22nd American Conference on Crystal Growth and Epitaxy (ACCGE-22)

and

20th US Workshop on Organometallic Vapor Phase Epitaxy (OMVPE-20)

Virtual Conference

AUGUST 2 - 4, 2021

All times MDT (Mountain Daylight Time)
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SCIENTIFIC PROGRAM

Fundamentals of Crystal Growth
Chairs:
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Israel Institute of Technology
Invited Speakers
Maria Sushko
PNNL
James De Yoreo
PNNL
Peter Vekilov
University of Houston
Jeffrey Rimer
University of Houston
Modeling of Crystal Growth Processes
Chairs:
Talid Sinno
University of Pennsylvania
Invited Speakers
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University of Minnesota
Lijun Liu
Xi’an Jiaotong University, China
Julia Dschemuchadse
Cornell University
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Berlin, Germany
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National Taiwan University
Taipei, Taiwan
Bulk Crystal Growth
Chairs:
Aleksandar Ostrogorsky
Illinois Institute of Technology
Invited Speakers
Robert Feigelson
Stanford University
Zhiqiang Mao
Pennsylvania State University
Andrew Novoselov
II-VI Aerospace & Defense
Biological and Biomimetic Materials
Chairs:
David Kisailus
UC Irvine
Jinhui Tao
Pacific Northwest National Laboratory
Invited Speakers
Atsushi Arakaki
Tokyo University of Agriculture and Technology
Keynote Speakers:
Helmut Colfen (University of Konstanz, Germany)
Lara Estroff (Cornell University, USA)
Rajesh Naik (Air Force Research Lab, USA)
Invited Speakers:
Hermann Ehrlich (Technische Universitat, Freiberg, Germany)
Laurie Gower (University of Florida, USA)
Michiko Nemoto (Okayama University, Japan)
Fabio Nudelman (University of Edinburgh, UK)
Boaz Pokroy (Technion Institute of Technology, Israel)
Abe Satoshi (Tokyo Institute of Technology, Yokohama, Japan)
Ruikang Tang (Zhejiang University, China)
Takafumi Ueno (Tokyo Institute of Technology, Japan)
Kimberly Weirich (Clemson University, USA)
Dongfeng Xue (Chinese Academy of Sciences, Shenzhen, China)
Shuai Zhang (University of Washington)

**Thin film growth, epitaxy, and superlattices**

Chairs:
Ferdinand Scholz
University of Ulm, Germany
Masakazu Sugiyama
University of Tokyo

Invited Speakers:
Dr. Ewa Grzanka
Institute of High Pressure Physics, Polish Academy of Sciences Warsaw, Poland
“Studies towards InGaN QW homogenization and decomposition via metal vacancies”

Prof. Dr. Kimberly Dick Thelander
Centre for Analysis and Synthesis, NanoLund, Solid State Physics Lund University, Sweden
“Understanding the dynamics of III-V nanostructure growth with in-situ TEM”

Prof. Motoaki Iwaya
Meijo University, Nagoya, Japan
“MOVPE and in situ analysis for hetero-junctions, tunnel-junctions and DBRs”

**Lattice-mismatched epitaxy and alternative epitaxial substrates**

Chairs:
David Lackner
Fraunhofer ISE

Invited Speaker
Vladimir Tassev
Air Force Research Laboratory
2D materials, surfaces and interfaces
Symposium Chair: Kevin M. Daniels
(University of Maryland)
Co-chairs: Cheng Gong (University of Maryland) and Soaram Kim (University of Maryland)
List of invited speakers for the Symposium:
Jimmy Kotsakidis, Monash University
Andrew May, Oak Ridge National Laboratory
Angela Hight Walker, National Institute of Standards and Technology
Matthias Batzill, University of South Florida
Shoufeng Lan, Texas A&M University
Xianglin Ke, MICHIGAN STATE UNIVERSITY
Ziqiang Qiu, UC Berkeley
Xi Ling, Boston University
Liuyan Zhao, University of Michigan
Paola Barbara, Georgetown University
Petr Neugebauer, CEITEC
Cheng Gong, University of Maryland
Soaram Kim, University of Maryland
Trevor Rhone, Rensselaer Polytechnic Institute
Peter Sutter, University of Nebraska-Lincoln

**Nanocrystals, quantum dots, and nanowires**

Chairs:
Jonathan Owen
Columbia University

Invited Speakers
Celso de Mello Donega
Benjamin Abecassis
Sanjit K. Ghose
BNL

David J. Norris
ETH Zurich
Sandrine Ithurria
Abstract Book - ACCGE-22//OMVPE-20

**Advanced Crystal Growth Technology and Equipment**
Chairs:
Rajan Rengarajan  
II-VI, Inc

Jeganathan Kulandaivel  
Bharathidasan University

Invited Speakers
Danilo Crippa  
LPE S.P.A  
"A novel 200mm Silicon Carbide Epitaxial Reactor for Power Devices: equipment and process perspectives"

Siddha Pimputkar  
Lehigh University  
“Pushing the Boundary on Nitride-Synthesis Equipment Technology”

Dharmalingam Prabhakaran  
Oxford University  
“Synthesis and Discovery of Quantum Materials”

**Advanced OMVPE techniques: equipment, epitaxy, and characterization**
Chairs:
Bernard Paquette  
National Research Council, Canada

III-V Epitaxial Growth for Devices  
Chairs:  
Luke Mawst  
University of Wisconsin-Madison

Nelson Tansu  
The University of Adelaide, Australia

Invited Speakers
Enrica Mura,  
Tyndall National Institute, Ireland

Josh Brown  
BluGlass Ltd, Australia

Kerstin Volz  
Philipps-Universität Marburg, Germany

**III-V Wide Bandgap Nitride Semiconductors and Devices**
Chairs:  
Ramon Collazo  
NC State University

Ronny Kirste  
Adroit Materials Inc

Invited Speakers
Anthony Rice  
Sandia National Laboratories, USA

Rafael Dalmau  
HexaTech, Inc. USA

**III-Vs on Silicon**
Chairs:  
Bill McMahon  
National Renewable Energy Lab

Invited Speakers
Tyler Grassman  
The Ohio State University

Invited Speakers
Eugenio Del Re  
Univ of Rome-la Sapienza, Italy

Chunhui Yang  
Harbin Institute of Technology, PR China

Benoît Boulanger  
University Grenoble, FRANCE

Peter Schunemann  
BAE Systems  
**Advanced OMVPE: novel materials and devices**  
Chairs:  
Ryan Lewis  
McMaster University
Thomas Hannappel
Technische Universität Ilmenau

**Narrow Bandgap Semiconductors and Devices**
Chairs:
Simon Watkins
Simon Fraser University

Invited Speakers
James Gupta
National Research Council of Canada
Sergey Suchalkin
Stony Brook University, Stony Brook, NY

**Silicon Carbide and Gallium Oxide Materials and Devices**
Chairs:
Govindhan Dhanaraj
Pallidus Inc
Michael Dudley
Stony Brook University, Stony Brook, NY
Balaji Raghothamachar
Stony Brook University, Stony Brook, NY

Invited Speakers
Zbigniew Galazka
LEIBNIZ-INSTITUT FÜR KRISTALLZÜCHTUNG, Germany
Victor Veliadis
Executive Director and CTO, Power America and NC State University
Roberto Fornari
Università di Parma, Italy
Elif Balkas
Wolfspeed, USA
Andrew Allerman
Sandia
Allen Brady
Alex Galyukov
STR US, Inc.

**Materials for photovoltaics and other energy technologies**
Chairs:
John Geisz
National Renewable Energy Lab

Invited Speakers
David Lackner
Fraunhofer Institute for Solar Energy Systems ISE
Freiburg, BW, Germany
Mohan Narayanan
Clean Energy Associates
Denver, CO
Parthiv Daggolu
Leading Edge Equipment Technologies
Wilmington, Massachusetts
Eric Colegrove
NREL

**Characterization techniques for bulk and epitaxial crystallization**
Chairs:
Michael Dudley
Stony Brook University

Invited Speakers
Xianrong Huang
Advanced Photon Source
Argonne National Laboratory, USA
Sakiko Kawanishi
Tohoku University, Japan
Maria Tsoutsouva
Norwegian University of Science and Technology, Norway.

Invited Speakers
Takeshi Yoshikawa
University of Tokyo, Japan
Fumihiro Fujie
Nagoya University, Japan
Jaime Frietas, Jr.
NRL, USA
Sage Bauers  
NREL, USA

Nadeemullah Mahadik  
NRL USA

Christian Reimann  
Fraunhofer Inst., Germany

**Symposium on Twisted Crystals**

Chairs:  
Bart Kahr  
New York University

Invited Speakers

Stephanie Lee  
NYU

David Amabilino  
U. Nottingham

Willem Noorduin  
AMOLF Amsterdam

Eli Sutter  
University of Nebraska-Lincoln

Yuzhou Zhao  
PhD Student U. Wisconsin

**Symposium on Metal Nanoparticle Nucleation and Growth**

Chairs:  
Hong Yang  
Invited Speakers

Ou Chen  
Brown University (USA)  
Hongyou Fan  
Sandia National Lab  
Sara Skrabalak  
Indiana University

Jianping Xie  
National University of Singapore

Symposium on Nucleation and Growth in Microfluidics  
Chairs:

Stéphane Veesler  
CINaM

Nadine Candoni  
CINaM

Romain Grossier  
CINaM

Invited Speakers

Simon Kuhn  
KU Leuven  
Leuven, Belgium  
Charline Gerard  
Technologie Servier  
Orléans, France

**Third Symposium on Ferroelectric Crystals and Textured Ceramics**

Chairs:  
Zuo-Guang Ye  
Simon Fraser University

Shujun Zhang  
University of Wollongong, Australia

Invited Speakers

Yunfei Chang  
Harbin Institute of Technology, China

Sandy Cochran  
University of Glasgow, UK

Lynn Ewart  
Naval Undersea Warfare Center, USA

Peter Kabakov  
University of Wollongong, Australia

Ho-Yong Lee  
Ceracomp Inc., South Korea

Fei Li  
Xi'an Jiaotong University, China

Yuji Noguchi  
Kumamoto University  
Kumamoto, Japan
Fifth Symposium on 2D and Low Dimensional Materials
Symposium Chair: Kevin M. Daniels
(University of Maryland)
Co-chairs: Cheng Gong (University of Maryland) and Soaram Kim (University of Maryland)

Boron Nitride Epitaxial Growth and Characterization Symposium
Chairs:
Siddha Pimputkar
Lehigh University

James Edgar
Kansas State University

Invited Speakers

Ishwara B. Bhat
Rensselaer Polytechnic Institute, USA,
"Properties of Hexagonal Boron Nitride Grown on Sapphire and Silicon Substrates"

Jianlin Liu
University of California, Riverside, USA,
"Two-dimensional hexagonal boron nitride: from molecular beam epitaxial growth to devices"

Sergei Novikov
University of Nottingham, UK,
"High-temperature MBE of hBN for single-photon emitters, deep-ultraviolet and lateral heterostructures."

Michael Snure
Air Force Research Lab, USA,
"Development of CVD grown hBN for scalable 2D electronics"

Takashi Taniguchi
International Center for Materials Nanoarchitectonics (NIMS), Japan,
"Synthesis of BN crystals by using solvent growth and their defect characterization"

Symposium on Detector Materials: Scintillators and Semiconductors
Chairs:
Henry Chen
Brimrose Corporation

Ei Ei Brown
US DEVCOM Army Research Laboratory

Invited Speakers

R. Radhakrishnan Sumathi
Leibniz-Institute Berlin, Germany

Irfan Kuvvetli
Technical University of Denmark
Kgs Lyngby, Denmark

Shariar Motakef
CapeSym

Kevin Pritchard
National Institute of Standards and Technology

Luis Stand
University of Tennessee - Knoxville

Krishna C. Mandal
University of South Carolina, Columbia
"High-resolution nuclear radiation detectors on 4H-SiC epitaxial layers"

Mark Derzon
Gold Standard Radiation Detection, Inc.,
"Suggested Material and Semiconductor Research to Improve Detectors for National Security and Civil Defense"

Rastgo Hawrami
Fisk University
"Latest Development on Advanced TI-based Scintillator Crystals for Radiation Detection and Medical Imaging"

Elsa Ariesanti
Fisk University
"Advanced Inorganic Halide Ceramic Scintillators."

Henry Chen
Brimrose Technology Corp.
"Mercurous Bromine Hg2Br2 as the next generation scintillator for space mission, high energy physics, defense and security applications"
DATA-DRIVEN STUDIES OF MAGNETIC VAN DER WAALS MATERIALS

Presenting Author: Trevor David Rhone

Topic: 2D materials, surfaces and interfaces

Format: Invited

Session: 2, 1

Date: 8/3/2021

Time (in MDT): 10:30:00 AM

Authors: Trevor David Rhone, Rensselaer Polytechnic Institute, Troy, New York, United States Wei Chen, Brookhaven National Laboratory, New York, United States Shaan Desai, Oxford University Steven Torrisi, Harvard University, Massachusetts, United States Daniel Larson, Harvard University, Massachusetts, United States Amir Yacoby, Harvard University, Massachusetts, United States Efthimios Kaxiras, Harvard University, Massachusetts, United States

When the dimensionality of an electron system is reduced from three dimensions to two dimensions, new behavior emerges. This has been demonstrated in gallium arsenide quantum Hall systems since the 1980’s, and more recently in van der Waals (vdW) materials, such as graphene. The discovery of vdW materials with intrinsic magnetic order in 2017 has given rise to new avenues for the study of emergent phenomena in reduced dimensions. These materials are at the forefront of condensed matter physics research. How many vdW magnetic materials exist in nature? What are their properties? How do these properties change with the number of layers? A conservative estimate for the number of candidate vdW materials (including monolayers, bilayers and trilayers) exceeds ~10^6. In this talk, we will use materials informatics (machine learning combined with materials science) as a tool to efficiently explore this large materials space and attempt to discover magnetic vdW materials with desirable spin properties. We will focus on crystal structures based on monolayer 

Cr<sub>2</sub>Ge<sub>2</sub>Te<sub>6</sub>, of the form

A<sub>2</sub>B<sub>2</sub>X<sub>6</sub>, which are studied using density functional theory (DFT) calculations and machine learning methods. Magnetic properties, such as the magnetic moment are determined. The formation energies are also calculated and used to estimate the chemical stability. We show that machine learning methods, combined with DFT, can provide a computationally efficient means to predict properties of vdW magnetic materials. In addition, data analytics provides insights into the microscopic origins of magnetic ordering in two dimensions. We also explore how our study of magnetic monolayers [1] can be extended, with proper modification, to multilayer vdW materials. This non-traditional approach to materials research paves the way for the rapid discovery of magnetic vdW materials that are chemically stable.<br />

2D MAGNETS AND 2D MAGNETISM

Presenting Author: Cheng Gong

Topic: 2D materials, surfaces and interfaces

Format: Invited

Session: 2, 3

Date: 8/3/2021

Time (in MDT): 11:00:00 AM

Authors: Cheng Gong, University of Maryland, College Park, College Park, Maryland, United States

Magnetism, one of the most fundamental physical properties, has revolutionized significant technologies such as data storage and biomedical imaging, and continues to bring forth new phenomena in emerging materials of reduced dimensionalities. The recently discovered magnetic 2D van der Waals materials provide ideal platforms to enable the atomic-thin, flexible, lightweight magneto-optical and magnetoelectric devices. Though many have hoped that the ultra-thinness of 2D magnets should allow an efficient control of magnetism, the state-of-the-art has not achieved notable breakthroughs to this end. In this talk, I will speak on our experimental discovery of the first 2D ferromagnet, and discuss on promising strategies towards the efficient electrical and optical control of 2D magnetism.
AMBIENT EFFECTS ON METALLIC TWO-DIMENSIONAL MAGNETS

Presenting Author: Zhiyin Tu

Topic: 2D materials, surfaces and interfaces

Format: Contributed

Session: 2, 5

Date: 8/3/2021

Time (in MDT): 11:30:00 AM

Authors: Zhiyin Tu, University of Maryland, College Park, Maryland, United States
Ti Xie, University of Maryland, College Park, Maryland, United States
Yeonghun Lee, The University of Texas at Dallas, Richardson, Texas, United States
Jinling Zhou, University of Maryland, College Park, Maryland, United States
Alemayehu S. Admasu, The State University of New Jersey, Piscataway, New Jersey, United States
Yu Gong, College of Charleston, Charleston, South Carolina, United States
Nagaraja Valanoor, University of New South Wales, Sydney, Australia
John Cumings, University of Maryland, College Park, Maryland, United States
Sang-Wook Cheong, The State University of New Jersey, Piscataway, New Jersey, United States
Ichiro Takeuchi, University of Maryland, College Park, Maryland, United States
Kyeongjae Cho, The University of Texas at Dallas, Richardson, Texas, United States
Cheng Gong, University of Maryland, College Park, Maryland, United States

The emergent magnetic two-dimensional (2D) materials provide ideal solid-state platforms for a broad range of applications including miniaturized spintronics, nonreciprocal optics, and magnetoelectric sensors. Owing to the general environmental sensitivity of 2D magnets, the understanding of ambient effects on 2D magnetism is critical. Apparently, the nature of itinerant ferromagnetism potentially makes metallic 2D magnets insensitive to environmental disturbance. Nevertheless, our systematic study showed that the Curie temperature of metallic 2D Fe$_3$GeTe$_2$ decreases dramatically in the air but thick Fe$_3$GeTe$_2$ exhibits self-protection. Remarkably, we found the air exposure effectively promotes the formation of multiple magnetic domains in 2D Fe$_3$GeTe$_2$, but not in bulk Fe$_3$GeTe$_2$. Our first-principles calculations support the scenario that substrate-induced roughness and tellurium vacancies boost the interaction of 2D Fe$_3$GeTe$_2$ with the air. Our elucidation of the thickness-dependent air-catalyzed evolution of Curie temperatures and magnetic domains in 2D magnets provides critical insights for chemically decorating and manipulating 2D magnets.
GRAPHENE QUANTUM DOTS BOLOMETERS FOR STUDIES OF SINGLE MOLECULE MAGNETS

Presenting Author: Paola Barbara

Topic: 2D materials, surfaces and interfaces

Format: Invited

Session: 3, 1

Date: 8/3/2021

Time (in MDT): 1:00:00 PM

Authors: Paola Barbara, Georgetown University, Washington, Dist. of Columbia, United States  Luke St. Marie, Georgetown University, Washington, Dist. of Columbia, United States  Lubomir Havlicek, Central European Institute of Technology, Brno University, Brno, Czech Republic  Jakub Hruby, Central European Institute of Technology, Brno University, Brno, Czech Republic  Amjad Alqahtani, Georgetown University, Washington, Dist. of Columbia, United States  Davonne Henry, Georgetown University, Washington, Dist. of Columbia, United States  Antonin Sojka, Central European Institute of Technology, Brno University, Brno, Czech Republic  Jorge Navarro, Central European Institute of Technology, Brno University, Brno, Czech Republic  Rachael Myers-Ward, US Naval Research Laboratory (NRL), Washington, Dist. of Columbia, United States  D. Kurt Gaskill, Institute for Research in Electronics and Applied Physics, University of Maryland, College Park, Maryland, United States  Abdel El Fatimy, Ecole Centrale Casablanca, Casablanca, Morocco  Amy Liu, Georgetown University, Washington, Dist. of Columbia, United States  Ivan Nemec, Central European Institute of Technology, Brno University, Brno, Czech Republic  Petr Neugebauer, Central European Institute of Technology, Brno University, Brno, Czech Republic

Abstract: Single molecule magnets (SMMs) are clusters of magnetic ions or single ions embedded in a ligand shell and they can be modeled as single-spin quantum systems. Their spectra have an energy barrier to magnetization reversal yielding magnetic bistability at low temperature and widely spaced spin states, making them very attractive for high-density data storage, molecular spintronics and quantum computing. SMMs are mostly studied in bulk samples, i.e. single crystals or powder pellets. However, since most applications require SMMs deposited on surfaces, it is important to understand whether the interaction between the ligand shells and the surfaces may substantially alter the SMM properties. Here we use epitaxial graphene on SiC patterned into quantum dots to probe the properties of SMMs. Since the detectors are designed with the graphene surface fully exposed, SMMs can be deposited directly on the graphene. The graphene quantum dots serve as highly sensitive photodetectors for in-situ electron paramagnetic resonance (EPR) spectroscopy of the SMMs, to measure whether the spectra of SMMs on the graphene surface are modified with respect to the spectra of SMMs in bulk samples. The interaction between the SMMs and the graphene also affects the transport properties of the quantum dot. We study this effect and the EPR spectra for Mn{Osub<sub>CCHCl</sub>}_{12} and H{Osub<sub>4</sub>CCHCl}_{12}, as well as for a version of these SMMs with modified carboxylate ligands. References: 1. El Fatimy, A.; Myers-Ward, R. L.; Boyd, A. K.; Daniels, K. M.; Gaskill, D. K.; Barbara, P. Nature Nanotechnology 2016, 11, (4), 335-340. 2. El Fatimy, A.; Nath, A.; Kong, B. D.; Boyd, A. K.;


THE IMPACT OF GROWTH CONDITIONS ON THE MAGNETISM OF FE-GE-TE MATERIALS

Presenting Author: Andrew May

Topic: 2D materials, surfaces and interfaces

Format: Invited

Session: 3, 3

Date: 8/3/2021

Time (in MDT): 1:30:00 PM

Authors: Andrew May, Oak Ridge National Lab, Oak Ridge, Tennessee, United States

Layered materials composed of magnetic slabs held together by van der Waals bonds are heavily exploited for studies of device-oriented physics in exfoliated samples. Demonstrating control over the physical properties of bulk crystals by tuning structures and chemistry is a key challenge for the continued development of device functionality as well as for testing various materials physics concepts. Crystal growth is a critical component in these endeavors, in part because the crystalline symmetries and defects can be dictated by the growth conditions. Of the cleavable magnetic materials, several metallic Fe-Ge-Te phases are especially interesting due to their relatively high Curie temperatures (from ≈150 to over 300K). This talk will examine the important role that crystal growth has played in revealing the interplay of structure and properties in the Fe$_3$GeTe$_2$ and Fe$_5$GeTe$_2$ systems. For crystals of Fe$_{3-x}$GeTe$_2$, the growth conditions dictate the stoichiometry of the crystals, while the structure of Fe$_{5-x}$GeTe$_2$ is complicated by a stacking-related instability as well as sublattice disorder that can be manipulated through thermal processing and chemistry. This talk will therefore encourage the development of greater synthetic control to allow for rational tuning of the properties in complex van der Waals phases.
SYNTHESIS AND CHARACTERIZATION OF MANGANESE (IV) SELENIDE ON MN AND MNO<sub>2</sub> SEEDED GRAPHENE AND SILICON

Presenting Author: Ihteyaz Avash

Topic: 2D materials, surfaces and interfaces

Format: Contributed

Session: 3, 5

Date: 8/3/2021

Time (in MDT): 2:00:00 PM

Authors: Ihteyaz A. Avash, University of Maryland, College Park, Maryland, United States  Michael Pedowitz, University of Maryland, College Park, Maryland, United States  Kevin M. Daniels, University of Maryland, College Park, Maryland, United States

Although transition metal dichalcogenides (TMD) have been in the forefront of scientific research in recent years due to their curious shift of various electronic and mechanical properties near monolayer limit, only a handful of them have been found to display ferromagnetic properties. Among them, MnSe<sub>2</sub> is of special interest, since its monolayer 1T-polytype has been found to display long-range magnetic ordering and high magnetic moments near room temperature conditions, making it uniquely qualified for various spintronic applications. In this study, we attempt to grow 2D heterostructure of MnSe<sub>x</sub> on epitaxial graphene (EG) and SiO<sub>2</sub> substrates using several variants of the chemical vapor deposition (CVD) methodology.

In our first approach, we use traditional one-step CVD technique, where selenium (Se) powder precursor was used alongside either MnO<sub>2</sub> or manganese acetate (MnAc) powder inside the CVD chamber for direct growth of MnSe<sub>x</sub> on EG or SiO<sub>2</sub> substrate. In the second approach, we use a two-step CVD technique, where δ-phase MnO<sub>2</sub> is first electrodeposited on EG or SiO<sub>2</sub> substrate. In the third approach, magnetron sputtering deposition is used to deposit a 7nm layer of Mn on SiO<sub>2</sub>, which is then selenified via CVD using only Se powder precursor. In the third approach, magnetron sputtering deposition is used to deposit a 7nm layer of Mn on SiO<sub>2</sub>, which is then selenified via CVD using only Se powder precursor. In the third approach, magnetron sputtering deposition is used to deposit a 7nm layer of Mn on SiO<sub>2</sub>, which is then selenified via CVD using only Se powder precursor.

The samples were characterized via Raman, SEM and AFM tools. For both precursor combinations of the first approach, the process yielded low grain size and growth density, albeit slightly better yield for MnAc compared to MnO<sub>2</sub>. The second approach was found to produce significantly higher MnSe<sub>x</sub> yield. Raman analysis for the growth on SiO<sub>2</sub> substrate showed a shift of characteristic peak from 259 to 253 cm<sup>-1</sup> with growth temperature increasing from 450<sup>o</sup>C to 800<sup>o</sup>C, indicating to the presence of a hybrid structure of MnSe<sub>x</sub> with α-MnSe component becoming more dominant with increasing temperature. For growth on EG, MnSe<sub>2</sub> phase was more prevalent as raman peak was found at 267 cm<sup>-1</sup> for 450<sup>o</sup>C growth temperature. In the third approach, presence of growth has only been observed for 800<sup>o</sup>C growth temperature, which yielded a growth characterized by raman peak at 254 cm<sup>-1</sup> indicating the dominant presence of α-MnSe phase. The two-step CVD techniques utilized in this study show a lot of promise, and once optimized, should lead to wafer scale synthesis of MnSe<sub>2</sub> based spintronic devices.
TRANSFORMATION OF BIRNESSITE MnO$_2$ ON EPITAXIAL GRAPHENE/SILICON CARBIDE TO Mn$_3$O$_4$ ON EPITAXIAL GRAPHENE/SILICON CARBIDE VIA SIMPLE HEAT TREATMENT

**Presenting Author:** Michael Pedowitz  
**Topic:** 2D materials, surfaces and interfaces  
**Format:** Contributed  
**Session:** 3, 6  
**Date:** 8/3/2021  
**Time (in MDT):** 2:15:00 PM

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The rising ubiquity of electronic infrastructure around the world has generated a need for low-cost, environmentally safe, and high-performance device materials. To meet these needs a variety of novel materials have been proposed including mixed-valence manganese oxides (MnO$_x$), which have attracted significant interest due to their easily accessible redox couples (Mn$^{+2}$/Mn$^{+3}$, Mn$^{+3}$/Mn$^{+4}$) and novel magnetic properties. Due to this, MnO$_x$ based devices have been proposed in catalysis, electrochemical energy storage, gas sensing, and data storage. Among these MnO$_x$ materials, hasumannite (Mn$_3$O$_4$) has been of particular interest due to its chemical stability, spinel structure, and novel magnetic properties. Mn$_3$O$_4$’s low inherent conductivity ($10^{-7}$ to $10^{-8}$ S), however, has limited its application to a wide variety of applications. To overcome this challenge heterostructures have been formed between graphene and Mn$_3$O$_4$, which seek to couple the inherent conductivity of graphene with the properties of Mn$_3$O$_4$. In this work, we document the transformation of thin-film δ-MnO$_2$ on quasi-freestanding bilayer epitaxial graphene/silicon carbide to Mn$_3$O$_4$ on quasi-freestanding bilayer epitaxial graphene/silicon. The initial δ-MnO$_2$ was deposited via electrodeposition on epitaxial graphene (EG) synthesized on semi-insulating 6H silicon carbide substrates (SiC) utilizing 10mM manganese acetate (Mn(CH$_3$CO$_2$)$_2$) solution in a three-electrode electrochemical cell with a platinum counter electrode and a silver/silver chloride reference electrode (Ag/AgCl). The resulting films were then annealed at temperatures ranging from 50°C to 400°C for 2Hr in air to produce the Mn$_3$O$_4$ on quasi-freestanding bilayer EG/SiC films. The annealed films were then characterized using Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM), and scanning force electron microscopy (SEM). Raman spectroscopy indicated that full transformation of δ-MnO$_2$ to Mn$_3$O$_4$ only occurred at 400°C, evidenced by a strong Raman band at 660cm$^{-1}$ and a weak band at 310cm$^{-1}$ which was consistent with the literature.
formal valence was approximately +2.67, consistent with $\text{Mn}_3\text{O}_4$. SEM revealed that the surface was made up of micron-sized platelets made up of accumulated nanoplatelets, which was confirmed by AFM. The use of epitaxial graphene is in contrast to previously reported methods, which rely on reduced graphene oxide, which significantly reduces the underlying graphene conductivity.<br />

MAGNON-PHONON HYBRIDIZATION IN THE QUASI-2D ANTIFERROMAGNET MnPSe₃

Presenting Author: Angela Hight Walker

Topic: 2D materials, surfaces and interfaces

Format: Invited

Session: 4, 1

Date: 8/3/2021

Time (in MDT): 3:00:00 PM

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Magnetic excitations in van der Waals (vdW) materials, especially in the two-dimensional (2D) limit, is an exciting research topic from both the fundamental and application perspectives. In MnPSe₃, a vdW material that hosts 2D, in plane antiferromagnetism (AFM), we correct an assignment from a one magnon scattering process to that from a continuum of two magnon excitations. Also, the hybridization of those excitations with two separate E₉ phonons was analyzed using temperature-dependent, magneto-Raman spectroscopy. A model was constructed that reproduces our observations and demonstrates that the phonons and two-magnon excitations interact strongly in the magnetically ordered state, dramatically affecting their lifetimes. Further, systematic studies of the effect of polarization and laser wavelength on the overall Raman scattering intensity in the AFM phase were performed. Our experimental and theoretical results points to the cause of spin-ordering-induced resonant Raman scattering effect in MnPSe₃.
Abstract Book - ACCGE-22//OMVPE-20

SPIN-INDUCED LINEAR POLARIZATION OF PHOTOLUMINESCENCE IN ANTIFERROMAGNETIC VAN DER WAALS NiPS$_3$

Presenting Author: Xi Ling

Topic: 2D materials, surfaces and interfaces

Format: Invited

Session: 4, 3

Date: 8/3/2021

Time (in MDT): 3:30:00 PM

Authors: Xi Ling, Boston University, Boston, Massachusetts, United States

Since the discovery of monolayer ferromagnets, magneto-optics plays a compelling role in revealing new physics of magnetism in the extreme nanoscale limit. Compared to ferromagnets, however, the studies of magneto-optics in 2D antiferromagnets are far more difficult due to the lack of net magnetic moments, despite their appealing natures for next-generation spintronic devices, due to their terahertz resonance, multilevel states, and absence of stray fields. The zero net magnetic moment of antiferromagnets makes the detection of the antiferromagnetic order and the investigation of fundamental spin properties notoriously difficult. Here, I will discuss an optical detection of Néel vector orientation through an ultra-sharp photoluminescence we recently discovered in the van der Waals antiferromagnet NiPS$_3$ from bulk to atomically thin flakes. The strong correlation between spin flipping and electric dipole oscillator results in a linear polarization of the sharp emission, which aligns perpendicular to the spin orientation in the crystal. By applying an in-plane magnetic field, we achieve manipulation of the photoluminescence polarization. Benefiting from the spin-correlated emission in NiPS$_3$, the Néel vector orientation can be optically detected as perpendicular to the PL polarization. Even though the manipulation of the PL polarization was only demonstrated in bulk NiPS$_3$, we anticipate similar results on few-layer flakes, in which the linearly polarized emission has also been demonstrated. Our report on the spin-correlated PL in vdW antiferromagnets – NiPS$_3$ will greatly advance future fundamental researches in magnetism and magneto-optics. Most of the prior optical spin-probe techniques for antiferromagnets are technically difficult to conduct and not suitable for ultrathin samples, since they require an ultrafast laser to induce the thermal or magnetic perturbation, and the amplitudes of signals are proportional to the thickness of samples. In contrast, the spin-induced polarization of PL demonstrated here using a steady-state microspectroscopy method offers an easy, fast, nondestructive strategy to determine the Néel vector orientation and investigate the spin properties of atomically thin antiferromagnets. We anticipate the conceptually new mechanism of spin-photon coupling will stimulate future theoretical and experimental studies in the field, promoting the development of opto-spintronic device and magnetic quantum information technology.
TWISTING ENGINEERING OF TWO-DIMENSIONAL MAGNETISM IN DOUBLE BILAYER CHROMIUM TRIIODIDE HOMOSTRUCTURES

Presenting Author: Liuyan Zhao

Topic: 2D materials, surfaces and interfaces

Format: Invited

Session: 4, 5

Date: 8/3/2021

Time (in MDT): 4:00:00 PM

Authors: Liuyan Zhao, University of Michigan, Ann Arbor, Michigan, United States

Twist engineering has emerged as one powerful venue to design and tailor the physical properties of two-dimensional (2D) materials. While it has led to tremendous success in modulating the charge degree of freedom, its power and potential in controlling the spin degree of freedom remain as a much less explored area, especially experimentally. In this talk, we use the archetypal 2D Ising magnet CrI$_3$ to fabricate twisted double bilayer (tDB) CrI$_3$ homostructures with well-controlled tunable twist angles, and demonstrate the successful twist engineering of 2D magnetic properties in such systems. Using polarized Raman spectroscopy, we successfully identify magneto-Raman signatures of a new magnetic ground state and carefully track its magnetic-field and twist-angle dependencies. We reveal that, while the very small (~ 0.5$^\circ$) and relatively large (~ 5.0$^\circ$) twist angle tDB CrI$_3$ can be approximated by the weighted linear superposition of contributions from bilayer-like and four-layer-like CrI$_3$, the intermediate (~ 1.1$^\circ$) twist angle tDB CrI$_3$ cannot be simply inferred from the bilayer and four-layer cases. But instead, it features a dramatic Raman circular dichroism suggesting the presence of a net magnetization that is absent in both bilayer and four-layer CrI$_3$, and lacks of sharp spin flip transitions indicating the noncollinear spin alignment that is in contrast to the collinear layered AFM state in bilayer and four-layer CrI$_3$. 
CHIRALITY, MAGNETISM, AND THEIR INTERPLAY

Presenting Author: Shoufeng Lan

Topic: 2D materials, surfaces and interfaces

Format: Invited

Session: 1, 1

Date: 8/4/2021

Time (in MDT): 8:30:00 AM

Authors: Shoufeng Lan, Texas A&M University, College Station, Texas, United States

Chirality, magnetism, and their interplay<br />The interplay between chirality and magnetism is of great interest in physics, chemistry, and mathematics since they share the circulating possession. The past few years also witnessed the surging development of the individual of them. For chirality, artificially structured materials exhibit optical rotation and circular dichroism that are several orders of magnitude larger than natural materials. For magnetism, experiments have verified the existence of long-range magnetic order in two-dimensional materials. In this talk, we present a series of engineered materials that exhibit a wide range of chiral phenomena in spectroscopy, imaging, optoelectronics, and nonlinear optics. We further integrate the engineered chiral materials with graphene and silicon into a monolithic polarimeter that can separate, analyze, and detect the full-Stokes polarization of light. Finally, we share the recent observation of an excitonic magneto-chiral effect in twisted bilayer van der Waals atomic crystals.<br />

References:
BEYOND 2D MATERIALS: LAYERED CRYSTALS WITH A TWIST

Presenting Author: Peter Sutter

Topic: 2D materials, surfaces and interfaces

Format: Invited

Session: 1, 3

Date: 8/4/2021

Time (in MDT): 9:00:00 AM

Authors: Peter Sutter, University of Nebraska-Lincoln, Lincoln, Nebraska, United States  Eli Sutter, University of Nebraska-Lincoln, Lincoln, Nebraska, United States

Two-dimensional (2D) crystals have attracted significant interest due to novel properties that arise in atomically thin materials. Much less explored are layered crystals and heterostructures that, assembled from 2D building blocks, lie between the monolayer and bulk limits. In the growth of such van der Waals crystals, phenomena such as spontaneous phase separation, transformations between different crystal polymorphs, hybrid dimensionality, and introduction of defects provide unprecedented opportunities for controlling morphology, interface formation, and novel degrees of freedom such as interlayer twist. But going beyond a single layer also poses extraordinary challenges, both due to the diversity and complexity of the possible few-layer structures and the difficulty of probing functionality such as optoelectronics at the relevant length scales. Here, we discuss recent research that addresses these challenges by combining in-situ microscopy of growth and processing with advanced materials characterization and optoelectronic spectroscopy at the ultimate resolution limit. We focus on group IVA chalcogenides, an emerging class of layered crystals with multiple stable polymorphs of different chalcogen content that have shown promising properties for energy conversion, information processing, and optoelectronics. By tuning the anion chemical potential, self-organization processes are activated that yield complex van der Waals heterostructures such as wrap-around core-shell structures[1] and layer stacks or superlattices incorporating one or multiple twisted interfaces.[2] Combining materials with different cation species produces atomically stitched heterostructures[3] and alloys[4] that provide fundamental insight into interface formation, strain effects, and alloying in few-layer van der Waals crystals. Nanometer-scale cathodoluminescence spectroscopy in STEM shows emerging optoelectronic and photonic properties, such as interfacial charge separation, valley-selective luminescence, and the excitation of propagating photonic modes. Our results highlight the rich sets of materials architectures and functionalities that can be realized in van der Waals crystals beyond the 2D limit. References: [1] P. Sutter, J. Wang, and E. Sutter, Adv. Mater. 31, 1902166 (2019). [2] P. Sutter, R. Ibragimova, H.-P. Komsa, B.A. Parkinson, and E. Sutter, Nat. Commun. 10, 5528 (2019). [3] E. Sutter, J. Wang, and P. Sutter, ACS Nano 14, 12248 (2020). [4] P. Sutter, L. Khosravi Khorashad, C. Argyropoulos, and E. Sutter, Adv. Mater. 33, 2006649 (2021).
ELECTRONIC AND MAGNETIC PROPERTIES OF QUASI-2D TOPOLOGICAL MAGNETS

Presenting Author: Xianglin Ke

Topic: 2D materials, surfaces and interfaces

Format: Invited

Session: 1, 5

Date: 8/4/2021

Time (in MDT): 9:30:00 AM

Authors: Xianglin Ke, Michigan State University, East Lansing, Michigan, United States

Magnetic topological materials have been a focal point of research in recent years. In this talk, we will present our recent electronic transport, thermal transport, and neutron scattering studies of some quasi-2D magnets. We will show that ferromagnetic Kagome metal Fe$_3$Sn$_2$ manifests topological properties arising from the synergic effects of Berry phase in both real space and momentum space. It exhibits large topological Nernst effect and topological Hall effect associated with the non-zero spin chirality of Skyrmion lattice; Additionally, it exhibits prominent anomalous thermal Hall effect and anomalous Nernst effect with features similar to the anomalous Hall effect. We will also present topological electronic properties and topological magnetic excitations of RMn$_6$Sn$_6$ which hosts quasi-2D ferromagnetic Kagome lattice.
CR$_{(1+\delta)}$TE$_2$ INTERCALATION COMPOUNDS AS FERROMAGNETIC VAN DER WAALS MATERIALS

Presenting Author: Matthias Batzill

Topic: 2D materials, surfaces and interfaces

Format: Invited

Session: 2, 1

Date: 8/4/2021

Time (in MDT): 10:30:00 AM

Authors: Matthias Batzill, University of South Florida, Tampa, Florida, United States

The Cr-Te system is known for its ferromagnetic properties. These materials can be characterized as a 1T-CrTe$_2$ transition metal dichalcogenide layers with additional Cr-atoms ($\delta$) interspersed in between the layers—sometimes also called a self-intercalated compound. Here we discuss the growth of this material by molecular beam epitaxy on van der Waals substrate. Films grow in van der Waals epitaxy, i.e. rotationally aligned with the substrate but with a van der Waals gap between the layers. Film thickness as thin as a single bilayer CrTe$_2$ with a single intercalation layer can be obtained. Importantly these films remain ferromagnetic to this ultrathin limit with a Curie temperature of ~150K. Generally, self-intercalated compounds may be considered alternative 2D materials and control of the intercalation may be used to tune their properties.
MAGNETIC STRIPE DOMAINS AND SKYRMIONS IN VAN DER WAALS FE\textsubscript{3}GeTe\textsubscript{2}

Presenting Author: Zi Q. Qiu

Topic: 2D materials, surfaces and interfaces

Format: Invited

Session: 2, 3

Date: 8/4/2021

Time (in MDT): 11:00:00 AM

Authors: Zi Q. Qiu, University of California at Berkeley, Berkeley, California, United States

Magnetic long-range order in 2D films is usually attributed to the existence of magnetic anisotropy because an isotropic two-dimensional (2D) Heisenberg system does not carry long-range order at finite temperature. The emerging van der Waals (vdW) magnetic materials offer a great opportunity to exam this fundamental issue in 2D magnetic systems. In this talk, I will report our recent study on vdW ferromagnetic Fe\textsubscript{3}GeTe\textsubscript{2} system which represents many vdW ferromagnetic materials with perpendicular magnetization. Magnetic imaging using Photoemission Electron Microscopy (PEEM) shows the formation of magnetic stripe domains in Fe\textsubscript{3}GeTe\textsubscript{2} with the stripe width increasing drastically as the film thickness decreases. We show that this behavior resembles the general property of the so-called spin reorientation transition (SRT) in conventional magnetic ultrathin films due to the competition between perpendicular magnetic anisotropy and the dipolar magnetic interaction. Then the knowledge of SRT naturally leads to the discovery that a magnetic interlayer coupling between Fe\textsubscript{3}GeTe\textsubscript{2} and Co/Pd multilayers converts the chiral magnetic stripe domains into topological skyrmions.
EPITAXIAL GRAPHENE BASED SENSOR FOR RAPID DETECTION OF COVID-19 FROM EXHALED BREATH AEROSOL

Presenting Author: Soaram Kim

Topic: 2D materials, surfaces and interfaces

Format: Invited

Session: 3, 1

Date: 8/4/2021

Time (in MDT): 1:00:00 PM

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On March 12, 2020, COVID-19 was classified as a pandemic by the World Health Organization (WHO), which is an emerging human infectious disease and causes respiratory illnesses of varying severity from the common cold to fatal pneumonia in both humans and animals [1]. As of April 11, 2021, more than 135,000,000 cases of COVID-19 have been confirmed around the world, resulting in 2,900,000 deaths, while about 22% of cases have resulted from the United States of America (USA), and the total deaths in the USA are about 567,000 [2]. The current primary diagnosis of COVID-19 is real-time reverse transcription-polymerase chain reaction (RT-PCR), which is the fastest and most reliable method, spreading around the world. However, the RT-PCR needs the RNA preparation process, which causes a decrease of accuracy as well as sensitivity, and takes over 3 h to complete the diagnosis of COVID-19. Thus, the direct detection of viral antigens from human to environmental conditions without the RNA sample preparation process is required for ultra-fast and highly accurate immunological diagnostic methods in the future. Two-dimensional (2D) materials such as graphene is promising for the next generation of electronics, i.e., biological and chemical sensors in environmental and safety monitoring and medical health care systems [3]. In addition, atomically thin 2D graphene has an extremely high surface-to-volume ratio which is the most vital parameter for sensing applications. Here we have fabricated a heterostructure of SARS-CoV-2 S1 spike antibodies and epitaxial graphene (EG) on 6H silicon carbide (SiC) substrate for COVID-19 detection. We have combined the advantages of high sensitivity and fast response time of graphene with the high selectivity of antibodies to develop a high sensitivity COVID-19 sensor. To synthesize bilayer EG on 6H SiC, the Si thermal sublimation method, followed by H<sub>2</sub> intercalation, was used [4]. After that, reactive ion etching (RIE, CF<sub>4</sub>) was used to prepare a simple pattern, and the metal electrode (Ti/Au = 30/220 nm) was deposited using an e-beam evaporator. Then, the crosslinker and SARS-CoV-2 S1 spike antibodies were immobilized on graphene/SiC directly. Samples were investigated by atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS), and Raman spectroscopy to confirm EG substrate integrity and its
heterostructure bonding on EG. Lastly, the electrical response of the sensor was measured using the Gamry 3000 Source/Measure Unit to investigate the sensor performance with clinical samples.
INCREASING THE MAGNESIUM INTERCALATION RATE FOR THE GRAPHENE ON SILICON CARBIDE SYSTEM

Presenting Author: Jimmy Kotsakidis

Topic: 2D materials, surfaces and interfaces

Format: Invited

Session: 3, 3

Date: 8/4/2021

Time (in MDT): 1:30:00 PM

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Graphene has not only expanded our understanding of fundamental condensed matter physics, but is a material that may directly enable future technological advancement through use in electrical devices. To enable this transition, research over the past decade has focused on ways to modulate the electrical properties of graphene via electrostatic gating, surface chemical doping, atom substitution, stacking or intercalation. Of these methods, intercalation, i.e., the insertion of atoms or molecules underneath the graphene, has achieved some of the highest doping levels in graphene. Intercalation experiments are typically carried out using graphene epitaxially synthesized on silicon carbide. In this case, the graphene sits atop of a carbon ‘buffer’ layer (which has a structure similar to graphene, but due to partial covalent bonding to the SiC surface, has a dissimilar electronic structure). When graphene on silicon carbide is intercalated, the intercalants typically go underneath the buffer layer, bonding to the SiC surface and liberating the buffer layer, which becomes another graphene layer.

Recently, we have demonstrated that magnesium and calcium can intercalate graphene on 6H-SiC(0001) [1]. Here, the magnesium (or calcium) intercalates between the buffer layer and the SiC surface to form a Mg-silicide/Ca-silicide and results in a highly n-type doped graphene [1][2]. Surprisingly, we found that while Ca-intercalated graphene was not air-stable, Mg-intercalated graphene was relatively stable in ambient atmosphere for at least six hours. Furthermore, Mg was unable to intercalate hydrogen intercalated quasi-freestanding bilayer graphene on 6H-SiC(0001) - opening up the possibility of hybrid Mg/H intercalation to create localized n-p type junctions. However, multiple Mg-intercalation steps were necessary to fully intercalate the sample. This implies Mg is a difficult atom to intercalate - potentially due to its high vapor pressure and weak binding forces to carbon. Thus,
although Mg induces desirable electrical properties in graphene, its difficulty to intercalate underneath epitaxial graphene on SiC remains an engineering obstacle for device fabrication. In this talk, I will review our recent results regarding the alkali earth (Ca and Mg) intercalation of graphene on 6H-SiC(0001), and then discuss how the engineering obstacle posed by magnesium can be overcome. We believe our intercalation method could be extended to other difficult-to-intercalate atoms such as antimony and zinc, or other high vapor pressure species yet to be intercalated.

CONTACTLESS MILLIMETER WAVE METHOD FOR QUALITY ASSESSMENT OF LARGE AREA GRAPHENE

Presenting Author: Petr Neugebauer

Topic: 2D materials, surfaces and interfaces

Format: Invited

Session: 3, 5

Date: 8/4/2021

Time (in MDT): 2:00:00 PM

Authors: Petr Neugebauer, Central European Institute of Technology, Brno, Czech Republic

We demonstrate that microwave absorption experiments offer a route for efficient measurements of transport properties for fast and accurate quality control of graphene. This contactless characterization method can be used to quickly evaluate transport properties over large areas without recourse to complex lithographic methods making it suitable as a probe of quality during wafer scale fabrication. In particular, we demonstrate that absorption measurement of transport properties is sensitive to inhomogeneities in sample transport properties. This is in contrast to traditional methods using electrical contacts which tend to overestimate transport properties due to the formation of preferential conducting channels between the electrodes. Here we compare Shubnikov-de Haas oscillations simultaneously detected by microwave absorption and by conventional contact Hall bar measurements in fields up to 15 T on quasi-free standing, large area (25 mm$^2$) monolayer graphene. We find that although the evaluated charge carrier densities from both measurements are similar, the mobility differs considerably due to electronic transport inhomogeneity. Finally, we give some perspectives on the application of the method to other materials, showing the case of graphite as an example, and comparing our results with conventional transport experiments.
UNIDIRECTIONAL EPITAXY OF TMD MONOLAYERS ON SAPPHIRE

Presenting Author: Joan Redwing

Topic: 2D materials, surfaces and interfaces

Format: Contributed

Session: 4, 1

Date: 8/4/2021

Time (in MDT): 3:00:00 PM

Authors: Joan Redwing, Penn State, University Park, Pennsylvania, United States Haoyue Zhu, Penn State, University Park, Pennsylvania, United States Tanushree Choudhury, Penn State, University Park, Pennsylvania, United States Nicholas Trainor, Penn State, University Park, Pennsylvania, United States Thomas McKnight, Penn State, University Park, Pennsylvania, United States Benjamin Huet, Penn State, University Park, Pennsylvania, United States Anushka Bansal, Penn State, University Park, Pennsylvania, United States

Wafer-scale synthesis of semiconducting transition metal dichalcogenide (TMDs) monolayers is of significant interest for device applications to circumvent size limitations associated with the use of exfoliated flakes. Promising results have been demonstrated for epitaxial films deposited by vapor phase techniques such as CVD and MOCVD. However, the three-fold symmetry of TMDs such as MoS$_2$ and WSe$_2$, results in two energetically equivalent domain alignments, often referred to as 0° and 60° domains, when grown on substrates such as c-plane sapphire and graphene. The oppositely oriented domains give rise to inversion domain boundaries (IDBs) upon coalescence which exhibit a metallic character and are generally undesirable. In this study, we demonstrate the epitaxial growth of unidirectional TMD monolayers on 2” diameter c-plane sapphire substrates with a significantly reduced density of inversion domains. Steps on the sapphire surface are shown to break the surface symmetry giving rise to a preferred domain orientation. Metalorganic chemical vapor deposition (MOCVD) was used for the epitaxial growth of WSe$_2$ and WS$_2$ monolayers on c-plane sapphire in a cold-wall horizontal quartz-tube reactor. The as-received sapphire substrates, which are miscut ~0.2° toward the m-axis, consist of steps with sub-1 nm step height separated by 50-70 nm wide terraces. A three-step nucleation-ripening-lateral growth process, carried out at temperatures ranging from 850°C to 1000°C, was used to achieve epitaxial films using W(CO)$_6$, H$_2$Se and H$_2$S as precursors in a H$_2$ carrier gas. Nucleation was observed to occur at the terrace edge and the growing domains align epitaxially with the underlying (0001) sapphire lattice. As a result of the nucleation process, the domains grow with a zig-zag edge facing the terrace edge which imparts a preferential direction to the domains. The percentage of domains with a preferred direction ranges from 75%-86% depending on MOCVD growth conditions. Continued lateral growth for times ranging from 10-30 minutes results in fully coalesced TMD monolayers that are epitaxially oriented on the sapphire, as assessed by in-plane x-ray diffraction, with a reduced density of inversion domain boundaries. The results demonstrate the important role of surface structure in nucleation and epitaxial growth of TMD monolayers.
MOLYBDENUM DISULFIDE BASED SYNAPTIC DEVICE FOR NEUROMORPHIC COMPUTING

Presenting Author: Sungjun Kim

Topic: 2D materials, surfaces and interfaces

Format: Contributed

Session: 4, 2

Date: 8/4/2021

Time (in MDT): 3:15:00 PM

Authors: Sungjun Kim, Sungkyunkwan University, Suwon, Korea, Republic of; Jin-Hong Park, Sungkyunkwan University, Suwon, Korea, Republic of; Keun Heo, Jeonbuk National University, Jeonju, Korea, Republic of

Here, we investigate the effects of the formation temperature of a ferroelectric material and the nature of the contact metals on the operating performance of a FeFET-based artificial synapse, in terms of its updating energy, dynamic range (DR), nonlinearity (NL), symmetricity, cycle-to-cycle variation (CCV), and relative standard deviation (RSD) in the long-term potentiation and depression (LTP/D) characteristic curves. The synaptic device consists of poly(vinylidene fluoride-trifluoroethylene) (P(VDF-TrFE)) as a gate dielectric and molybdenum disulfide (MoS$_2$) as a channel material. These materials have a very low amount of surface defects due to the absence of dangling bonds, thereby providing a gate-channel interface with very few defects. Subsequently, we also study the influence of the synapse characteristics on the training and recognition performance of a multi-layer perceptron (MLP)-based neural network by using handwritten digits MNIST database.
ULTRATHIN GAN CRYSTAL REALIZED THROUGH NITROGEN SUBSTITUTION OF LAYERED GAS

Presenting Author: Jun Cao

Topic: 2D materials, surfaces and interfaces

Format: Contributed

Session: 4, 3

Date: 8/4/2021

Time (in MDT): 3:30:00 PM

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Bulk GaN has been utilized as an important wide bandgap semiconductor in many applications, especially in high-power electronics. Two-dimensional (2D) GaN, with enlarged bandgap compared to the bulk counterpart, offers great promise to enhance existing functions and brings new opportunities for compact electronics. Although several methods have been developed to synthesize 2D GaN recently, their practical applications are hampered by either harsh growth conditions (e.g., high temperature and ultrahigh vacuum) or lacking control of the thickness of ultrathin GaN with both high crystallinity and satisfactory area. Here, we report the synthesis of few-nanometer thin GaN crystals via \textit{in situ} atomic substitution of layered GaS flakes at a relatively low temperature (590 °C). GaN with tunable thicknesses from 50 nm down to 0.9 nm (two atomic layers) is achieved by applying the atomic substitution reaction to GaS with different numbers of layers. The as-synthesized ultrathin GaN flakes retain morphology inherited from the GaS flakes and show high crystallinity. From photoluminescence (PL) spectroscopy measurements, we observe the band edge PL of 2D ultrathin GaN is blue-shifted as compared with bulk GaN, suggesting the increased bandgap with the decrease of thickness. This work demonstrates a promising way to access ultrathin GaN of high crystallinity and tunable thicknesses under mild growth conditions, paving the way for its future explorations on fundamental physics and device applications.
Towards a Mechanistic Understanding of the Formation of 2D-GaN Via MOCVD

Presenting Author: Anushka Bansal

Topic: 2D materials, surfaces and interfaces

Format: Contributed

Session: 4, 4

Date: 8/4/2021

Time (in MDT): 3:45:00 PM

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Recent work has experimentally demonstrated a pathway to artificially stabilize 2D forms of traditionally 3D group-III nitrides by encapsulating them between epitaxial graphene (EG) and SiC. Using metalorganic chemical vapor deposition (MOCVD), gallium adatoms delivered to the surface using trimethylgallium (TMGa) as a precursor, penetrated between EG and the SiC substrate and were transformed into 2D GaN\(_{x}\) via exposure to ammonia (NH\(_{3}\)) at moderate temperatures. It was found that defects in the graphene layer formed prior to intercalation using He/O\(_2\) plasma treatment plays a key role as they enable large lateral coverage area of intercalant, but the nature of the defects has remained elusive. Moreover, EG is grown by heating SiC substrates to temperatures above 1200°C under ultra-high vacuum that results in the sublimation of Si atoms from the SiC surface, leading to the surface reconstruction of C atoms forming graphene. Since the EG formation process depends on sublimation and surface reconstruction which are impacted by the presence of SiC surface steps, the number of layers of EG varies across the sample surface. Such non-uniformity in the EG thickness can directly impact defect formation and intercalation processes for Ga and N. In this study, the impact of graphene thickness on the defect formation and 2D-GaN\(_{x}\) intercalation is investigated. It is found that the nature of defects formed using He/O\(_2\) plasma treatment depends on the EG thickness on SiC. Thinner regions of graphene get chemically functionalized with O forming C=O, C-OH bonds, whereas thicker regions of graphene do not get chemically modified. The oxygen functionalized defective thinner graphene is found to be crucial for the formation of 2D GaN\(_{x}\) at the EG/SiC interface. In the absence of NH\(_{3}\) exposure, Ga intercalates in regions of thicker, non-functionalized defective graphene and the thinner chemically functionalized regions result in Ga droplet aggregation on the surface but negligible intercalation. However, in presence of NH\(_{3}\) exposure, Ga and N both intercalate in the thinner regions of oxygen functionalized defective graphene leading to the formation of 2D-GaN\(_{x}\) at the EG/SiC interface, while thicker regions of graphene have 2D-Ga only intercalated. By modifying
the EG process to produce thin buffer layer graphene, uniformly intercalated 2D-GaN\(_x\) can be obtained across most of the substrate surface. Further studies are underway using density functional theory (DFT) and reactive force field (ReaxFF) modeling to understand the direct correlation between defect type and adatom intercalation (Ga,N) leading to the formation of 2D-GaN\(_x\).
HIGH TEMPERATURE CONVERSION AND CRYSTALLIZATION OF BORAZINE BASED HBN FILMS

Presenting Author: Jeffrey Kronz

Topic: 2D materials, surfaces and interfaces

Format: Contributed

Session: 4, 5

Date: 8/4/2021

Time (in MDT): 4:00:00 PM

Authors: Jeffrey W. Kronz, The Pennsylvania State University, University Park, Pennsylvania, United States
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Hexagonal boron nitride (hBN) is an attractive 2D material due to its insulating properties and layered 2D form. hBN films are traditionally grown by chemical vapor deposition on transition metal or insulating substrates, such as sapphire, by a direct deposition from multiple vapor-phase sources. An alternative approach employs a two-step single source process whereby a borazine film is deposited at low temperature and is followed by high temperature annealing to convert and crystallize into hBN. This allows for a stoichiometric deposition without the need to balance multiple precursors while utilizing a less toxic source. Once deposited, borazine follows a direct reaction path to form an amorphous BN film through dehydrogenation restructuring. Post-deposition high temperature annealing offers additional energy, which allows for the crystallization of amorphous BN, thus forming hBN. In this study, the effects of annealing temperature and time on borazine conversion to BN and subsequent crystallization into hBN were investigated. Raman spectroscopy demonstrated that the hBN $E_{2g}$ mode at 1367 cm$^{-1}$ increased in intensity and decreased in full-width half maximum (FWHM) up to 1400 °C. However, there was material loss from both the film and substrate, suggesting that annealing the borazine films above 1400 °C without fully completing the dehydrogenation process will cause the residual hydrogen in the film to react and etch both the BN film and sapphire substrate underneath. Scanning electron microscopy images revealed etching occurred only where the film was present on the sapphire substrate further supporting that the residual hydrogen in the borazine films is the cause of the etching. Using this information, we were able to demonstrate that by increasing the annealing time at lower temperatures the hydrogen etching can be mitigated which allowed for films to survive up to 1500 °C. Additionally, the hBN films displayed improved crystallinity when examined via x-ray diffraction. These results offer a direct route towards forming large area crystalline hBN using a single source method.
DIRECTIONAL ETCHING FOR HIGH ASPECT RATIO NANO-TRENCHES IN HEXAGONAL BORON NITRIDE BY CATALYTIC METAL PARTICLES

Presenting Author: Chen Chen

Topic: 2D materials, surfaces and interfaces

Format: Contributed

Session: 4, 6

Date: 8/4/2021

Time (in MDT): 4:15:00 PM

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Stimulated by the attractive performance of multi-dimensional heterostructures involving hexagonal boron nitride (\(<i>h</i>\)BN), intense attentions have been paid to creation of sharp boundary/interface, which theoretically could bring \(<i>h</i>\)BN nanostructures additional appealing physical properties. However, the lack of precise approach of synthesis limits further experimental investigation on \(<i>h</i>\)BN nano-structure. Here, we report systematic investigations on the directional etching of transitional metal nano-particles (NPs) on the surface of \(<i>h</i>\)BN to produce nano-trenches with sharp edges. It is found that, only Pt and Ir NPs can produce armchair-oriented nano-trenches at low \(H_{2}\) partial pressure, while other transition metals lead to zigzag-oriented nano-trenches. The density and width of the nano-trenches always increase with temperature and solution concentration while the etching orientation depends on both \(H_{2}\) partial pressure and temperature. The aspect ratio of nano-trenches may reach several thousand under optimized conditions. Our method shines a light on precise patterning of 2D crystals.
A NOVEL 200MM SILICON CARBIDE EPITAXIAL REACTOR FOR POWER DEVICES: EQUIPMENT AND PROCESS PROSPECTIVE

Presenting Author: Danilo Crippa

Topic: Advanced Crystal Growth Technology and Equipment

Format: Invited

Session: 3, 1

Date: 8/2/2021

Time (in MDT): 1:00:00 PM

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LPE is a small-medium enterprise based in Milan with almost 50 years of experience in Power Management equipment for silicon and silicon carbide. LPE has an application lab in Catania where the development of silicon carbide technology started in 2001. PE108, Fig. 2, is the last generation tool for silicon carbide substrate production. It embodies the know-how resulting from the continuous improvement of the previous equipment, leading, at the same time, the path to novel process opportunities. Those include the ability to process 200 mm silicon carbide substrates featuring a fully automated Cassette-to-Cassette (C2C) module, combined with a new generation high-temperature loading system aimed at minimizing the wafer transfer time. State-of-the-art real-time automation makes it ready for Industry 4.0, combining the flexibility needed in labs and the ease of use required in mass production. A basic process on 200 mm substrate has been anticipated in a prototype reactor (ACiS-M10) with a similar process chamber, yet equipped with a simpler gas flow injection and manual wafer loading. Thickness uniformity, evaluated on 49 points with an FTIR equipment, is around 0.8%. Type $<i>n</i>$ doping uniformity, evaluated on 49 points with a CV mercury probe, is outstanding in a 20 mm edge exclusion area. The upgrade of the gas injection system is expected to extend the same performance to the 5 mm edge exclusion area as well (Fig. 1). Tab. 1 summarizes process performances details. New results will be ready by the first half of 2021.

![Image](http://files.abstractsonline.com/CTRL/44/B/2E1/C0C/57A/48C/5A3/7A0/BD6/9B9/71E/BE/g1338_1.jpg)

![Table](http://files.abstractsonline.com/CTRL/44/B/2E1/C0C/57A/48C/5A3/7A0/BD6/9B9/71E/BE/g1338_1.jpg)

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New results will be ready by the first half of 2021.
No. points | edge exclusion | (Max-min)/avg | sigma/avg
----|----------------|------------|---------
49 | 5mm | 13.9% | 5.6% |
49 | 20mm | 2.5% | 0.9% |

Fig. 2: PE108 epi reactor
THERMAL LASER EPITAXY OF OXIDE FILMS

Presenting Author: Dong Yeong Kim

Topic: Advanced Crystal Growth Technology and Equipment

Format: Contributed

Session: 3, 3

Date: 8/2/2021

Time (in MDT): 1:30:00 PM


The growth of high-quality oxide heterostructures demands precise control of the deposition parameters and a high purity of the source materials. Thermal Laser Epitaxy (TLE) has been proposed as a promising technique for the growth of oxide heterostructures fulfilling these requirements. TLE utilizes thermal evaporation of pure elemental sources by laser-induced local heating. TLE therefore combines the advantages of molecular beam epitaxy and pulsed laser deposition. In the presentation, we show a variety of binary oxide thin films deposited by TLE from pure metal sources under oxidizing conditions. From sublimating elements to refractory elements, a wide range of elemental sources form polycrystalline oxide thin films on unheated Si (100) substrates. We will also demonstrate the first epitaxial growth of binary oxide films by TLE. In this heteroepitaxial growth, the films were deposited on laser-heated oxide substrates. Our results evince that TLE is well suited for oxide film growth and has a great potential for the epitaxy of oxide heterostructures.
PUSHING THE BOUNDARY ON NITRIDE-SYNTHESIS EQUIPMENT TECHNOLOGY

Presenting Author: Siddha Pimputkar

Topic: Advanced Crystal Growth Technology and Equipment

Format: Invited

Session: 3, 4

Date: 8/2/2021

Time (in MDT): 1:45:00 PM

Authors: Siddha Pimputkar, Lehigh University, Bethlehem, Pennsylvania, United States

Nitrides are a fascinating class of functional materials, though are still largely unexplored due to stringent synthesis constraints: of the 447 predicted thermodynamically stable ternary nitrides less than have been synthesized. New approaches and improved equipment designs are required to extend our ability to access unexplored synthesis parameter space. Even for currently synthesized nitrides, in particular group III-nitrides (III-N), further refinement and developments are needed to further scale, increase growth rates, improve upon the material quality and reduce cost of their synthesis to further promote technological advances. Three different advances in technology used for the synthesis of single-crystal nitrides will be discussed: new autoclave technologies for ammonothermal growth of nitrides, new in situ technologies for Na-flux growth of nitrides and the development of a novel high-pressure spatial chemical vapor deposition (HPS-CVD) tool designed to operate up to 100 atm. Examples of GaN synthesis using the former two approaches will be presented along with the strengths of the new autoclave and system designs. The latter approach will be presented by way of an overview of the new synthesis platform along with current, preliminary computational fluid dynamics (CFD) modeling of the internal chamber intended to be used for prototyping the apparatus.
FABRICATION OF NIR TRIGGERED AND NIR EMITTING DOWN CONVERSION SYSTEM - A CANDIDATE FOR OPTICAL IMAGING APPLICATION

Presenting Author: Karthickraja D.

Topic: Advanced Crystal Growth Technology and Equipment

Format: Contributed

Session: 3, 6

Date: 8/2/2021

Time (in MDT): 2:15:00 PM

Authors: Karthickraja D., Periyar University, Salem, India Karthi S., Henan University, Kaifeng, China Kumar G.A., University of Texas at San Antonio, San Antonio, Texas, United States Girija E.K., Periyar University, Salem, India

FABRICATION OF NIR TRIGGERED AND NIR EMITTING DOWN CONVERSION SYSTEM: A CANDIDATE FOR OPTICAL IMAGING APPLICATION

Bioimaging refers to noninvasive visualization of the living tissues. When compared to conventional imaging modalities, optical imaging mode has gained the attention of researchers owing to its advantages including low cost, portability, nonionizing radiation, high sensitivity and resolution, real time imaging, fast data acquisition and possibility for multimodal imaging. Advanced developments in the past decades include fluorescent quantum dots (QDs) and rare earth ions doped inorganic nanoparticle contrast agents. Despite the advantages like biological and photostability in addition to tunable emission wavelength and improved penetration depth QDs suffer from the concern of toxicity issue to living tissues. Some major issues in fluorescence imaging involve autofluorescence, low penetration depth etc. To circumvent these limitations there is demand for the development of near infrared (NIR) excited and NIR emissive biocompatible fluorescence probes. By utilizing NIR-to-NIR Stokes luminescent process and systematic engineering of a biocompatible nanoparticle the advantage of the NIR biological window region added to deep tissue penetration, low background noise, and low phototoxicity can be achieved. Here, we report the synthesis of optimum concentration of Nd<sup>3+</sup> and Yb<sup>3+</sup> doped calcium fluoride (CaF<sub>2</sub>) nanoparticles by wet precipitation method. Optical characterization of the nanoparticle revealed that in spite of the fact that the energy transfer takes place from Nd<sup>3+</sup> to Yb<sup>3+</sup>, the intensity of emission was found to be weak which is due to the generation of lattice defects associated with the doping of trivalent cations (Nd<sup>3+</sup> and Yb<sup>3+</sup>) for divalent host cations (Ca<sup>2+</sup>). Tailoring these defect centres by charge compensation approach through co-doping optimum concentration of monovalent Na<sup>+</sup> ion and optimizing the heat treatment duration resulted in significant enhancement of emission intensity and life time. Penetration depth obtained from <i>ex vivo</i> fluorescence imaging experiment was 14 mm. The fabricated phosphor may be a potential contrast agent for deep tissue NIR imaging.
Recent advances in techniques for growing and characterising evermore perfect crystals of a wide range of novel quantum materials lie at the roots of much of today's advanced technology. The main challenges in bulk crystal growth often come from high melting point, anisotropic segregation and an incongruent phase diagram. To overcome this task new instrument development is needed; it will open a new avenue in bulk growth particularly with oxide and intermetallic compounds. In this talk we will highlight some of the capabilities added to the optical floating-zone technique enabling us to grow higher valency state transition metal oxides under high oxygen partial pressure.
INVESTIGATION OF LASER-INDUCED PHASE-SEPARATED DROPLET OF AQUEOUS GLYCINE USING NON-PHOTOCHEMICAL LASER-INDUCED NUCLEATION AND DYNAMIC LIGHT SCATTERING

Presenting Author: Omar Gowayed

Topic: Advanced Crystal Growth Technology and Equipment

Format: Contributed

Session: 4, 3

Date: 8/2/2021

Time (in MDT): 3:30:00 PM

Authors: Omar Yasser Gowayed, New York University, Brooklyn, New York, United States Tahany Moosa, New York University, Brooklyn, New York, United States Angelica Moratos, New York University, Brooklyn, New York, United States Tianyi Hua, New York University, Brooklyn, New York, United States Tasfia Tasnim, New York University, Brooklyn, New York, United States José Fuentes-Rivera, New York University, Brooklyn, New York, United States Stephen Arnold, New York University, Brooklyn, New York, United States Janice Aber, New York University, Brooklyn, New York, United States Bruce Garetz, New York University, Brooklyn, New York, United States

Tightly focusing a continuous-wave, near-infrared laser beam at the air/solution interface of a mm-thick layer of glycine in D₂O forms a crystal through a nucleation process known as gradient-force laser-induced nucleation. However, when this same beam is focused at the glass/solution interface of a film of aqueous glycine a laser-induced phase-separated (LIPS) solution droplet is formed instead. In addition to providing insight into the light-matter interactions of glycine nanodroplets in solution, the LIPS droplet has peculiar properties: it is visible beyond the focal region of the attracting beam, it has much higher glycine concentration than the surrounding solution, and it does not nucleate for as long the laser is focused at the glass/solution interface. In order to better understand the LIPS droplet, two optical experiments were conducted: (1) nonphotochemical laser-induced nucleation (NPLIN) of a LIPS droplet using a single near-infrared (NIR) unfocused high-powered (0.4 GW/cm²) nanosecond laser pulse and (2) dynamic light scattering (DLS) of a LIPS droplet using a low-power continuous-wave (cw) blue laser beam (5 mW/cm²) and a modular, custom built, in-situ DLS apparatus. The NPLIN experiments revealed that NPLIN could nucleate crystals within a LIPS droplet and that the LIPS droplet was observed to be more labile to spontaneous nucleation than a control solution for the first 40 min of relaxation. The resulting crystals were analyzed using powder X-ray diffraction, and 100% of crystals formed within the LIPS droplet induced by NPLIN and by spontaneous nucleation were α-glycine. Additionally, the observation of nanodroplets in motion through DLS revealed that the application of optical tweezers at the glass/solution interface forms a relatively monodisperse collection of large nanodroplets (&lt 400nm) concentrated around the focal point of the beam with smaller particles (&gt 100nm) expelled from the LIPS droplet within the first two minutes of laser exposure. These experiments allow for a better understanding of the LIPS droplet and the interaction of optical tweezers with nanodroplets and nanoclusters in solution. This understanding will help in studying the fundamental nature of metastable nanodroplets. More practically, laser-induced phase-separation makes possible the nucleation-free separation of large nanodroplets from small clusters, facilitating materials technologies such as high purity, polymorphically selective
nucleation of crystals and co-crystals used for pharmaceuticals, dyes, and photovoltaics.
EXPLORING A NEW CLASS OF EXPERIMENTS TO STUDY DYNAMICS IN DOPED AND UNDOPED Na<sub>x</sub>CoO<sub>2</sub> BULK SINGLE CRYSTALS GROWN BY OFZ TECHNIQUE

Presenting Author: Uthayakumar Sivaperumal

Topic: Advanced Crystal Growth Technology and Equipment

Format: Contributed

Session: 4, 4

Date: 8/2/2021

Time (in MDT): 3:45:00 PM

Authors: Uthayakumar Sivaperumal, Department of Physics, Royal Holloway University of London Egham, TW20 0EX, United Kingdom and ISIS Pulsed Neutron and Muon Source, STFC Rutherford Appleton Laboratory, Didcot, Oxfordshire OX11 0QX, United Kingdom. Dan Porter, Diamond Light Source, Harwell Science and Innovation Campus, Didcot, Oxfordshire OX11 0DE, United Kingdom. David Voneshan, Department of Physics, Royal Holloway University of London Egham, TW20 0EX, United Kingdom and ISIS Pulsed Neutron and Muon Source, STFC Rutherford Appleton Laboratory, Didcot, Oxfordshire OX11 0QX, United Kingdom. Jon Goff, Department of Physics, Royal Holloway University of London Egham, TW20 0EX, United Kingdom.

Exploring a new class of Experiments to study dynamics in doped and undoped Na<sub>x</sub>CoO<sub>2</sub> bulk single crystals grown by OFZ technique

S.Uthayakumar<sup>1</sup>, D. G. Porter<sup>2</sup>, David J. Voneshan<sup>1</sup> and J P Goff<sup>3</sup> <sup>1</sup>Department of Physics, Royal Holloway University of London Egham, TW20 0EX, UK and ISIS Pulsed Neutron and Muon Source, STFC Rutherford Appleton Laboratory, Didcot, Oxfordshire OX11 0QX, UK. <sup>2</sup>Diamond Light Source, Harwell Science and Innovation Campus, Didcot, Oxfordshire OX11 0DE, UK. <sup>3</sup>Department of Physics, Royal Holloway University of London Egham, TW20 0EX, UK. The research on thermoelectric (TE) materials is one of the most rapidly-growing research areas in materials science. Semiconductor TE which encompass elements that are harmful, such as Pb,Bi or Sb have essentially reached the limit of their development from a materials perspective. Therefore the synthesis of new TE materials with improved performance are mandatory to identify new sustainable energy solutions. Oxide based TE have recently emerged as an attractive alternative, since they are environmentally clean. The development of Na<sub>x</sub>CoO<sub>2</sub> is particularly promising, since it has emerged as among the best P-type TE materials, where the shortage of alternatives is particularly acute [1,2]. To achieve large power factor we adopted doping strategy which eventually led to a reasonable improvement in the electrical conductivity and also lowered the thermal conductivity by modifying the electronic structure. Doping Na<sub>x</sub>CoO<sub>2</sub> with divalent ions was reported to lead to dramatic improvement in the thermoelectric performance [3-5]. In our previous neutron Laue diffraction measurements evidenced a kaleidoscope of Na ion patterns as a function of Na 'x', and we were able to rationalise the magnetic and TE properties which are responsible for the TE performance [6,7]. The present study is to optimize the growth conditions and study the fundamental properties of doped Na<sub>x</sub>CoO<sub>2</sub> bulk single crystals on the atomic scale. This study also likely to have
MODIFIED FZ TECHNIQUE FOR OXIDES CRYSTAL GROWTH

Presenting Author: Michael Gonik

Topic: Advanced Crystal Growth Technology and Equipment

Format: Poster

Session: ,

Date:

Time (in MDT):

Authors: Michael Gonik, Centre for Material Researches, Alexandrov, Russian Federation Florin Baltaretu, Technical University of Civil Engineering, Bucharest, Romania

Mostly, the oxide crystals are grown with use of containers made of noble metals. It means that any appreciable overheating of a melt causes its significant evaporation and dissociation yielding in strong interaction of the oxide products with the container material. As a result, the container exposed to be damaged, with a metal being incorporated into the melt and influencing the origination a number of defects in the growing crystal. Such an effect is more typical for the Cz technique, which is characterized by the intensive convection, large open melt surface and high temperature of the crucible walls, especially, in case of inductive heating. From this point of view, the best variant is to grow crystal from the thin melt layer in the presence of the submerged heater providing temperature control in the melt-crystal interface vicinity. Such an approach in FZ configuration was previously successfully applied in Si crystal growth [1]. Now we offer this technique for oxides growth by using a special design of the heater with a casing made of Pt, Rh or Ir. The melt under the heater is suspended by forces of surface tension, while charge from above is realized by melting the feeding rod. To better supply the growth process with fresh melt, the heater, unlike the similar AHP one [2], has a through-hole along its centerline and two heaters elements on the both top and bottom surfaces of it. Besides, the heater may have the arbitrary shape, for example, square one to fit those used in a device. Based on the example of TeO$_2$, steady-state meniscus stability, as well as the melt flow dynamics in process are considered in the paper. The mathematical 2D axisymmetric model taken into account continuity equation, laminar flow (Navier-Stokes), including surface tension effects, the equation for the transport of the fluid interface. The Level Set Method applied for a two-phase gas-liquid domain allows the smooth variation of density and dynamic viscosity across this interface. The numerical calculations, from one hand, made it possible to estimate the appropriate value of the heater height, as well as relations of the translating rate for top and bottom rods to provide the modes of enlarged and constant diameter during the crystal growth.[1] M.A. Gonik and A. Cröll. CrystEngComm, 2013, 15 (12), 2287-2293.[2] V.D. Golyshev, M.A. Gonik, V.B. Tsvetovsky, J. Cryst. Growth, 198/199, 1999, p.501-506.
GALLIUM DOPED SILICON THROUGH CHANNELS PROCESSED BY THERMOMIGRATION

Presenting Author: Boris Seredin

Topic: Advanced Crystal Growth Technology and Equipment

Format: Poster

Session:

Date:

Time (in MDT):

Authors: Boris Seredin, Platov South-Russian State Polytechnic University (NPI), Nowocherkassk, Russian Federation; Andrey Lomov, Valiev Institute of Physics and Technology of RAS Russia, Moscow, Russian Federation; Stepan Martyushov, Technological Institute for Superhard and Novel Carbon Materials, Troitsk, Russian Federation; Alexander Malibashev, Platov South-Russian State Polytechnic University (NPI), Nowocherkassk, Russian Federation; Victor Popov, Platov South-Russian State Polytechnic University (NPI), Nowocherkassk, Russian Federation

An array of through vertical $p$-channels in single-crystal silicon wafers can be get by thermomigration (Temperature gradient zone melting -ThM). By aluminum thermomigration concentration of acceptors is $\sim 10^{19}$ cm$^{-3}$ (ThM at 1400K) are created usually. It is known that the concentration can be extended by using gallium atoms as a ligature. Technical problem associated with gallium instabilities of migrating molten zone what make difficulties for using in thermomigration process. In this work we present a process to create gallium zones on silicon plate. Chemical etched parallel grooves 100μm width and 50μm depth were filled with gallium micropowder and its melting were carried out in a vacuum at a temperature of $\sim 350$ K. The reasons leading to defectiveness of gallium zone were clarified: incomplete filling of the recess with the charge, powder sticking to the masking coating, uneven filling of the recess. It is shown that the observed defects of the zones are related to the particle size, the temperature of the crucible heating, and the speed of plate movement. The sample with gallium doped channels in the matrix of the silicon plate Si(111) were obtained in vacuum. The channels were formed based on the technique proposed above at $T(\text{ThM}) = 1400$–$1500$ K, and $G = 50$–$100$ K/cm for 60 min. The characterization of samples with stably moving gallium molten zones were performed by the X-ray rocking curve (Bragg geometry, 333 reflection, copper radiation) and projection Lang topography on silver radiation. We found that a characteristic type of structural defects near channel on surface wafer is half-loops dislocations. The values of deformations ($10^{-5}$ - $10^{-4}$) in the channels and crystal plane tilt (20-30 arcsec) at the boundary of the channel close to its appearance on the surface of the plate are determined. The gallium concentration equal to $C_{\text{Ga}} \sim 1.9 \times 10^{19}$ cm$^{-3}$ is get. It shows that, under equal conditions, the concentration of acceptor impurity in the $p$-channel of gallium is twice as high as aluminum. Experimental studies of the electrophysical properties of the obtained vertical Si(Ga) $p$-channels are carried out. It is found that their electrical conductivity ($\sim 0.02$ ohms cm) is proportional to the impurity concentration in the channel and the aspect ratio of the channel width to its length. The barrier electrical capacity of the $p$-$n$ junctions adjacent to them is estimated, its values are in the range of 10-100 pF.
BIO-INSPIRED MINERALIZATION FOR MEDICAL APPLICATIONS

Presenting Author: Helmut Coelfen

Topic: Biological and Biomimetic Materials

Format: Invited

Session: 2, 1

Date: 8/2/2021

Time (in MDT): 10:30:00 AM

Authors: Helmut Coelfen, University of Konstanz, Konstanz, Germany

Biomineralization yields materials with unsurpassed properties although they are usually made of materials with poor properties like calcium carbonate or phosphate or silica. The secret is the precisely engineered organic-inorganic hybrid structure, which is often hierarchical over several levels. Therefore, Biominerals can serve as valuable archetypes for useful materials. In this presentation, examples will be given, how Bioinspiration can lead to advanced materials for medical applications.

The first example is dental materials based on polyacrylic acid-calcium coacervates and polyallylamine-phosphate coacervates. It is shown that these materials form a continuous interface with the existing tooth and therefore demonstrate their potential for dental application.

The second example is a bio-inspired material targeted to replace amalgam as dental tooth filling material. It is built from a gelatin-hydroxyapatite composite, which is crosslinked and supplemented by a calcium phosphate cement resulting in a material with the mechanical properties of dentin. First applications as a root sealer are shown.

The third example is osseointegrative coatings for bone implants inspired by bone. Bone-inspired materials based on gelatin, but also on polysaccharides as well as purely synthetic implant coatings are shown.
GIANT BIOMINERALS

Presenting Author: Hermann Ehrlich

Topic: Biological and Biomimetic Materials

Format: Invited

Session: 2, 4

Date: 8/2/2021

Time (in MDT): 11:15:00 AM

Authors: Hermann Ehrlich, TU Bergakademie Freiberg, Freiberg, Germany

Giant bones of whales (Cetacea) represent the largest biomineral-based constructs known. The existence of such macrobiominerals with still unknown mechanisms for biomineralization, is an example of a groundbreaking phenomenon unexplored in nature. The goal is to study how the manipulation of inorganic materials by organic macromolecules enables cetaceans to create enormous biominerals, where occlusion of biomacromolecules within individual crystals generates superior hyperdense, or, alternatively, macroporous hierarchically structured architectures with specific mechanical properties which definitively played significant roles in the survival of the largest mammals on Earth over the 60 million years of their evolution. By focusing on two different biomineralogical scenarios, hypermineralized and lipid-rich, porous bones, our research strategy will bring together an array of disciplines ranging from anatomy, palaeontology, biomineralogy, chemistry, to solid-state physics, materials science and even biomimetics. Consequently, our objective with regard to “large-scale biomimetics” includes the goal of proposing the key way for industrial production and design at ambient conditions of “3D Ca-lipid-collagen composites” using naturally occurring sources of each component, is a challenging task. However, the fact that whale bones represent examples of large-scale biocomposites which has been synthesized in situ at 36.6°C highly motivate us to resolve these outstanding questions.
MORPHOLOGICAL COMPLEXITY OF GROWING CALCITE CRYSTALS DURING COCCOLITH FORMATION

Presenting Author: Assaf Gal

Topic: Biological and Biomimetic Materials

Format: Contributed

Session: 2, 6

Date: 8/2/2021

Time (in MDT): 11:45:00 AM

Authors: Assaf Gal, Weizmann Institute of Science, Rehovot, Israel Emanuel M. Avrahami, Weizmann Institute of Science, Rehovot, Israel

The ability of organisms to produce inorganic minerals with elaborate morphologies has fascinated scientists for centuries. Coccolithophores are an abundant group of unicellular algae that cover themselves in such biominerals, composed of calcite crystals, known as coccoliths. Coccoliths are produced intracellularly in a specialized vesicle, and highly vary in shape, size and number between different species. Although the alternating nucleation pattern was elucidated, it does not account for the fascinating stages of coccolith growth, in which the crystal units gradually interlock. In order to investigate the morphogenesis of the coccolith crystals, we extracted intracellular coccoliths at arrested growth stages. We utilized the heavily calcifying species <i>Calcidiscus leptoporus</i>, and investigated its growing coccoliths using SEM, TEM and STEM-tomography. The results provide high-resolution 3D data of the growing coccoliths at several growth stages, showing the gradual departure in crystal shape from small rhombs to the ultimate labyrinthine, interlocking units. Interestingly, the complex crystal morphology is the result of anisotropic growth of the stable rhombohedral facets of calcite without any other set of crystallographic planes. We propose that in the confined volume of the coccolith vesicle local chemical conditions can lead to anisotropic growth of chemical equivalent crystal facets that result in the convoluted morphology.
HOW ADDITIVES CONTROL THE STABILITY AND CRYSTALLIZATION PATHWAYS OF AMORPHOUS CALCIUM CARBONATE

Presenting Author: Zhaoyong Zou

Topic: Biological and Biomimetic Materials

Format: Contributed

Session: 3, 1

Date: 8/2/2021

Time (in MDT): 1:00:00 PM

Authors: Zhaoyong Zou, Wuhan University of Technology, Wuhan, China, Zhengyi Fu, Wuhan University of Technology, Wuhan, China

Amorphous calcium carbonate (ACC) is widely known as a metastable precursor for the formation of crystalline biominerals with unique morphologies and remarkable mechanical properties. It has been shown that biological macromolecules and inorganic ions are critical in directing the formation and transformation of ACC, however, the underlying mechanisms are not yet clear. Here, I will present our recent work unravelling the effect of different additives on the stability and crystallization pathways of ACC. For the stability of ACC, we show that while adsorption of poly(Aspartic acid) (pAsp) on the surface of ACC nanoparticles is effectively inhibiting calcite nucleation from the surface, bulk incorporation of inorganic ions like phosphate ions act to modify the ion mobility therefore delaying crystal propagation. For the crystallization pathways in solution, we find that both phosphate ions and pAsp are effective in stabilizing the surface of ACC nanoparticles and can promote the formation of calcite via a particle attachment crystallization mechanism or vaterite via a pseudomorphic transformation mechanism. Thus, new insights on controlling the stability and crystallization processes of amorphous materials are provided and it may have great implications for understanding the biomineralization process.
DESIGNED INTERFACES BETWEEN PROTEINS AND INORGANIC CRYSTALS FOR TEMPLATED ASSEMBLY AND CO-ASSEMBLY

Presenting Author: Sakshi Yadav

Topic: Biological and Biomimetic Materials

Format: Contributed

Session: 3, 2

Date: 8/2/2021

Time (in MDT): 1:15:00 PM


Previously (Pyles, H., Zhang, S., De Yoreo, J.J., Baker, D.; Nature 2019) we have shown we could use Rosetta to design proteins that exhibited a lattice match to mineral surfaces. We discovered that we could exploit those interactions to generate a variety of ordered 2D phases (micrometer-long wires and extensive honeycomb arrays) that were strongly dependent on electrolyte type and concentration and several other factors. Comparison to Monte Carlo simulations of non-interacting colloidal rods demonstrates that these phases are not predicted and thus must result from the competition between the designed interfaces (protein-protein and protein-substrate) and the colloidal forces, while machine learning analysis shows that the orientation dependent energy landscape is both complex and also dependent on electrolyte type and concentration. Moving beyond a system of homogeneous protein building blocks, we are now using the power of co-assembly to both investigate the role of complementarity and frustration in defining order and to generate higher-order assemblies.
DAILY COCA-COLA INTAKE VERSUS THE CRYSTALLIZATION OF STRUVITE - THE MAIN COMPONENT OF INFECTIOUS URINARY STONES

Presenting Author: Jolanta Prywer

Topic: Biological and Biomimetic Materials

Format: Contributed

Session: 3, 3

Date: 8/2/2021

Time (in MDT): 1:30:00 PM

Authors: Jolanta Prywer, Institute of Physics, Lodz Univeristy of Technology, Lodz, Poland  Mikołaj Skubisz, Institute of Physics, Lodz University of Technology, Lodz, Poland  Ewa Mielniczek-Brzóska, Institute of Chemistry, Health & Food Sciences, Jan Długosz University in Częstochowa, Częstochowa, Poland

Infectious urinary stones are easily formed in the urine of humans whose urinary tract is infected with urease-producing microorganisms. Struvite crystals (magnesium ammonium phosphate hexahydrate; NH₄MgPO₄ · 6H₂O; Fig. 1, arrow 1) are the main component of these stones. In the case of this kind of stones, it is not enough to eliminate the infection itself. Microorganisms can survive in already formed stone by building into its structure. When stones are crushed, for example with high-energy ultrasound waves, microorganisms are released into the urinary tract, which causes disease recurrence after treatment in 60% of cases. The results to date indicate that even dead microorganisms can be centres of heterogeneous nucleation, accelerating the recrystallization. Additionally, in recent years, an intense increase in the incidence of infectious urinary stones has been observed, especially in populations living in highly developed countries. In these countries, urolithiasis affects up to 20% of the population, depending on the geographical region studied. The question is: what factors are associated with the progressive increase in the incidence of infectious urolithiasis in highly developed countries? In highly developed countries human may be exposed to various adverse factors originating in the environment in which human lives (water, air), originating from food, medications taken and household chemical products. Could Coca-Cola intake be such a risk factor for infectious urolithiasis? Consuming carbonated drinks in excess, especially those containing phosphoric acid, such as Coca-Cola, is associated with diseases such as hypertension and diabetes. Daily consumption of this type of beverages also has a real impact on the increased risk of developing chronic kidney diseases [1,2]. In this article, we present studies of the effects of phosphoric acid, the main ingredient of Coca-Cola and other carbonated drinks, on the nucleation and growth of struvite - the main component of infectious urinary stones. The purpose of these studies is to assess whether the consumption of this type of drink is a risk factor in relation to this type of urolithiasis.

References

[1] Y. Shutto,


ARCHITECTED BIOMINERALIZED IMPACT RESISTANT BI-CONTINUOUS NANOPARTICLES

Presenting Author: David Kisailus

Topic: Biological and Biomimetic Materials

Format: Contributed

Session: 3, 5

Date: 8/2/2021

Time (in MDT): 2:00:00 PM

Authors: David Kisailus, University of California at Irvine, Irvine, California, United States  Wei Huang, University of California at Irvine, Irvine, California, United States

Nature utilizes available resources to construct lightweight, strong and tough materials under constrained environmental conditions. The impact surface of the fast-striking dactyl club from the mantis shrimp is an example of one such composite that evolved the capability to localize damage and avoid catastrophic failure from high-speed collisions during its feeding activities [1-3]. Here we report a biomineralized composite coating composed of densely packed ~65 nm bi-continuous nanoparticles of hydroxyapatite (HAP) integrated within an organic matrix [4]. The mesocrystalline HAP nanoparticles are assembled from small highly aligned nanocrystals guided by the biomineral templating proteins. Under high strain rate (~10^4 s^-1) impacts, particles rotate and translate, while the nanocrystalline networks fracture at low angle grain boundaries, form dislocations, and undergo amorphization. The interpenetrating organic network provides additional toughening, as well as significant damping, with loss coefficient ~0.02. A rare combination of stiffness and damping is therefore achieved, outperforming many engineered materials.

STRUCTURE-MECHANICAL PROPERTIES OF THE MULTIPHASE, WEAR RESISTANT BIOMINERALIZED TEETH FROM A ROCK-GRINDING MOLLUSK

Presenting Author: Devis Montroni

Topic: Biological and Biomimetic Materials

Format: Contributed

Session: 3, 6

Date: 8/2/2021

Time (in MDT): 2:15:00 PM

Authors: Devis Montroni, UCI, Irvine, California, United States  Wen Yang, UCI, Irvine, California, United States  Taifeng Wang, UCI, Irvine, California, United States  David Kisailus, UCI, Irvine, California, United States

Biogenic materials exhibit astonishing mechanical properties compared to synthetic analogues. This difference is mostly due to the fine controlled multi-scale architectural and compositional features present in these matrices. Among them, a high damage tolerance was observed in the abrasion resistant teeth of chitons.<sup>[1,2]</sup> In this study, we characterized the composition, structure, and mechanical properties of the mineralized radular teeth of <i>Chiton articulatus</i>. This species, commonly called sea cockroach, is an herbivorous marine mollusk endemic of the rocky intertidal shores of the Mexican Tropical Pacific and has both ecological and economical importance.<sup>[3]</sup> The radular tooth of this species presents a scoop-like morphology adapted to collect coralline algae from rocky surfaces. In each tooth, a hard magnetite region was observed on the leading edge, while a softer apatite region (likely presenting a minor fluorapatite phase) was observed on the trailing edge. A transition region, composed of goethite and lepidocrocite, is present between the two regions. In the apatite region a rod-based nanostructure, organized in layers, was observed running parallel to the trailing edge and gradually bend towards the leading edge. These rods changed in composition while transitioning to the from the Ca-rich region to the Fe-rich transition region. In the magnetite region the rod-based laminated structure bends to become parallel to the leading edge and the rod morphology is substituted by particles. The analysis of the complex architecture and composition in the teeth of <i>C. articulatus</i> is a fundamental initial step in the understanding of the multiphase biomineralization of this matrix. Moreover, these unique features observed might contribute in future design of wear-resistant composite materials.<br />

STRUCTURAL DEVELOPMENT AND TOPOTACTIC PHASE TRANSFORMATION OF MESOCRYSTALLINE IRON OXIDE PHASES IN MOLLUSK TEETH

Presenting Author: Taifeng Wang

Topic: Biological and Biomimetic Materials

Format: Contributed

Session: 4, 1

Date: 8/2/2021

Time (in MDT): 3:00:00 PM

Authors: Taifeng Wang, UC Irvine, Irvine, California, United States  David Kisailus, UC Irvine, Irvine, California, United States  Wei Huang, UC Irvine, Irvine, California, United States  Wen Yang, UC Irvine, Irvine, California, United States

Biological organisms naturally synthesize complex, hierarchical, multifunctional materials through mineralization processes at ambient conditions and under physiological pH. One such example are the ultrahard and wear-resistant radular teeth found in mollusks, which are used to scrape against rock for food. Here, we reveal the biomineralization-controlled structural development of the hard, outer magnetite-containing shell of the teeth. Specifically, we identify the formation of a series of mesocrystalline iron oxide phases, templated by chitin-binding proteins. The initial mesocrystalline domains undergo a solid-state phase transformation without any noticeable architectural changes. Additional growth via Ostwald ripening is then observed to form nearly single crystalline rod-like elements. In order to corroborate our observations of mineralization in the biological system, we have synthesized magnetite nanoparticles using bioinspired polymer matrices. The results from these experiments will help to shine light on the manufacture of engineering materials with controlled microstructure for high performance applications.
Biominerals formed by living organisms exhibit excellent properties, such as photonic-crystal like properties, good wear resistance and biocompatibility. These biominerals are sometimes difficult to reproduce artificially. How do organisms synthesize such high-performance biominerals under ambient conditions? Previous studies have shown that organisms control the formation of biominerals by secreting scaffolding proteins and catalyzing proteins when and where they are needed. Revealing the proteins that regulate biomineralization will contribute to the development of novel functional materials. By using genomic-based approaches, we have identified several biomineralization-related proteins. In the first part of the talk, I will present a study on the proteins involved in silica (SiO$_2$) cell wall formation in diatoms. The unique porous architectures of silica cell wall offer promise to produce next generation materials for various applications. In this study, to identify the silica formation-related proteins that are universally present in diatoms, the first extensive comparative analysis of genes from eight diatom species was conducted. These analyses revealed a diatom-specific SET domain protein methyltransferase family as well as a novel diatom-specific silica matrix protein. Expression analysis showed that these proteins were upregulated in response to silicon, indicating that these proteins are involved in silica cell wall formation. In the second part of the talk, I will describe a recent work on the proteins involved in ultrahard teeth formation in chitons. Chitons have a feeding organ called the radular teeth, in which magnetite (Fe$_3$O$_4$) is deposited on the cusps of the large lateral teeth. It has been shown that chiton teeth exhibit the largest hardness and stiffness amongst any biological minerals. To elucidate the proteins regulating the teeth mineralization of chitons, we previously conducted transcriptome and proteome analysis of the chiton *C. stelleri* and twenty-two proteins specifically expressed in mineralized cusp that may be involved in teeth formation were identified. In this study, to clarify the teeth mineralization proteins conserved in chitons, the transcriptome data of radular tissues from five chiton species were compared. As a result, the proteins conserved between chitons that are highly expressed in radular tissues were identified. These proteins include the previously identified mineralized cusp-specific proteins and the iron storage protein. The relevance of these proteins for teeth mineralization will be discussed.
CROSSLINKING OF INORGANIC IONIC OLIGOMERS FOR NONCLASSCIAL CONSTRUCTIN OF MINERALS

Presenting Author: Ruikang Tang

Topic: Biological and Biomimetic Materials

Format: Invited

Session: 4, 5

Date: 8/2/2021

Time (in MDT): 4:00:00 PM

Authors: Ruikang Tang, Zhejiang University, Hangzhou, China  Zhaoming Liu, Zhejiang University, Hangzhou, China

Biomineralization can produce biological inorganic materials with complicated structures and optimized properties, which cannot be achieved by classical crystallization routes in laboratories. Inspired by polymeric materials with moldable dimensions and continuous structures that can be readily manufactured by crosslinking monomers or oligomers, we suggest a nonclassical construction of continuously structured inorganic materials by crosslinking ionic oligomers. Using calcium carbonate as a model, we obtain a large quantity of its oligomers, in which triethylamine (TEA) acts as a capping agent for stabilization. The removal of TEA can initiate the controllable cross-linking of the oligomers to achieve the fast construction of pure monolithic calcium carbonate and even single crystal, which is attributed to the resulting continuous internal structure. The gel-like characteristic of oligomer precursors can ensure moldable construction for materials, even those with structural complexity and variable morphologies. The discovery of ionic oligomers and their crosslinking provides a new nonclassical strategy for material construction and arises from a fusion of classic inorganic and polymer chemistry by employing the same pathway for material manufacturing. By a control of in-situ crosslinking of calcium phosphate oligomers on natural enamel, an amorphous precursor layer with continuous internal structure can be deposited to induce epitaxial phase-transformation-based crystal growth of enamel apatite, which mimics crystal-amorphous biomineralization frontier in biogenic tissue development. As a result, the damaged enamel can be recovered perfectly since the newly grown layer can share the exactly same hierarchical structure and mechanical properties as the natural enamel. Furthermore, the calcium phosphate oligomers can be injected into biological bone tissues to promote remineralization of mineral-deficient collagens, which can turn the osteoporotic bone to healthy one due to their ultrasmall size effect (less than 1 nm). These achievements follow that the nonclassical route of inorganic oligomer crosslinking provides a promising approach for artificial construction and regenerations of biominerals.
PROTEIN IONIC LIQUID BASED MATERIALS

Presenting Author: Naik Rajesh

Topic: Biological and Biomimetic Materials

Format: Invited

Session: 2, 1

Date: 8/3/2021

Time (in MDT): 10:30:00 AM

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Biology offers inspiration, solutions, and opportunities for creating biomimetic materials and devices that can address material challenges and needs. However, biological systems are limited in their ability to carry out functions, to operate outside of ambient and aqueous conditions, and optimally control the formation of non-natural materials. For example, proteins readily denature and aggregate in non-aqueous solvents and at high temperatures, rendering them inactive. Alternatively, the conversion of biomolecules into water-free protein ionic liquids has greatly expanded the ability of proteins to operate and function under non-biological conditions as well as provided new forms of biological materials. In this talk, we will discuss the use of protein ionic liquids for the stabilization of labile biomolecules, creation of functional bio-composites with inert plastics, and non-traditional synthesis of nanomaterials. In all, protein ionic liquids provide unique capabilities and new applications of biological materials.
DISORDERED FILAMENTS MEDIATE THE FIBRILLOGENESIS OF TYPE I COLLAGEN IN SOLUTION

Presenting Author: Fabio Nudelman

Topic: Biological and Biomimetic Materials

Format: Invited

Session: 2, 4

Date: 8/3/2021

Time (in MDT): 11:15:00 AM

Authors: Fabio Nudelman, University of Edinburgh, Edinburgh, United Kingdom

Collagen type I is one of the major structural proteins in mammals, providing tissues such as cornea, tendon, bone, skin, and dentin with mechanical stability, strength, and toughness. The collagen fibril is characterised by the highly organised arrangement of the molecules in staggered parallel arrays that give rise to a periodicity of 67 nm along the fibril axis. Fibril formation is a multi-scale, self-assembly process that is driven by electrostatic interactions between the molecules, leading to fibrils that can be several microns long. Little is known, however, about the self-assembling mechanisms during collagen fibrillogenesis, in particular how such ordered structures arise from the association of single molecule building blocks. This issue is fundamental to understanding the structural basis of imperfect fibril formation in congenital disorders such as <i>osteogenesis imperfecta</i>, as well as the mineralisation mechanisms during bone formation.<br />Here, we studied the mechanisms of collagen self-assembly from the molecular to the micron scales using a combination of time-resolved cryo-transmission electron microscopy (cryoTEM) and molecular dynamics (MD) simulations. We developed a coarse-grained MD model to gain insight into the first steps of self-assembly, the initial aggregation of the collagen molecules, which is not observable with electron microscopy. CryoTEM was used to characterize the different stages in the formation of fibrils by promoting fibrillogenesis <i>in vitro</i> and collecting samples at different time points, which were then plunge-frozen in liquid ethane.<br />We show that collagen assembly is a multi-step process in which the molecules first aggregate into dimers and trimers, which then organize into 4 nm-thick filaments that are devoid of short-range order. These filaments subsequently aggregate, first as disordered, loosely packed fibrils which then become denser and compact. The appearance of the 67 nm periodicity is gradual and starts with the alignment of adjacent filaments at the N-terminal end of the molecules. Our results provide significant insights in the mechanisms of collagen self-assembly, and will help us to understand the formation of collagenous tissues in the body, such as cornea, bone, skin, and tendons, as well as elucidate how mutations in the amino-acid sequence affect fibril structure.
TWO STEP NUCLEATION OF FIBRILS OF THE TUMOR SUPPRESSOR P53

Presenting Author: David Yang

Topic: Biological and Biomimetic Materials

Format: Contributed

Session: 2, 6

Date: 8/3/2021

Time (in MDT): 11:45:00 AM

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Cancer is one of the leading causes of death worldwide. The protein p53 is an important tumor suppressor and is known as the guardian of the genome. This protein is a transcription factor that binds to DNA and controls multiple signaling pathways to determine the cell fate. More than 50% of human cancers are related to mutations in the p53 DNA-binding domain. Recent studies suggest that p53 aggregation is a key factor in cancer development and the majority of the p53 mutants have an exaggerated propensity to aggregate. Mechanistic details on the nucleation and growth of p53 amyloid fibrils, however, are missing. Here we explore the aggregation mechanism of the p53 R248Q mutant by combining immunofluorescent 3D confocal microscopy of breast cancer with light scattering from solutions of the purified protein and molecular simulations to probe the mechanisms of phase behavior and aggregation. We establish that R248Q p53 forms anomalous condensates which host nucleation of amyloid fibrils. We also demonstrate that in contrast to dense liquids of other partially disordered proteins, the p53 clusters are driven by the structural destabilization of the core domain and not by interactions of its extensive disordered region. The proposed two-step aggregation pathway is supported by data on the aggregation of a protein construct in which we removed the disordered domains and left intact the ordered DNA binding domain of p53. Two-step nucleation of mutant p53 amyloids suggests means to control fibrillization and the associated pathologies through modifying the cluster characteristics. In a broader context, our findings exemplify interactions between distinct protein phases that activate complex physicochemical mechanisms operating in biological systems.
SELF-ORGANIZATION IN COMPOSITE BIOPOLYMER LIQUID CRYSTALS

Presenting Author: Weirich Kimberly

Topic: Biological and Biomimetic Materials

Format: Invited

Session: 3, 1

Date: 8/3/2021

Time (in MDT): 1:00:00 PM

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Complex mixtures of macromolecules self-organize to form the soft and active biological materials that structure the cellular cytoplasm. Ordered assemblies of cytoskeletal filaments, such as stress fibers and mitotic spindles, orchestrate the complex mechanical behavior of cells. Key to understanding these exquisite mechanics is elucidating the physical principles of self-organization in these systems. We recently reported dense condensates of cytoskeletal filaments that form liquid crystal condensed phases, where structure arises from the anisotropy of the filaments. Here, we discuss emergent self-organization in composites of these liquid crystals with biological polymers of different rigidities and activity, and the shape changes that result from confinement. Our results highlight the role of anisotropy in the self-organization of biological materials and suggest physical mechanisms of controlling shape change in bio-inspired, soft materials.
AMYLOID-LIKE AMELOGENIN NANORIBBONS TEMPLATE MINERALIZATION VIA A LOW ENERGY INTERFACE OF ION BINDING SITES

Presenting Author: Susrut Akkineni

Topic: Biological and Biomimetic Materials

Format: Contributed

Session: 3, 4

Date: 8/3/2021

Time (in MDT): 1:45:00 PM

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Protein scaffolds direct the organization of amorphous precursors that transform into mineralized tissues, but the templating mechanism remains elusive. Motivated by knowledge gaps in biomineralization of tooth enamel, wherein amyloid-like amelogenin nanoribbons guide mineralization of apatite filaments, we investigated the impact of nanoribbon structure and chemistry on amorphous calcium phosphate (ACP) nucleation. Using full-length amelogenin and peptide analogs with an amyloid-like domain, large 2D arrays of nanoribbon were self-assembled on graphite and characterized by in situ atomic force microscopy and molecular dynamics simulations. All sequences substantially reduce nucleation barriers by creating low-energy interfaces, while phosphoserines along the length of nanoribbons dramatically enhance kinetic factors associated with ion binding. Furthermore, the predicted distribution of hydrophilic residues at the amyloid-solution interface matches the structure of the multi-ion clusters comprising ACP. Therefore, nanoribbons generate energetically and stereochemically favorable interfaces for formation of apatite filaments via ACP. These findings provide crucial insights into structure-function relationships underlying amelogenin biomineralization and a generalizable system for synthesizing hybrid materials.
DIVERSE ASSEMBLY OF SHORT SEQUENCE PEPTOIDS ON MOS2

Presenting Author: Shuai Zhang

Topic: Biological and Biomimetic Materials

Format: Invited

Session: 3, 5

Date: 8/3/2021

Time (in MDT): 2:00:00 PM


Peptoid is a class of biomimetic polymer inspired by peptide, with compatible bio-functions but better thermal and chemical stabilities. It has unique capabilities for creating hierarchical assemblies at solid-liquid interfaces, serving as templates for convincing applications in molecular recognition, fabrication of bio-hybrid materials, (bio)mineralization, energy conversion, storage, and transportation of matter and information, etc. In this talk, I will present the most recent achievements of assembling short peptoid oligomers on MoS$_2$. Using substrates with different hydrophilicity and adjusting the sizes of peptoid hydrophobic side chains and the dehydration process, we demonstrated that peptoid assembly on MoS$_2$ could have diverse phases, including the monolayer hybrid film with high crystallinity, single-/multi-strands ribbons, and lamella patterns. We further found that these phases can co-exist with each other in a complicated phase diagram. It is clear that the peptoid-peptoid interaction, peptoid-solvent interaction, and peptoid-MoS$_2$ interaction, mediated by pH, play crucial roles in this multi-phase assembly. These results improve the knowledge of designing hierarchical architectures with biomolecules at solid-liquid interfaces. It also provides opportunities to optimize the performance of semiconductor devices in the future.
THE GROWTH MECHANISM AND CONTROL PARAMETERS OF AMYLOID B FIBRILS

Presenting Author: Yuechuan Xu

Topic: Biological and Biomimetic Materials

Format: Contributed

Session: 4, 1

Date: 8/3/2021

Time (in MDT): 3:00:00 PM

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The Growth Mechanism and Control Parameters of Amyloid β Fibrils

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Amyloid-β (Aβ) peptide forms fibrils and plaques in the brains of Alzheimer’s disease patients. Along with findings suggesting oligomers might constitute the neurotoxic agent, amyloid fibrillization is still extensively explored. Amyloid fibrillization is a complex process, in which structural transformation of associating protein chains accompanies aggregation. To elucidate the transition state of fibrillization, we combine time-resolved in situ atomic force microscopy with coarse-grained molecular dynamics simulations. Our experiments reveal urea increases the solubility of Aβ peptide and the growth rate of the fibrils. The behavior contradicts the common notion that higher solubility correlates with slower growth rate. We attribute this counterintuitive behavior to the presence of an activated complex, in which a monomer is nonspecifically bound to the fibril tip before transforming to a growth-competent conformation. The response of the growth kinetics to increasing urea concentration suggests up to four monomers are recruited in the transition state. The conjecture of a complex transition state is supported by the distinct growth rates of freshly-cleaved fibrils, for which a transition state consisting of a single monomer is enforced. Further tests of the transition state focused on the E22Q mutant. The Aβ E22Q exhibits a lower solubility; however, the kinetic constant increases ~15 times. Characterizations of fibril growth rates in the presence of urea and of freshly-cleaved fibrils suggested one or two frustrated monomers in the transition state. This behavior confirms the role of the E22 residue in the frustrated contacts that constrain the growth of Ab fibrils. Numerical simulations employing predictive coarse-grained protein force field (AWSEM) were combined with atomic-level MD simulations of selected configurations along the reaction coordinate for association of a monomer to the fibril end. The model results reproduce the correlation between the urea effects on the fibril stability and its rate of growth and support the conclusion of the significance of a transition state based on non-native prematurely formed contacts between the fibril end and a docked monomer.
POLYMORPH TRANSFORMATIONS AND DRUG ACTIVITY IN AMYLOID-BETA FIBRIL GROWTH

Presenting Author: Sima Mafimoghaddam

Topic: Biological and Biomimetic Materials

Format: Contributed

Session: 4, 2

Date: 8/3/2021

Time (in MDT): 3:15:00 PM

Authors: Sima Mafimoghaddam, University of Houston, Houston, Texas, United States Yuechuan Xu, University of Houston, Houston, Texas, United States Peter Vekilov, University of Houston, Houston, Texas, United States

The accumulation of the protein fragment amyloid-β (Aβ) outside neurons in the brain is one of the main hallmarks of Alzheimer’s disease. Aβ peptides can aggregate into both soluble oligomers and insoluble fibrils and plaques. In parallel with recent focus on neurotoxic Aβ oligomers and other pathology pathways, the structures and mechanism of Aβ fibril formation are still actively explored. Deeper understanding of the mechanisms of Aβ fibrillization and its response to Alzheimer’s drugs can guide us to more efficient treatments. Bexarotene, an FDA approved drug for cutaneous T cell lymphoma, is one of several small molecules that show promising results in reducing Aβ aggregates in the brain but its mechanism of action remains elusive. The bulk kinetics of fibrillization reveals that bexarotene delays the primary nucleation of fibrils without impacting secondary nucleation and growth. For molecular level insight on how bexarotene operates, we monitor the response of fibril growth to bexarotene by time-resolved <i>in situ</i> atomic force microscopy. The fibril growth rates are indifferent to bexarotene as high as 1 μM, concurrently with bulk fibrillization results. We find that Aβ fibrils generated in presence of bexarotene engage in three surprising behaviors. First, the structural details of the bexarotene fibrils diverge from that of normal Aβ fibrils, suggesting that bexarotene may enforce a distinct fibril polymorph. Second, fibrils generated in the presence of bexarotene kill primary rat hippocampal neurons almost half as efficiently as normal Aβ fibrils. Third, the rate of growth of bexarotene seeds from pure Aβ solutions correlate sublinearly with the peptide concentration and saturation occurs at higher concentrations, in contrast to the linear correlation obtained with normal seeds. We hypothesize that this nonlinear behavior manifests a unique activated complex for growth of the polymorph promoted by bexarotene. The complex delays the transformation of the Aβ monomers into their bulk fibril structure. Urea, known to impair hydrophobic contacts both in the fibril structure and in the activated complex, increases the solubility of fibrils generated in presence of bexarotene, as expected. Surprisingly, urea does not stimulate or suppress the fibril growth rates and ratifies that the activated complex employed by bexarotene seeds is unique. The suggested polymorph transformation driven by bexarotene presents a novel mode of action of drugs that suppress pathological aggregation not only in Alzheimer’s, but also for myriad distinct pathologies that originate with protein condensation.
PROTEIN CRYSTALLIZATION INDUCED BY SURFACE PLASMON RESONANCE OF GOLD NANO PARTICLES

Presenting Author: Tetsuo Okutsu

Topic: Biological and Biomimetic Materials

Format: Contributed

Session: 4, 4

Date: 8/3/2021

Time (in MDT): 3:45:00 PM

Authors: Tetsuo Okutsu, Gunma University, Kiryu, Gunma, Japan  
Asuka Ito, Gunma University, Kiryu, Gunma, Japan  
Tomohiko Sato, Gunma University, Kiryu, Gunma, Japan  
Hiroaki Horiuchi, Gunma University, Kiryu, Gunma, Japan

We studied protein crystallization induced by surface plasmon resonance. We have studied photo-induced crystallization of proteins with gold nanostructures. We found a phenomenon in which crystallization is induced by a mechanism that does not involve the reaction. This phenomenon was explained by the mechanism of molecular trap by surface plasmon resonance. Protein adsorbs on gold nanoparticles. When surface plasmon resonance of gold nanoparticles is induced, the amount of adsorption further increases. When gold nanoparticles are placed close together, gap mode plasmon resonance is induced between the nanoparticles. Crystallization is most induced when the plasmon resonance of this gap mode is induced. From this, it is concluded that the protein was trapped in the gap of the nanoparticles by the electric field generated by plasmon resonance, concentrated and crystallized.
DESIGN OF IN-CELL PROTEIN CRYSTALS FOR DEVELOPMENT OF BIO-SOLID MATERIALS

Presenting Author: Satoshi Abe

Topic: Biological and Biomimetic Materials

Format: Invited

Session: 4, 5

Date: 8/3/2021

Time (in MDT): 4:00:00 PM

Authors: Satoshi Abe, Tokyo Institute of Technology, Yokohama, Japan  Takafumi Ueno, Tokyo Institute of Technology, Yokohama, Japan

The development of biomaterials using protein assemblies has attracted much attention in the field of bio-nanotechnology. Protein crystals, which have a highly ordered arrangement of protein molecules, have great potential for applications in molecular storage, separations, and catalysis. It is known that some proteins can be crystalized in living cells. An in-cell protein crystal is a useful template for fabricating functional materials because it is highly stable under harsh conditions, and has high designability. We have previously established the in-cell engineering of polyhedra crystals (PhC) for immobilization of exogenous enzyme and metal complexes.<sup>[1]</sup> Here, we report the fabrication of porous crystals by deleting amino acid residues located on the intermolecular contact region of polyhedrin monomer to facilitate the selective accumulation of organic compounds, and immobilize two exogenous enzymes.<sup>[2][3]</sup> The engineered crystals immobilizing two enzymes were demonstrated to promote cascade reactions with high reactivity, thermostability, and recycling. We have recently established a method for fabricating supramolecular protein assemblies in engineered protein crystals <i>via</i> site-specific intermolecular disulfide bond formation.<sup>[4]</sup> The bundled filament structure was constructed from the crystals by cross-linking of molecules with auto-oxidation of introduced cysteinyl thiols after isolation of the crystals from living cells.<sup>[5]</sup> These results suggest the possibility of using in-cell protein crystals to design the bio-solid materials for developing further applications in bio-nanomaterial science.<i>br /></i>[1] S. Abe <i>et al</i>., <i>Adv. Mater.</i> 2015 <i>27</i>, 7951-7956. S. Abe <i>et al</i>., <i>Phys. Chem. Chem. Phys.</i> 2018 <i>20</i>, 2986-2989.[2] S. Abe <i>et al</i>., <i>ACS Nano</i> 2017 <i>11</i>, 2410-2419.[3] T. K. Nguyen <i>et al</i>., <i>ACS Appl. Nano Mater.</i> 2021 <i>4</i>, 1672-1681.[4] H. Negishi <i>et al</i>., <i>Chem. Commun.</i> 2018 <i>54</i>, 1988-1991. T. K. Nguyen <i>et al</i>., <i>Chem. Sci.</i> 2019 <i>10</i>, 1046-1051.[5] S. Abe <i>et al</i>., <i>Angew. Chem. Int. Ed.</i> <i>in press</i>.
HARNASSING CONFINEMENT AND SURFACES TO PATTERN CRYSTAL GROWTH

Presenting Author: Lara Estroff

Topic: Biological and Biomimetic Materials

Format: Invited

Session: 2, 1

Date: 8/4/2021

Time (in MDT): 10:30:00 AM

Authors: Lara A. Estroff, Cornell University, Ithaca, New York, United States  Damian Palin, Trinity College Dublin, Dublin, Ireland  Konrad Hedderick, Cornell University, Ithaca, New York, United States  Assaf Gal, Weizmann Institute of Science, Rehovot, Israel

Often in biomineralization, crystal growth in confinement is coupled with functionalized and patterned organic substrates to direct the location and morphology of the final crystalline structures. In this presentation, I will focus on our recent efforts to use confinement within anisotropic gel networks to mold calcite crystals and the use of block copolymers to template the surface confined precipitation of crystalline transition metal oxides with periodicities on the order of 50 nm. For both of these strategies, I will present results related to the formation mechanisms and internal structures of the resulting nanostructured crystals. I will also discuss recent studies of templated growth in a model system of coccolith formation using fluid cell AFM. Taken together, these studies have the potential to lead to design criteria for polymer-reinforced crystalline materials with unique structure-property relationships. In addition, insights provided by this work may help to elucidate the formation mechanism(s) and properties of biogenic single crystals with incorporated organic material.
USING OLD TRICKS ON NEW MATERIALS

Presenting Author: Boaz Pokroy

Topic: Biological and Biomimetic Materials

Format: Invited

Session: 2, 4

Date: 8/4/2021

Time (in MDT): 11:15:00 AM

Authors: Boaz Pokroy, Technion Israel Institute of Technology, Hiafa, Israel

In the course of biomineralization, organisms produce a large variety of functional biogenic crystals that exhibit fascinating mechanical, optical, magnetic and other characteristics. More specifically, when living organisms grow crystals they can effectively control polymorph selection as well as the crystal morphology, shape, and even atomic structure. Materials existing in nature have extraordinary and specific functions, yet the materials employed in nature are quite different from those engineers would select. I will show how specific strategies used by organisms in forming structural biogenic crystals, and can be applied biomimetically so as to form new structural materials with new properties and characteristics. I will mainly concentrate on the entrapment of organic molecules into single crystals of functional materials so as to tailor and manipulate their electronic and other physical properties in ways that could not be done previously.
POLYCATION-POLYANION COACERVATION PROCESSES REGULATE A MORPHOLOGICAL SWITCH OF BIOINSPIRED SILICA

Presenting Author: Hang Zhai

Topic: Biological and Biomimetic Materials

Format: Contributed

Session: 2, 6

Date: 8/4/2021

Time (in MDT): 11:45:00 AM

Authors: Hang Zhai, Weizmann Institute of Science, Rehovot, Israel  Assaf Gal, Weizmann Institute of Science, Rehovot, Israel

Diatoms are unicellular microalgae that produce cell walls composed of biosilica. These biosilica structures exhibit a complex 3D architecture (Figure 1A). Unusual positively-charged long-chain polyamines (LCPAs) and negatively-charged proteins (e.g., silaffins) that were extracted from diatom silica are involved in biosilification. However, bioinspired silica synthesized in-vitro using similar polyelectrolytes usually form spheres with diameters ranging from 200 to 2000 nm rather than continuous fibers/networks. It is still unclear how diatoms control the intricate architecture of their biosilica. To address this issue, we used polyallylamine (PAH) and polyacrylic acid (PAA) to establish a polycation-polyanion system similar to LCPAs-silaffins. PAH (5 mM) or PAA (5 mM) alone cannot accelerate silica precipitation from supersaturated solutions (100 mM silicic acid, pH 5.0) (Figure 1B). Only the coupled PAH-PAA system can precipitate silica. As was shown before, directly adding silicic acid to PAH-PAA mixtures induces the formation of spheres containing 49% (mass) SiO$_2$ (Figure 1C). In contrast, when first introducing only PAH to the silicic acid source, followed by the addition of PAA, fibrous structures with 67% SiO$_2$ are formed (Figure 1D). We revisited the chemical interactions underlying this observed difference. Optical and transmission electron microscope observations show that PAH directly reacts with PAA to form a [PAH-PAA] coacervate spheres that are silicified upon silicic acid addition. However, when PAH is interacting with silicic acid first, the coacervates that form upon addition of PAA are more dilute and contribute to the formation of silica-rich fibers. These observations highlight the role of polymer coacervation in biosilification, which may improve our understanding of how positively-charged LCPAs and negatively-charged silaffins act in diatom biosilification.
CRYSTAL GROWTH AND BIOMINERALIZATION VIA COLLOID ASSEMBLY AND TRANSFORMATION

Presenting Author: Laurie Gower

Topic: Biological and Biomimetic Materials

Format: Invited

Session: 4, 1

Date: 8/4/2021

Time (in MDT): 3:00:00 PM

Authors: Laurie Gower, University of Florida, Gainesville, Florida, United States

Our biomimetics lab uses <i>in vitro</i> model systems to examine the role of biopolymers in modulating crystal growth, and particularly crystals involved in the calcification of biological tissues. This includes the calcium phosphates found in bones and teeth of invertebrates, calcium carbonates found in the shells and exoskeletons of invertebrates, and calcium oxalates found in kidney stones and plants. Much of our work has been founded on the discovery of a polymer-induced liquid-precursor (PILP) mineralization process that is induced with polyanionic peptides and proteins. Since this discovery, we demonstrated that many of the enigmatic microstructural features found in biominerals can be reproduced in the beaker, ranging from thin aragonite tablets mimicking mollusk nacre to intrafibrillar mineralization of collagen to emulate bone’s interpenetrating organic-inorganic nanostructure. This then formed the basis of our hypothesis that many biominerals may be formed by a similar non-classical crystallization mechanism. While this hypothesis was originally met with skepticism given the prevalent perspective of proteins having defined globular 3D shapes and functions involving molecular recognition (such as enzymes), more recently it has come to be recognized that the highly charged nature of the soluble fraction of biomineralization proteins causes them to fall in the category of intrinsically disordered proteins. This therefore allows many biomineralization features to be emulated using relatively simple polyelectrolyte-ion interactions. However, the PILP namesake has been confusing since recent biomineralization studies demonstrate that the amorphous precursor particles that fuse to form biominerals are apparently not in a truly liquid state since there is a remnant colloidal texture found in biominerals. This is the case in our <i>in vitro</i> PILP system as well. Thus, while they fill space, unlike that expected for solid particles, their fusion suggests the precursors have a gel-like consistency. This two-step crystallization mechanism has come to be referred to as the particle attachment mechanism, or in the biomineralization literature, particle accretion. Therefore, I will lead a discussion (hopefully with audience feedback) on the relevance of the physical state of the amorphous precursor, the influence of surfaces and matrices on this state and kinetics of transformation, and how these all influence the colloid assembly and transformation of the precursor phase, both of which are stages critical to creating the exquisite non-equilibrium morphologies found in biominerals.
BIO-INSPIRED SYNTHESIS OF IMPACT-RESISTANT BI-CONTINUOUS ZINC OXIDE NANOPARTICLES

Presenting Author: Wei Huang

Topic: Biological and Biomimetic Materials

Format: Contributed

Session: 4, 4

Date: 8/4/2021

Time (in MDT): 3:45:00 PM

Authors: Wei Huang, University of California Irvine, Irvine, California, United States  Taige Hao, University of California Irvine, Irvine, California, United States  David Kisailus, University of California Irvine, Irvine, California, United States

Biomineralized composites found in natural organisms such as nacre, antler and the dactyl club of mantis shrimp show remarkable toughness and impact resistance. For example, during feeding activities, the dactyl clubs of the mantis shrimp can reach an impact speed of ~20 m/s at an acceleration of ~10,000g yet do not fail. We revealed that the surfaces of these clubs consist of a thin veneer of hydroxyapatite/chitin-based bi-continuous nanoparticles that absorb large amounts of energy and thus, protect the underlying structure from impact damage. It is likely that during the biomineralization process, nucleating peptides bound to chitin template the formation of hydroxyapatite, yielding these bi-continuous nanoparticles that provide multiscale toughening mechanisms. Inspired by the exquisite control of these biomineralized structures, we utilized block co-polymer templates to synthesize bi-continuous ZnO nanoparticles. By modulating the fraction of precursor and block co-polymer, the resulting morphologies of these nanoparticles could be tuned. The resulting nanocomposite particles were then coated on quartz and carbon fiber composite substrates and subjected to nanoimpact testing at high strain rates. The results of these tests validate our observations in the biological structure, demonstrating a ~70% decrease of damage area and thus protecting the underlying substrates. We discuss the mechanisms of nanoparticle formation as well as their toughening mechanisms and their potential for use in multiple applications.
CRYSTAL ENGINEERING OF ELECTRODE MATERIALS TOWARDS HIGH PERFORMANCE ELECTROCHEMICAL ENERGY STORAGE

**Presenting Author:** Dongfeng Xue

**Topic:** Biological and Biomimetic Materials

**Format:** Invited

**Session:** 4, 5

**Date:** 8/4/2021

**Time (in MDT):** 4:00:00 PM

**Authors:** Dongfeng Xue, Shenzhen Institute of Advanced Technology, Chinese Academy of Sciences, Shenzhen, China

Bio-inspired crystallization strategies were employed to the growth of electrode materials for high performance electrochemical energy storage. Upon multi-valence metal salts, colloidal electrode materials were created and shown as promising flexible supercapattery applications. Core-shell infrastructures were crystallized for lithium-ion battery electrode materials. In this talk, I will share some of our recent advances in bio-inspired crystallization towards high performance electrochemical applications.
BIFURCATED TRANSITION STATE FOR THE GROWTH OF THE THREEFOLD POLYMORPH OF AMYLOID BETA FIBRILS

Presenting Author: Ted Kim

Topic: Biological and Biomimetic Materials

Format: Poster

Session: ,

Date:

Time (in MDT):

Authors: Ted Kim, University of Houston, Houston, Texas, United States  Sima Mafimoghaddam, University of Houston, Houston, Texas, United States  Peter Vekilov, University of Houston, Houston, Texas, United States

Alzheimer’s disease ranks as the third leading cause of death amongst adults over the age of 60 behind heart disease and cancer. The accumulation of amyloid plaque and neurofibrillary tangles causes the irreversible degradation and destruction of neurons that drastically shrinks brain tissue. Amyloid plaques are due to the buildup of insoluble amyloid beta (Aβ) fibrils formed from self-assembled propagation of peptides. Studies have shown that Aβ can take shape as soluble oligomers or insoluble fibrils with different morphologies. Aβ fibrils attain numerous structures, called polymorphs, both in patients’ brains and in vitro. Prior observations reveal that in agitated solutions the twofold polymorph of Aβ40 fibrils dominates, whereas the threefold polymorph of Aβ40 fibrils preferentially forms in the quiescent solutions. Previous atomic force microscopy (AFM) studies have demonstrated that the twofold symmetric Aβ40 polymorph grows steadily at broad ranges of peptide solution concentrations. It was also established that the fibril growth rate is determined by an activated complex, comprised by a peptide chain partially bound to the fibril tip and folded in a conformation distinct from that in the fibril bulk; the rearrangement of the intermediate configuration of the incoming peptide to the structure in the bulk fibril constitutes the transition state for growth [1]. We employ time-resolved in situ AFM to monitor the growth of seeds nucleated in quiescent solutions that belong to the threefold polymorph. We find that at low peptide concentrations, the fibrils growth bifurcates between two regimes. Growth either completely stalls or it proceeds at a rate, which is reproducible for the chosen solutions concentration. Similar observations of “stop and go” kinetics with other fibril-forming proteins have been attributed to two conformations of the soluble protein chains, growth complement, which supports growth, and growth incompetent, which caps the fibril tips and prevent association of growth competent chains. The recorded consistently steady growth of the two-fold Aβ40 fibrils, however, challenges the presence of growth-incompetent conformations in Aβ40 solutions. We put forth that stalled growth of the three-fold Aβ40 fibrils is due to an activated complex in which the incoming peptide folds into a conformation that cannot transform into the bulk fibril structure. The lifetime of that conformation of the activated complex defines the length of the period of stalled growth of the fibril. Our finding illuminates the complex interplay between fibril structures and the associated transition states during the growth of amyloid β fibrils.
HIGH-TEMPERATURE MBE OF HBN FOR SINGLE-PHOTON EMITTERS, DEEP-ULTRAVIOLET AND LATERAL HETEROSTRUCTURES.

Presenting Author: Sergei Novikov

Topic: BN Epitaxial Growth and Characterization

Format: Invited

Session: 2, 1

Date: 8/2/2021

Time (in MDT): 10:30:00 AM

Authors: Sergei V. Novikov, University of Nottingham, Nottingham, United Kingdom T. S. Cheng, University of Nottingham, Nottingham, United Kingdom J. Wrigley, University of Nottingham, Nottingham, United Kingdom J. Bradford, University of Nottingham, Nottingham, United Kingdom T. James, University of Nottingham, Nottingham, United Kingdom J. Thomas, University of Nottingham, Nottingham, United Kingdom A. Summerfield, University of Nottingham, Nottingham, United Kingdom C. J. Mellor, University of Nottingham, Nottingham, United Kingdom A. N. Khlobystov, University of Nottingham, Nottingham, United Kingdom L. Eaves, University of Nottingham, Nottingham, United Kingdom C. T. Foxon, University of Nottingham, Nottingham, United Kingdom P. H. Beton, University of Nottingham, Nottingham, United Kingdom A. N. Khlobystov, University of Nottingham, Nottingham, United Kingdom P. H. Beton, University of Nottingham, Nottingham, United Kingdom

Research studies on the growth and properties of hexagonal boron nitride (hBN) have recently attracted a lot of attention. First, the band gap of hBN is about 6 eV and that has triggered the interest in hBN as a wide gap material for deep-ultraviolet device (DUV) applications. Secondly, the lattice parameter of hBN is very close to that of graphene. The surface of hBN is atomically flat and can provide an ideal chemically inert dielectric substrate for 2D-structures.<br />We have studied a new molecular beam epitaxy (MBE) technology for the growth of graphene and hBN monolayers at extremely high growth temperatures up to 1850°C. This high-temperature (HT) MBE approach offers new opportunities in the burgeoning fields of DUV materials, 2D materials and related van der Waals heterostructures. We have developed HT-MBE growth of hBN at the temperatures from 1250°C to 1700°C. We have demonstrated that by growing hBN on highly oriented pyrolytic graphite (HOPG) substrates it is possible to produce monolayer and few-layer thick boron nitride with atomically flat hBN surfaces, which are essential for future 2D and DUV applications. The hBN coverage can be reproducibly controlled by the growth time, substrate temperature and boron to nitrogen flux ratios. However, decreasing the epitaxy temperature below 1250°C, rapidly degrades the optical properties of the hBN layers.<br />Together with our colleagues from the University of Montpellier (France) we combined deep-ultraviolet photoluminescence and reflectance spectroscopy with atomic force microscopy to reveal the presence of a direct energy gap of 6.1 eV in single atomic hBN layers, thus experimentally confirming a crossover to direct gap in the hBN monolayer limit [1].<br />hBN has recently attracted the interest of the quantum technology community since defects in hBN have been reported to act as visible single-photon emitters (SPEs). Together with our colleagues from the University of Technology Sydney (Australia) we have experimentally demonstrated that the SPEs in hBN are carbon related [2].<br />We have recently shown that lateral heterojunctions between regions of graphene (G) and hexagonal boron nitride can be grown using HT-MBE. Sequential
HT-MBE growth of hBN, graphene and a second cycle of hBN growth results in the formation of monolayer thick lateral hBN-G-hBN heterostructures, in which a strip of graphene is embedded between monolayers of hBN.

TWO-DIMENSIONAL HEXAGONAL BORON NITRIDE: FROM MOLECULAR BEAM EPITAXIAL GROWTH TO DEVICES

Presenting Author: Jianlin Liu

Topic: BN Epitaxial Growth and Characterization

Format: Invited

Session: 2, 3

Date: 8/2/2021

Time (in MDT): 11:00:00 AM

Authors: Jianlin Liu, University of California, Riverside, Riverside, California, United States
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Two-dimensional (2D) hexagonal boron nitride (h-BN) plays a significant role in nanoscale electrical and optical devices because of its superior properties. However, the difficulties in the controllable growth of high-quality films hinder its applications. In this presentation, we report molecular beam epitaxial growth of high-quality 2D h-BN monolayer and few-layer thin films and their metal-insulator-metal (MIM) devices. Various epitaxy tools, in particular, chemical vapor deposition, have been used to grow 2D h-BN. Molecular beam epitaxy (MBE), which has a capability of the deposition at the atomic layer thickness and in-situ growth monitoring using reflective high-energy electron diffraction (RHEED), is an excellent alternative for 2D h-BN growth. Besides the tuning of traditional growth parameters such as growth temperature, growth time, etc., we have introduced a new growth parameter, namely, tuning the carbon impurity level in the selected transition metal substrates such as Co and Ni to adjust the catalytic strength of the substrates. This method has significantly reduced random 3D h-BN adlayer grain growth and led to single-crystalline wafer-scale 2D h-BN films with uniform thickness. It is found that the carburization of Ni substrates with different surface orientations leads to different kinetics of h-BN growth. While the carburization of Ni (100) enhances the h-BN growth, the speed of the h-BN growth on carburized Ni (111) reduces. In addition, we have demonstrated that electropolishing plays an important role in drastically increasing the speed of h-BN film growth. 1-in<sup>2</sup> monolayer single-crystal h-BN films are obtained within 1 hour by MBE. Density functional theory (DFT) simulations were used to understand the thermodynamics of 2D h-BN growth. MIM devices based on 2D molecular beam epitaxial h-BN films have been fabricated. Direct tunneling and breakdown characteristics are comprehensively studied. High breakdown electric field of 12 MV/cm is routinely demonstrated. Failure mechanism and reliability of ultrathin h-BN are analyzed. “Effective” tunneling area is found to be orders of magnitude smaller than physical device area of these atomic layer thin devices. Finally, low-energy deposition of aluminum electrode on epitaxial monolayer h-BN thin films on Ni were carried out to fabricate robust nanocapacitors. The quantum-capacitance effect has been studied.
H-BN OR R-BN - WHICH POLYTYPE OF SP\(^2\)-BN DID YOU GROW?

**Presenting Author:** Hans Högberg

**Topic:** BN Epitaxial Growth and Characterization

**Format:** Contributed

**Session:** 2, 5

**Date:** 8/2/2021

**Time (in MDT):** 11:30:00 AM

**Authors:** Hans Göran Högberg, Linköpings universitet, Linköping, Sweden  Henrik Pedersen, Linköpings universitet, Linköping, Sweden  Mikhail Chubarov, Infineon, Austria  Laurent Souqui, University of Illinois at Urbana-Champaign, Urbana, Illinois, United States  Sachin Sharma, Linköpings universitet, Linköping, Sweden

sp\(^2\)-hybridized BN (sp\(^2\)-BN) have two different crystal structures: hexagonal BN (h-BN) and rhombohedral BN (r-BN). h-BN exhibits an ABAB... stacking sequence of the basal planes while an ABCABC... stacking sequence is observed in r-BN. The a-axis in h-BN and r-BN are equally long with 2.504 Å and both phases show identical spacing between the basal planes with 3.333 Å. In h-BN, each next basal plane is rotated 180° around the c-axis ([0001]) with respect to the previous basal plane, while in r-BN, each next basal plane is shifted along the [1-100] direction by 1.45Å. We have recently shown,\(^1\) by using van der Waals corrected density functional theory, that r-BN is the most stable phase at the high temperature and low-pressure conditions used in chemical vapor deposition (CVD). For 0001 oriented and epitaxial sp\(^2\)-BN films the identical a-axis and spacing between the basal planes along the c-axis for both r-BN and h-BN makes phase determination a challenge. Several reports in the literature show very poor phase determination and material properties may have been assigned to the wrong polytype. We have shown that the phase determination requires either very high quality careful thin film XRD methods such as grazing-incidence diffraction of non-specular reflections or high-resolution transmission electron microscopy.\(^2\) From thermally activated CVD at temperatures about 1500 °C, we have in a series of publications demonstrated epitaxial growth of sp\(^2\)-BN films on Al\(<sub>2</sub>\)-BN films on Al\(<sub>2</sub>\)-SiC\(<sub>2</sub>\)-SiC\(<sub>2</sub>\) substrates as well as on magnetron sputtered epitaxial ZrB\(<sub>2</sub>\)-SiC\(<sub>2</sub>\) films on 4H-SiC\(<sub>2</sub>\). We find that growth from TEB on Al\(<sub>2</sub>\)-BN films on Al\(<sub>2</sub>\)-SiC\(<sub>2</sub>\) substrates results in an initial about 4 nm thick nucleation layer of h-BN followed by growth of r-BN, while growth from TMB results direct nucleation of r-BN.\(^3\) For SiC\(<sub>2</sub>\) and ZrB\(<sub>2</sub>\)-SiC\(<sub>2</sub>\) substrates, we find direct nucleation of r-BN on both substrates.\(^4\)\(^5\)

\(^1\) H. Pedersen et al. Thermodynamic stability of hexagonal and rhombohedral boron nitride under chemical vapor deposition conditions from van der Waals corrected first principles calculations. \(\textit{J. Vac. Sci. Technol. A}\) 2019, \(\textit{37}\), 040603.

\(^2\) M. Chubarov et al. Review Article: Challenge in determining the crystal structure of epitaxial 0001 oriented sp\(^2\)-BN films. \(\textit{J. Vac. Sci. Technol. A}\) 2018, \(\textit{36}\), 030801.


\(^4\) L. Souqui et al. Rhombohedral boron nitride epitaxy on ZrB\(<sub>2</sub>\)-SiC\(<sub>2</sub>\). \(\textit{J. Vac. Sci. Technol. A}\) 2021, \(\textit{39}\), 013405.
DEVELOPMENT OF CVD GROWN HBN FOR SCALABLE 2D ELECTRONICS

Presenting Author: Michael Snure

Topic: BN Epitaxial Growth and Characterization

Format: Invited

Session: 3, 1

Date: 8/2/2021

Time (in MDT): 1:00:00 PM

Authors: Michael Snure, Air Force Research Laboratory, Wright Patterson AFB, Ohio, United States

After more than a decade since its emergence as a two dimensional (2D) material, hexagonal boron nitride (hBN) continues to generate significant interest for optical, electrical, chemical, and thermal applications. As an ultrawide bandgap insulator, hBN is unique among the very large and diverse number of 2D materials finding adoption as tunneling barriers, dielectrics, deep UV and quantum emitters, as well as substrate and passivation layers. All this interest has driven a growing amount of research on synthesis methods capable of scalably producing mono- to many-layer thick films. Out of the numerous methods reported, chemical vapor deposition (CVD) has demonstrated to be one of the most promising approaches for achieving high quality large area hBN films. With the wide variety of control knobs available in the CVD process—pressure, temperature, precursor type, substrate selection, etc.—there are numerous fundamental questions about how each can affect growth mechanisms, nucleation, and crystallization. To this motivation, I will review some of the various CVD processes for growth of mono-few layer hBN layer, which for simplicity, will be discussed based on substrate type (metallic and non-metallic) and precursor selection. This overview aims to shows how the most critical control knobs are used to achieve extremely high quality hBN films. Additionally, I will discuss and compare the properties of these CVD films and give some important examples of their application. Because even though we have seen amazing progress in the area of hBN synthesis the majority of reports on hBN characterization and devices rely on flakes exfoliated from bulk sources.
Hexagonal boron nitride (hBN) is a wide bandgap semiconductor (Eg ~ 6eV) with sp2-hybridized atomic sheets of boron and nitrogen. This material has attracted much attention for its properties such as high resistivity, high thermal conductivity (2000 Wm⁻¹K⁻¹), and stability in aggressive chemical environments and at high temperatures (up to 1000 °C). hBN, an insulating isomorph of graphene, has a small (1.7%) lattice mismatch to graphene and is expected to be atomically smooth and free from dangling bonds because of its sp2-hybridized bonding and weak interplanar Van der Waals bond. Hence, hBN is an excellent candidate to be used as a supporting substrate and gate dielectric for graphene based electronics. hBN is also an emerging material for deep UV photonics and for solid state thermal neutron detector application, since 10B, a constituent element of hBN, has a large thermal neutron capture cross section (3840 barns). This talk will present the results on the growth and characterization of thick (>12μm) hexagonal boron nitride (hBN) and its use for solid-state thermal neutron detection. The hBN epilayers were grown by metalorganic chemical vapor deposition on sapphire and silicon substrates at a temperature of 1350 °C. The films were characterized using standard techniques like x-ray diffraction for crystalline structure and optical transmission for bandgap determination. The thick epilayers can easily be lifted-off from the substrate to get a free standing epilayer. This property has made processing of this material extremely challenging since wet processing was found to delaminate the epilayer from the substrate. Therefore a fully dry processing technique was developed using thin contact masks and processed without any standard lithography. Using this newly developed processing, the films were processed to fabricate large area neutron detectors and characterized to determine electron and hole mobility lifetime products and for their efficiency in neutron detection. This work is supported by the US Department of Homeland Security, DNDO office, under the grants ECCS-1348269 and 2013-DN-077-ER001.
Hexagonal Boron Nitride (hBN), belonging to the family of 2-dimensional (2D) materials, is a group III-nitride wide bandgap semiconductor that has a layered crystal structure very similar to graphite. Due to its extraordinary physical properties, such as high resistivity, high thermal conductivity, high dielectric breakdown field, stability in the air up to 1000°C, and large bandgap ($E_{g} \sim 5.9$ eV), hBN appears to be a promising material for emerging applications, including deep ultraviolet (DUV) optoelectronics, single photon emitters (SPEs), neutron detectors, etc. There is also significant interest in monolayer and few-layer hBN as an encapsulating/dielectric layer for 2D devices based on graphene and transition metal dichalcogenides. While high-quality hBN bulk crystals are available for exfoliation, the size of the crystals is limited, consequently, there is continued interest in the epitaxial growth of large-area hBN films using chemical vapor deposition (CVD) to use it for practical applications. CVD of hBN layers on C-plane (0001) vs A-plane (11-20) of sapphire ($\alpha$-Al$_2$O$_3$) substrate is compared. High hBN deposition temperatures (>1200°C) and the use of an H$_2$ carrier gas substantially alters the C-plane sapphire surface and leaves the top layer(s) oxygen-deficient, most likely Al-rich, as analyzed using reflection high energy electron diffraction (RHEED). The surface morphology of the C-plane sapphire substrate is inhomogeneous with a high surface roughness that impacts hBN deposition causing non-uniform residual stress in the deposited films. Therefore, A-plane sapphire (11-20) was investigated to serve as an alternative substrate for hBN deposition. Unlike C-plane, A-plane of sapphire does not etch substantially under H$_2$ at high growth temperatures thus proving to be a stable alternative for the growth of high-quality hBN. The photoluminescence behavior of the hBN film, measured at room temperature (RT), obtained on C-plane and A-plane sapphire does not show any significant differences between them. They both appear to have common luminescence characteristics with a peak near 4.1 eV, which have been attributed to be a
donor-acceptor pair (DAP) transition of a shallow donor and a deep acceptor, $V_{N}$ and $C_{N}$ respectively. In addition, both of the samples had a peak near 5.3 eV, which has been identified as a quasi-DAP transition between $V_{N}$ and an unknown deep acceptor. These are both signature peaks seen for lower NH$_3$ growth. Moreover, the dielectric breakdown field of hBN deposited on A-plane sapphire was measured to be 5 MVcm$^{-1}$, agreeing well with early reports on mechanically exfoliated hBN flakes.
CHARACTERIZATIONS OF STRAINED HEXAGONAL BORON NITRIDE GROWN ON SAPPHIRE

Presenting Author: Shantanu Saha

Topic: BN Epitaxial Growth and Characterization

Format: Contributed

Session: 3, 6

Date: 8/2/2021

Time (in MDT): 2:15:00 PM

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Hexagonal boron nitride (h-BN) is a two-dimensional (2D) ultrawide bandgap semiconductor (~6 eV). Although theoretical investigations on strained h-BN were reported but its detailed experimental analysis is still missing. Hence, a thorough microscopic and spectroscopic characterizations and analysis of such h-BN films are needed as it will provide a fundamental understanding to pave the way for developing quantum technologies which demand defect-free h-BN. Different growth tools including chemical vapor deposition (CVD), metal-organic CVD (MOCVD), and molecular beam epitaxy (MBE) have already been used for h-BN growth. Non-metalorganic borazine \(\text{B}_3\text{H}_6\text{N}_3\) is a carbon-free precursor and can minimize the defects in h-BN. In this work, multilayer h-BN was grown on sapphire by the CVD method in a MOCVD reactor at 1500°C using this precursor and subsequent structural, vibrational, morphological and chemical analysis were done. X-ray diffractions (XRD), and Raman spectroscopy measurements were carried out for investigations of structural and vibrational properties. Morphological characterizations were investigated by using scanning electron microscopy (SEM), and atomic force microscopy (AFM). Standard 2θ/ω scan of XRD revealed two peaks around 26.7° and 41.7° which correspond to (0002)\(<i>h\text{-BN}\end{i}>\) and the (0006) sapphire crystal planes, respectively. An increase of 0.7% c-axis lattice constant was observed which could be due to a residual strain from the cooling process after the growth. Raman measurements confirmed peak at 1368 cm\(^{-1}\) which corresponds to the \(<i>E</i>\text{-mode of h-BN}\). No splitting of this peak supports the presence of biaxial strain in the film which was further supported by the morphological analysis. SEM and AFM measurements showed presence of the wrinkles with some hillocks in the films. Appearance of wrinkles is common when a van-der Waals (vdW) material is under in-plane strain. Stoichiometric h-BN films with excellent uniformity was confirmed by X-ray photoelectron spectroscopy (XPS) confirmed. Our systematic and comprehensive characterization studies of borazine-based h-BN are believed to bring new insights. Borazine can minimize the possibility of presence of carbon-impurities and showed a new way of achieving defect-free h-BN. This will lead to develop single photon emitters through deterministic point defects. More details of the characterizations including high resolution transmission electron microscopy (HRTEM) will be discussed during the presentation.
Two-dimensional (2D) hexagonal boron nitride (h-BN) is highly appreciated for its atomically smooth surface and absence of dangling bonds, which could be employed as an ideal 2D dielectric for 2D electronic/optoelectronic devices\cite{1,2}. Although wafer-scale monolayer single crystalline h-BN has been achieved in the past few years\cite{3–5}, the limited thickness could not efficiently screen the surrounding disturbance and keep the intrinsic properties of 2D crystals\cite{6}. To date, the exploration of novel properties such as twistronics of 2D layered materials relies on the exfoliated h-BN flakes. Controllable synthesis of large-scale multilayer h-BN is still challenging. Here, we report a vapor–liquid–solid growth (VLSG) method to achieve uniform multilayer h-BN by using a molten Fe$_{82}$B$_{18}$ alloy and N$_2$ as reactants\cite{7}. Different from the self-limited growth mechanism of monolayer h-BN on catalytic metal such as cooper surface\cite{5}, liquid Fe$_{82}$B$_{18}$B$_{18}$ not only supplies boron source but promotes gaseous nitrogen converting into nitrogen atoms and further reserves the atoms in the molten “reservoir”\cite{8}. Subsequently, B-N associates gradually formed and enabled the epitaxially growth of h-BN multilayers on a c-face sapphire substrate. In situ ambient X-ray photoemission spectroscopy (APXPS) and X-ray diffraction (XRD) are employed to explore how B-N bonding initially forms in Fe-B alloy and the epitaxial relationship between the multilayer h-BN and sapphire was suggested by cross-sectional transmission electron microscopy (TEM) and electron backscattered diffraction (EBSD). The mechanical strength of the multilayer h-BN was investigated and the values of Young’s modulus were approximately 1.04 ± 0.1 TPa. Besides, the applicability of the multilayer h-BN as a dielectric has been considered. Graphene sandwiched between as-grown h-BN multilayers was patterned into a Hall bar configuration, and the electronic performance of graphene was evaluated, the carrier mobility of graphene at 300 K under
different magnetic fields was in the range of $0.5 \sim 1 \text{m}^2\text{V}^{-1}\text{s}^{-1}$. The approach herein demonstrates the feasibility for large-area fabrication of van der Waals 2D materials and heterostructures.

H-BN CHARACTERIZATION USING 4D STEM-IN-SEM AND AFM

Presenting Author: Elisabeth Mansfield

Topic: BN Epitaxial Growth and Characterization

Format: Contributed

Session: 4, 2

Date: 8/2/2021

Time (in MDT): 3:15:00 PM

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Hexagonal boron nitride (hBN) is of broad interest for two-dimensional (2D) materials-based electronics, optoelectronic, and nanophotonic device applications. Because monolayers exfoliated from bulk hBN crystals are the highest structural quality, they are the best source for 2D device applications. Thus, it is surprising that the structural properties of bulk hBN crystals has received so little attention. In this contribution, defects prevalent in hBN crystals grown at atmospheric pressure from metal solutions were identified. Cross-sections of the hBN crystals were examined by 4-dimensional (4D) scanning transmission electron microscopy in a scanning electron microscope (STEM-in-SEM) to garner information about defects in the bulk. Figure 1a shows an annular dark-field (ADF) STEM image of a cross-section obtained from directly under a surface fold. A large subsurface void and twin boundaries were revealed. Moreover, the diffraction pattern (DP) from the region indicated in red shows a ring of spots suggestive of polycrystalline structure. In contrast, the DP from the adjacent region indicated in green shows a row of spots suggesting large coherent domains characterized by wide planes normal to the row direction. Figure 1b shows a split-screen SEM image of the crystal surface. Several features suggesting blister-like protrusions appeared using the off-axis detector (left side). The in-lens detector (Figure 1b, right side) suggests the presence of voids under the protrusions. Conventional AFM was used to confirm these features as protrusions, and CR-AFM showing locally reduced contact stiffness was consistent with sub-surface voids or delaminations below the protrusions. Identifying the defects in bulk hBN crystals is important for establishing the quality of the material, developing methods for improving the crystal growth, and considering how they will impact 2D heterostructure device fabrication and performance.
TOWARDS CHIRALITY CONTROL OF GRAPHENE NANORIBBONS EMBEDDED IN HEXAGONAL BORON NITRIDE

Presenting Author: Huishan Wang

Topic: BN Epitaxial Growth and Characterization

Format: Contributed

Session: 4, 3

Date: 8/2/2021

Time (in MDT): 3:30:00 PM

Authors: Huishan Wang, SIMIT, Shanghai, China Lingxiu Chen, SIMIT, Shanghai, China Li He, SIMIT, Shanghai, China Chen Chen, SIMIT, Shanghai, China Haomin Wang, SIMIT, Shanghai, China Jannik Meyer, Institute of Applied Physics, Tübingen, Germany

The integrated in-plane growth of graphene nanoribbons (GNRs) and hexagonal boron nitride (h-BN) could provide a promising route to achieve integrated circuitry of atomic thickness. However, fabrication of edge-specific GNRs in the lattice of h-BN still remains a significant challenge. Here we developed a two-step growth method and successfully achieved sub-5-nm-wide zigzag and armchair GNRs embedded in h-BN. Further transport measurements reveal that the sub-7-nm-wide zigzag GNRs exhibit openings of the bandgap inversely proportional to their width, while narrow armchair GNRs exhibit some fluctuation in the bandgap-width relationship. An obvious conductance peak is observed in the transfer curves of 8- to 10-nm-wide zigzag GNRs, while it is absent in most armchair GNRs. Zigzag GNRs exhibit a small magnetic conductance, while armchair GNRs have much higher magnetic conductance values. This integrated lateral growth of edge-specific GNRs in h-BN provides a promising route to achieve intricate nanoscale circuits.
SYNTHESIS OF BN CRYSTALS BY USING SOLVENT GROWTH AND THEIR DEFECT CHARACTERIZATION

Presenting Author: Takashi Taniguchi

Topic: BN Epitaxial Growth and Characterization

Format: Invited

Session: 4, 4

Date: 8/2/2021

Time (in MDT): 3:45:00 PM

Authors: Takashi Taniguchi, National Institute for Materials Science, Tsukuba, Japan

Hexagonal boron nitride BN (hBN) is chemically and thermally stable, and has been widely used as an electrical insulator and heat-resistant materials. By using high pressure and high temperature (HPHT) solution growth with solvent of Ba-BN system, high purity hBN with oxygen and carbon impurity less than SIMS detection limit i.e.10ppm level was obtained. In this paper, recent studies for properties of BN obtained at high pressure with respect to impurity control will be reported. Particularly the present issue to improve their properties further is to eliminate residual carbon and oxygen impurities in the range of 10ppb region.
GROWTH OF LARGE SAPPHIRE CRYSTALS: LESSONS LEARNED

Presenting Author: Andrew Novoselov

Topic: Bulk Crystal Growth

Format: Invited

Session: 2, 1

Date: 8/2/2021

Time (in MDT): 10:30:00 AM

Authors: Andrew Novoselov, II-VI Aerospace & Defense, Murrieta, California, United States

Sapphire, a colorful precious gemstone, is one of the most exciting crystal materials known to humankind from the beginning of time, but the 20th century brought new meaning to this word. Colorless artificial sapphire became a popular window material in science and technology because it can withstand substantial mechanical load, corrosive chemicals, high temperature, and radiation while keeping its pristine appearance and wide transmittance range [1]. However, the discovery of high-brightness GaN light-emitting diodes (LEDs) at the end of the 20th century turned a new page in the long history of sapphire [2].

The success of GaN LEDs depends on the availability of inexpensive but reliable substrates, and sapphire successfully competed with numerous alternatives. To satisfy the market’s appetite for enormous quantities of sapphire substrates, a number of already existing crystal growth technologies, such as the Czochralski (CZ) and Kyropoulos (KY) methods, the heat-exchanger method (HEM), edge-defined film-fed growth (EFG), and horizontal directional solidification (HDS), were further advanced to grow large sapphire crystals. They also provided the opportunity to increase the size of sapphire windows.

In this paper, I will review recent developments in large sapphire crystal growth for substrates and optical windows, and demonstrate useful tools applied to increase crystal size. References


CZOCHELRSKI GROWTH OF LARGE Li₂MoO₄ SINGLE CRYSTALS

Presenting Author: Matias Velazquez

Topic: Bulk Crystal Growth

Format: Contributed

Session: 2, 3

Date: 8/2/2021

Time (in MDT): 11:00:00 AM

Authors: Matias Velazquez, CNRS, SIMaP Laboratory, Saint Martin d'Hères, France, Abdelmounaim Ahmine, CNRS, SIMaP Laboratory, Saint Martin d'Hères, France, Thierry Duffar, CNRS, SIMaP Laboratory, Saint Martin d'Hères, France

Crucial experiments in the field of understanding the origin of neutrino mass and the direct detection of dark matter require the detection of extremely rare events, such as neutrinoless double beta decay ($2\beta0\nu$). Among the most powerful detectors of this decay are the scintillating bolometers that simultaneously generate a nuclear event and record it in the same crystal that constitutes their core. The most promising crystal to achieve this goal is lithium molybdate Li₂MoO₄ (LMO). The central part of a Czochralski (CZ) puller has been designed through numerical simulation in order to optimize the temperature field around the crystal [1]. Several massive LMO crystals (up to 1kg) were pulled (Fig. 1). They show a good crystal quality with dislocation density reaching ≈10⁴ cm⁻². One of the crystals that we developed fractured during its pulling (Fig. 2). In order to assess the fracture potential of LMO crystals during their growth, we developed a finite element calculation model of the temperature fields and thermoelastic stresses in the crystal during the Czochralski pulling and during the subsequent cooling. It was shown that the thermoelastic stresses during pulling of this crystal were below the rupture stress of LMO. It is finally concluded that the observed cracking was rather due to accidental vibration of the equipment.

Fig. 1: Li₂MoO₄ single crystal, 970 g and 50 mm in diameter
CZOCHRALSKI GROWTH OF HEAVILY ARSENIC DOPED, DISLOCATION FREE SILICON IN THE 110 ORIENTATION FOR POWERMOS DEVICES

Presenting Author: Joel Kearns

Topic: Bulk Crystal Growth

Format: Contributed

Session: 2, 4

Date: 8/2/2021

Time (in MDT): 11:15:00 AM

Authors: Joel K. Kearns, NASA Glenn Research Center, Cleveland, Ohio, United States

Heavily arsenic-doped, dislocation free silicon crystals were grown as part of process development to produce low resistivity crystals in <110> orientation for use as substrates for Trench power MOSFETs. Crystals of <110> orientation possess two vertical {111} planes running down the length of the crystal, so the planes are normal to the cut wafer surface. Preferential etching can be used to produce extremely flat vertical trench walls for a trench UMOS. However, <110> crystals are much more difficult to grow dislocation free than <100> or <111> orientation crystals. Because the {111} planes run down the length of the crystal, it is more difficult to eliminate seed-dip dislocations by Dash necking, so the crystal may not become dislocation free at all. Further, if dislocations are generated later by some disturbance, the crystal will slip back good material further than other orientations, again because of the vertical {111} planes. So such processes usually produce less usable material at a higher cost, regardless of resistivity. Four crystals were grown as a proof of concept process demonstration. Surprisingly on crystal twinned during growth, which is unusual for lightly doped silicon crystals. The crystal that generated a twin (A26-A) is compared to three other crystals (A26-B, A26-C, A26-D) grown using the same solidification conditions in the same crystal puller.
GAS BUBBLE FORMATION AND TRANSPORT IN CZOCHRALSKI GROWTH OF SI CRYSTALS WITH HORIZONTAL MAGNETIC FIELDS

Presenting Author: Alexey Kondratyev

Topic: Bulk Crystal Growth

Format: Contributed

Session: 2, 5

Date: 8/2/2021

Time (in MDT): 11:30:00 AM


During Czochralski growth of silicon there is experimental evidence for formation of gas bubbles and their transport across the melt with a probability of incorporation into the crystal. These bubbles assumingly form due to presence of micro-defects and cavities on the crucible surface as well as due to diffusion of CO and SiO$_2$ gases from the crucible wall into the melt [1, 2]. Original bubble nuclei with near-atmospheric pressure reside near the crucible surface once it was manufactured. At certain conditions, the nuclei can accumulate more gas atoms from the crucible and grow. Their size is limited by the linear size of the cavity, which ranges from several microns to several millimeters. The bubbles can join during motion so that the larger bubbles incorporate the smaller ones. The bubbles can be removed through the free surface of the melt but can also reach the crystallization interface and incorporate into the crystal. In the latter case they can negatively affect the growing material quality and even serve as a reason for polycrystalline grains formation. Upon reaching a certain size the bubbles can detach from the crucible surface. The rate at which the new bubbles appear on the surface depends on the rate of gas diffusion from the crucible, which is determined by the corresponding chemical potentials. A bubble incorporation into the crystal is possible if its linear velocity does not exceed the local crystallization rate, while the net force squeezes it to the crystal. We have suggested a 3D numerical model describing formation and transport of bubbles based on force balance equations, thermodynamics of bubble formation and incorporation into the crystal. The typical size of the cavities filled with gas is distributed according to the Gaussian law. The Stokes and buoyancy force, the Marangoni effect, shear stresses, and probability of bubble detachment from the crucible wall are estimated. The bubble trajectories in the melt are computed and a probability of bubble incorporation into the crystal is estimated for the growth of a 300 mm diameter Si crystal in an industrial furnace with horizontal magnetic field. [1] X. Huang, H. Kishi, S. Oishi, H. Watanabe, K. Sanpei, S. Sakai, and K. Koshikawa, Jpn. J. Appl. Phys. vol. 38 (1999) pp. l 353-l 355 [2] T. Minami, S. Maeda, M. Higasa, K. Kashima, J. Cryst. Growth 318 (2011) 196-199<a href="http://files.abstractsonline.com/CTRL/2E/F/8DF/174/5A3/478/9A5/9E2/FAC/S40/3FE/1C/g1245_1.png" target='_blank' address=no ><img src="http://files.abstractsonline.com/CTRL/2E/F/8DF/174/5A3/478/9A5/9E2/FAC/S40/3FE/1C/g1245_1.png" alt="" border="0" /></a></p>
CZOCZRALSKI GROWTH OF 550 MM DIAMETER SILICON CRYSTALS UNDER STRONG HORIZONTAL MAGNETIC FIELDS

Presenting Author: Alexey Kondratyev

Topic: Bulk Crystal Growth

Format: Contributed

Session: 2, 6

Date: 8/2/2021

Time (in MDT): 11:45:00 AM


Monocrystalline silicon ingots of 550 mm diameter are used for fabrication of mechanical parts for Dry Etch process on Semiconductor Fabrication in order to obtain a fully closed silicon chamber. The use of silicon guide ring in the reactive ion etch system improves etch uniformity by extending the plasma over the wafer surface and by focusing the electric field within the ring. Such a chamber prevents the graphite insulation impurities and yttrium atoms, that can emit from the cermet reactor walls, from reaching the wafer. Even a single metallic atom, reaching the wafer surface, can destroy the growing structure. Furthermore, inclusion of silicon mechanical parts into the reactor enables up to an order of magnitude increase of its operation cycle, avoiding interruption for cleaning. At present, there hardly seem to be an offer on the market for cylindrical parts of the silicon chamber as it should be cut out from a monocrystalline ingot which should be no less than 550 mm in diameter. Si ingots are produced by the Czochralski technique involving strong horizontal magnetic fields generated by direct current coils. Controlling the growth of large diameter crystals is always challenging due to strong thermal convection of the silicon melt characterized by high Grashof numbers. To suppress the instabilities arising due to buoyancy driven turbulence, horizontal magnetic fields are applied, that generate strong Lorentz forces due to high linear velocities at the crystal edge. The competing buoyancy and Lorentz forces can form complex melt flow structures that are difficult to govern and that complicate control over the growth. A variation of the growth parameters is performed both experimentally and numerically by computer modeling with CGSim software to provide a stable process without monocrystalline structure loss, minimize generation of defects in the crystal lattice and precipitation of impurities such as oxygen. The rate and direction of crucible rotation, vertical and angular position of the inductor coils and the heating regime are optimized. To resolve a melt turbulent flow inside the crucible an advanced RANS/LES approach using a novel hypothesis of turbulent flow anisotropy is applied. In particular, the model is characterized by the following features. A pressure-diffusion source term is introduced into the transport equation for the turbulent kinetic energy (TKE). Additional generation of TKE is considered on the melt surface due to thermocapillary and soluto-capillary effects. Turbulence is gradually damped near the crucible wall with increasing its rotation rate.
GROWTH AND SCINTILLATION PROPERTIES OF BaCl$_2$/NaCl/KCl EUTECTICS FOR RADIATION IMAGING APPLICATIONS.

Presenting Author: Yui Takizawa

Topic: Bulk Crystal Growth

Format: Contributed

Session: 3, 1

Date: 8/2/2021

Time (in MDT): 1:00:00 PM

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1. Introduction: Radiation detectors composed of scintillators and photodetectors such as CCD are widely used in X-ray imaging applications. In our research group, phase-separated scintillator fibers (PSSFs) of eutectic materials were reported for high resolution radiation imaging. In such PSSF structure the eutectic phases of higher refractive index scintillator fibers of several μm in diameter are surrounded by lower refractive index matrix materials. Such eutectic structure works as an optical waveguide. As a result, high resolution X-ray imaging can be achieved[1]. In this work, we searched the ternary eutectics containing BaCl$_2$/2NaCl/KCl ternary eutectics and their PSSFs structures were investigated.

2. Experimental procedure: The starting materials were prepared using BaCl$_2$/2NaCl/KCl ternary eutectics and their PSSFs structures were investigated. The details of BaCl$_2$/2NaCl/KCl eutectic composition were described in Ref.[2]. The starting powders were enclosed in a quartz tube with 3.8 mm inner diameter under high vacuum (~10$^{-4}$ Pa). Crystal growth was performed by the vertical Bridgman Stockbarger (VB) method. The pulling rates was 0.01 mm/min. The eutectic structures on transverse and vertical cross-section were observed.

3. Results & Discussion: The Tb doped and non-doped BaCl$_2$/2NaCl/KCl eutectics were grown by the VB method (Fig.1). Circular samples with 1 mm thickness were cut from the grown crystal. The cut surface was mechanically polished and the eutectic phase structure was observed by back scattered electron image (BEI). The BEI of transverse & vertical
cross-section of the eutectic are shown in Fig. 2. Tb:BaCl<sub>2</sub> scintillator fibers of 1-3μm diameter were surrounded by NaCl and KCl fiber phases although the fibers were winding along the growth direction. Here, refractive index of BaCl<sub>2</sub>, NaCl and KCl are 1.73, 1.54 and 1.49@550nm, respectively. The BaCl<sub>2</sub> scintillator fiber phase can have waveguiding function. In our presentation, relationship between chemical composition of starting materials, growth rate, and eutectic structure will be discussed. Details of scintillation properties, emission image map and radiation imaging using the grown eutectic plates will be also reported. Fig.2 BEI of BaCl<sub>2</sub>/NaCl/KCl eutectic on transverse (a) & vertical (b) cross-section. Fig.1 Photographs of the grown eutectics(a) and a wafer sample(b). Reference[1]K. Kamada et al, IEEE Trans. Nucl. Sci. 65(8) (2018) 2036-2040[2]E. Vortisch, Neues Jahrb. Mineral., Geol. Palaeontol., Beilageband, 38, (1914) 513-524.
MELT GROWTH AND SCINTILLATION PROPERTIES OF EU DOPED CAO SINGLE CRYSTALS BY CORE HEATING METHOD

Presenting Author: Kei Kamada

Topic: Bulk Crystal Growth

Format: Contributed

Session: 3, 2

Date: 8/2/2021

Time (in MDT): 1:15:00 PM

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Inorganic scintillators have been playing a major role in many fields of radiation detection, including astro-particle physics experiment, medical imaging, security, etc. The observation of neutrino-less double beta decay (0νββ) would be the most practical way to prove the Majorana nature of the neutrino and lepton number violation. The CANDLES experiment studies $^{48}$Ca double beta decay using 1000 CaF$_{2}$ scintillator in Kamioka observatory in Japan. The main advantage of $^{48}$Ca is that it has the highest Q-value (4.3 MeV) among all the isotope candidates for 0νββ. We are aiming to develop an inorganic scintillator including $^{48}$Ca with very good energy resolution for future 0νββ search experiment. For example, CaO is attractive host material for the above application due to high concentration of $^{48}$Ca. However CaO have generally high melting temperatures of 2572°C. Its boiling point of 2850°C is close to its melting point and make trouble due to its evaporation during crystal growth. Conventional growth techniques using Ir crucible such Chochralski, Bridgman-Stockbarger and micro-pulling down method are difficult to use for CaO crystal growth. In this study, we propose a novel indirect heating growth method using arc plasma and Ir metal melt for materials survey. Arc plasma preferentially head for metal due to the difference of electrical conductivity. We refer to this indirect heating growth method as the core heating (CH) method[1]. In this study Eu and non-doped CaO single crystals were grown by the CH method. Figure 1 shows an example photograph of the grown undope and Eu doped CaO crystals. These crystals shows enough transparency and size for luminescence and radiation response measurements. The Eu doped sample shows red Eu$^{3+}$ emission peaking at around 600-630 and 760-770 nm, respectively. Details of growth procedure, crystal phase, XRC, optical and scintillation properties will be presented. [1] K. J. Kim, K. Kamada, Crystals 2020, 10, 619
GROWTH OF IRON DOPED BETA GALLIUM OXIDE BY THE EDGE-DEFINED FILM-FED GROWTH (EFG) METHOD

Presenting Author: Drew Haven

Topic: Bulk Crystal Growth

Format: Contributed

Session: 3, 3

Date: 8/2/2021

Time (in MDT): 1:30:00 PM

Authors: Drew Haven, Saint-Gobain, Milford, New Hampshire, United States David Joyce , Saint-Gobain, Milford, New Hampshire, United States John Frank , Saint-Gobain, Hiram, Ohio, United States

Beta phase gallium oxide (β-Ga$_2$O$_3$) has seen a significant amount of attention in recent years as an ultra-wide bandgap semiconductor for next generation high power switching and high voltage RF electronics. This is due to its large band gap (E$_g$ = 4.8 eV), ability to be doped as an n-type semiconductor up to degenerate levels, high theoretical critical field strength of 8 MV/cm, and breakdown field 2-3 times larger than silicon carbide or gallium nitride. A major hindrance to the further development of this promising material is the lack of crystalline substrates, due to difficulties in the bulk crystal growth of gallium oxide. With Air Force Research Laboratory (AFRL) and National Renewable Energy Lab (NREL) support, Saint Gobain has undertaken a program aimed at growing gallium oxide by the Edge-defined Film-fed Growth (EFG) method. Saint-Gobain has successfully grown unintentionally doped (UID) and Fe-doped β-Ga$_2$O$_3$ ribbons, and fabricated wafers from this material. Preliminary details of growth, properties, and defects of the material will be reviewed.
AN EXPERIMENTAL APPROACH TO CONTROL BULK GAN GROWTH THERMODYNAMICALLY IN SITU BY THE NA FLUX METHOD

Presenting Author: Moahmmed Abo Alreesh

Topic: Bulk Crystal Growth

Format: Contributed

Session: 3, 4

Date: 8/2/2021

Time (in MDT): 1:45:00 PM

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In this study, we highlight the significance of nitrogen pressure monitoring of GaN growth by the sodium flux method. At UCSB system, GaN growth is correlated to the decrease of nitrogen pressure in a sealed reactor. Here, we demonstrate the system ability of monitoring and controlling the GaN growth thermodynamically in situ. By varying temperature and monitoring pressure, we were able to stop or start GaN growth in situ. In addition, this monitoring and control enabled us to calculate the Ga activity coefficient in the Na-Ga melt.
MOLTEN SALT SYNTHESIS OF NiO, MgO, AND THEIR MIXED OXIDES: DESIGNING NEW METHODS TO CONTROL CRYSTAL MORPHOLOGY

Presenting Author: Mariano Susman

Topic: Bulk Crystal Growth

Format: Contributed

Session: 3, 5

Date: 8/2/2021

Time (in MDT): 2:00:00 PM

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In several catalytic and absorption processes of industrial relevance, the crystal morphology and surface terminations of metal oxides play an important role; however, controlling these surface properties and studying their different behaviors in order to rationally optimize catalyst performance is not always feasible. In this presentation, we will discuss methods of preparing rock-salt metal oxides like MgO, NiO, and their solid solutions, (Mg,Ni)O by molten salt synthesis (MSS). Our findings reveal that MSS enables a high level of morphological control by altering the pathways of metal oxide crystallization. We will show that polar MgO(111) can be prepared using either alkali nitrates or chlorides. For NiO, the morphological diversity is much wider, including NiO octahedra and trapezohedra exposing NiO(311) and (611) facets in alkali chlorides. These high-index facets have not been previously reported for this material. Our findings also reveal that NiO(311) trapezohedral particles grow through a nonclassical crystallization pathway, and are stable under steaming and retain catalytic activity in oxidative dehydrogenation of ethane over long time on stream, indicating high morphological stability at reaction conditions without evidence of sintering. We will show that the judicious selection of alkali nitrates allows for the synthesis of NiO cubes, cuboctahedra, and octahedra. Moreover, we have discovered that the formation of (Mg,Ni)O solid solutions is distinctively favored in alkali chlorides whereas in nitrates segregation of the oxides takes place. The crystallization process in chlorides is mediated by the formation of molten phases comprised of KNaMCl (M=Mg, Ni) from which solid metal oxides form. Collectively, our findings reveal that diverse morphologies can be achieved through crystal engineering, thus allowing for the establishment of structure-performance relationships in a wide range of industrial catalytic processes.[1] M. D. Susman, H. N Pham, A. K. Datye, S. Chinta, J.D. Rimer; Chem. Mater. 2018 30, 2641-2650 “Factors governing MgO (111) Faceting in the thermal decomposition of oxide precursors”[2] M.D. Susman, H.N. Pham, X. Zhao, D.H. West, S. Chinta, P. Bollini, A.K. Datye; Angew. Chem. Int. Ed. 2020 59, 15119–15123 “Synthesis of NiO
Crystals Exposing Stable High-Index Facets”[3] M. D. Susman, S. Chinta, J. D. Rimer; Chem. Mater.<br>2021, “High-Index (Ni,Mg)O Crystallization during Molten Salt Synthesis” DOI:<br>10.1021/acs.chemmater.0c04837
GROWTH OF OPTICALLY TRANSPARENT GASB BULK CRYSTALS

Presenting Author: Partha Dutta

Topic: Bulk Crystal Growth

Format: Contributed

Session: 3, 6

Date: 8/2/2021

Time (in MDT): 2:15:00 PM

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GaSb is a III-V compound semiconductor substrate material most suitable for the growth of antimonide based quantum well and super-lattice layer photodetector structures due to its lattice matching characteristics with the device layers. For back side illumination devices, the substrate material must have high optical transmission. Unfortunately, GaSb has unusual optical transmission characteristics due to the presence of high density of equilibrium point defects (native defects such as vacancies and antisites) which makes the substrates practically opaque to radiation of below bandgap wavelengths where the devices operate. The GaSb substrate must be thinned after device fabrication complicating the device packaging process and often resulting in the introduction of defects in the device layers. Optically transparent GaSb is highly desirable for these applications as well as other infrared optical technologies. Two methods for enhancing the optical transmission of GaSb will be presented in this paper. In the first method, n-type dopants (Te, Se, S) has been used to compensate for the p-type native defects in GaSb crystals. The effect of Te, Se and S segregation on the wavelength dependent optical transmission characteristics of GaSb wafers extracted along the growth direction of the crystals will be discussed. In the second method, results of GaSb growth from gallium rich non-stoichiometric solution with growth temperature in the range of 400-550 °C will be presented. The effects of temperature gradient, synthesis duration and solution cooling rate on the optical transmission of GaSb will be presented. To eliminate the incorporation of gallium inclusions in the crystals, a continuous solute feeding process has been developed. The effectiveness of the solute feeding process on the reduction of gallium inclusion in the crystals will be presented. Using the solute feeding process, 2-3 mm thick crystals of 20 mm diameter GaSb has been successfully grown at temperature as low as 500 °C, which is approximately 200 °C lower than the melt growth temperature of GaSb. The reduced growth temperature results in lowering of native defect concentration, thereby enhancing the optical transparency of GaSb. For the growth of intrinsic (undoped) n-type GaSb, the growth temperature must be reduced below 400 °C. Challenges in solution growth at such low temperatures will be discussed along with the mitigating strategies.
The combination of magnetism and non-trivial band topology can generate potentially useful exotic quantum states of technological relevance, e.g., the quantum anomalous Hall insulator (QAHI). In this talk, I will present our recent studies on layered magnetic topological insulators (MnBi$_2$Te$_4$)(Bi$_2$Te$_3$)$_m$ (m=0, 1 & 2). This material system has recently attracted a great deal of interest, since it is predicted to provide access to a rich variety of novel topological quantum states, such as QAHI, axion insulators, high-order topological insulators and ideal Weyl semimetals [1-4]. Experimentally, intrinsic AFM insulators have been demonstrated for MnBi$_2$Te$_4$ (m=0) [3], MnBi$_4$Te$_7$ (m=1) [5] and MnBi$_6$Te$_{10}$ (m=2) [6]. Furthermore, both QAHI [7] and axion insulators [8] have been observed in 2D thin layers of MnBi$_2$Te$_4$. Our work [9-11] in this area has focused on the study of competing magnetic interactions of (MnBi$_2$Te$_4$)(Bi$_2$Te$_3$)$_m$ and the field-driven topological phase transition in Mn(Bi$_{1-x}$Sb$_x$)$_2$Te$_4$. While theory predicts the AFM phases are more stable than the FM phases in (MnBi$_2$Te$_4$)(Bi$_2$Te$_3$)$_m$, we have succeeded in synthesizing both AFM and FM phases for these compositions through finely tuning growth conditions and tuned their chemical potential to be close to their charge neutral points via Sb substitution for Bi. These materials provide rich opportunities for observing novel magnetic topological phases. From magnetotransport measurements on Mn(Bi$_{1-x}$Sb$_x$)$_2$Te$_4$, we have observed clear evidence of an ideal type-II FM Weyl state in the polarized FM phase. We find the field-driven AFM-to-FM transition induces an electronic structure reconstruction in lightly hole-doped samples, which results in a large intrinsic anomalous Hall effect and negative c-axis longitudinal magnetoresistance attributable to the chiral anomaly [11]. These results establish a promising platform for exploring the underlying physics of the long-sought, ideal time-reversal-symmetry breaking type II Weyl semimetal. References: [1] D. Zhang et al., Phys. Rev. Lett. 122, 206401 (2019). [2] J. Li et al., Science Advances 5, eaaw5685 (2019). [3] M. M. Otrokov et al., Nature 576, 416 (2019). [4] R.X. Zhang, F.C.Wu & S.D. Sarma, Phys. Rev. Lett. 124, 136407 (2020) [5] C. Hu, et al., Nat. Commun. 11, 1 (2020). [6] S. Tian et al., Phys. Rev. B 102, 035144 (2020) [7] Y. Deng et al., Science 367, 895 (2020) [8] C. Liu et al., Nat. Mater. 19, 5 (2020) [9] Lee et al., Phys.
CZOCHRALSKI GROWTH AND ELEMENTAL DISTRIBUTION IN THE MULTICOMPONENT GARNET (Lu<sub>1/4</sub>Yb<sub>1/4</sub>Y<sub>1/4</sub>Gd<sub>1/4</sub>)<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>

Presenting Author: Matheus Pianassola

Topic: Bulk Crystal Growth

Format: Contributed

Session: 4, 3

Date: 8/2/2021

Time (in MDT): 3:30:00 PM

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This work demonstrates the practical aspect of scalable growth of complex garnets and evaluates the implications of a multicomponent composition in the optical quality and elemental distribution of a Czochralski-grown crystal. A 30 mm-dia transparent (Lu<sub>1/4</sub>Yb<sub>1/4</sub>Y<sub>1/4</sub>Gd<sub>1/4</sub>)<sub>3</sub>Al<sub>5</sub>O<sub>12</sub> crystal was grown with a well-controlled shape. An increasing size and concentration of internal defects from seed to tail was observed via optical microscopy. Single-crystal and powder XRD indicate a single garnet phase with an increasing unit cell volume from seed to tail. EPMA results reveal an axial gradient of composition while the radial elemental distribution is relatively homogeneous. Preferential incorporation of smaller Lu<sup>3+</sup> and Yb<sup>3+</sup> was observed, while larger Gd<sup>3+</sup> ions are rejected by the crystal. Y<sup>3+</sup> ions have a relatively constant concentration throughout the crystal. The concentrations of three rare-earths and Y are closer to stoichiometric on the tail-side of the boule. In the micrometer scale, a homogeneous elemental distribution was observed via EDS elemental mapping.
EFFECTS OF MULTICOMPONENT COMPOSITIONS ON PHASE FORMATION IN MICRO-PULLING-DOWN GARNET CRYSTALS

**Presenting Author:** Matheus Pianassola

**Topic:** Bulk Crystal Growth

**Format:** Contributed

**Session:** 4, 4

**Date:** 8/2/2021

**Time (in MDT):** 3:45:00 PM

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In this work, we explore the effects of average ionic radius and pulling rate on the optical quality and phase composition of multicomponent garnet crystals grown by the micro-pulling-down method. Ten compositions were formulated from the system (Lu,Y,Ho,Dy,Tb,Gd)\(_3\)Al\(_5\)O\(_{12}\) with a range of rare-earth average ionic radius from 1.021 - 1.040 Å. Crystals were grown at either 0.05 or 0.20 mm/min. In general, crystals grown at 0.05 mm/min are more transparent and have a smoother surface. Optical microscopy images reveal an opaque central region in crystals with average ionic radii equal to or greater than 1.035 Å and 1.028 Å for crystals grown at 0.05 or 0.20 mm/min, respectively. Powder and single-crystal XRD reveal that crystals form a single garnet phase if the average ionic radius is equal to or shorter than a critical value; above this value, crystals form a mixture of garnet and perovskite. Slow pulling rates suppress the formation of secondary perovskite phases in crystals with intermediate average ionic radii. SEM/EDS measurements indicate typical eutectic microstructures closer to the outer edges of the crystals with large average ionic radii.
CRYSTAL GROWTH OF THE IRIDIUM-RHODIUM-RUTHENIUM ALLOY WIRES BY THE MICRO-PULLING-DOWN METHOD AND THEIR THERMOELECTRIC CHARACTERISTICS

Presenting Author: Rikito Murakami

Topic: Bulk Crystal Growth

Format: Contributed

Session: 4, 5

Date: 8/2/2021

Time (in MDT): 4:00:00 PM

Authors: Rikito Murakami, Graduate School of Engineering, Tohoku University, Sendai, Japan Kei Kamada, New Industry Creation Hatchery Center, Tohoku University, Sendai, Japan Katsunari Oikawa, Graduate School of Engineering, Tohoku University, Sendai, Japan Akira Yoshikawa, Institute for Materials Research, Tohoku University, Sendai, Japan

Thermocouples are widely used as an indispensable means for accurate temperature measurement in high temperature processes such as oxide single crystals, semiconductor crystal growth, and aerospace applications. Iridium-based thermocouples can be used in an atmosphere where a small amount of oxygen is present, and Ir/Ir-Rh thermocouples are currently commercially available. The Ir/Ir-Rh thermocouple can be used up to ~2423K, which is the melting point of Ir-Rh alloy wire. On the other hand, no noble metal thermocouple that can be used in the temperature range beyond 2423K can be commercially available. In such a temperature range, W-Re type thermocouples are candidates; however, they can only be used in inert or reducing atmosphere and have the disadvantage of becoming brittle after heating. We have addressed this problem by adopting the micro-pulling-down (μ-PD) method to make the thermocouple elements. The grown wires typically show unidirectional solidification microstructure or single crystal, thus the intergranular fracture reduce significantly. Recently, we have found that the fabricated Ir/Ir-20Ru thermocouple shows equivalent thermoelectromotive force characteristics with that of the commercially available Ir-40Rh/Ir thermocouple. While the Ir-Ru system is superior to the Ir-Rh system in terms of price (Ru: ~14 $/g, Rh: ~972 $/g as of April 1, 2021) and melting point, it has the problem of inferior oxidation resistance. In this study, we focused on the addition of rhodium, which has excellent oxidation resistance, to the iridium-ruthenium system and investigated its thermoelectric properties. In addition, we also investigated the Ru-Rh system without iridium. Iridium-ruthenium-rhodium and ruthenium-rhodium alloys were grown by the μ-PD method. Iridium, ruthenium, and rhodium powders with 99.9% purity were arc-melted in an Ar atmosphere. The button ingots were placed in a zirconia crucible with 0.5~0.7 mm diameter hole at the bottom and melted by induction heating in an Ar atmosphere. The iridium seed crystal was placed at the bottom of the crucible, and after the seed-touch process, the crystal was gently pulled down. Thermocouples were formed using Pt wire (99.99% purity) and their thermoelectric properties were measured in a tubular furnace. The thermoelectromotive force was measured by the comparison method with a calibrated R-type thermocouple (Pt/Pt-13%Rh) using a well-stirred ice-water mixture as reference junction. The EMF of each wire was obtained as a polynomial equation, and the EMF characteristics from room temperature to 2000 K were clarified for several thermocouples including previously unknown combinations.
SYNTHESIS AND DOMAIN STRUCTURES OF A VAN DER WAALS FERROMAGNETIC SEMICONDUCTOR VAGP$_2$Se$_6$ WITH A CHIRAL STRUCTURE

Presenting Author: Seng Huat Lee

Topic: Bulk Crystal Growth

Format: Contributed

Session: 4, 6

Date: 8/2/2021

Time (in MDT): 4:15:00 PM

Authors: Seng Huat Lee, Leixin Miao, Jingyang He, V. Gopalan, Nasim Alem, Zhiqiang Mao

The exploration of 2D van der Waals (vdW) materials has attracted enormous interest. The lattice symmetry often plays a pivotal role in generating exotic functional properties in 2D materials, e.g., the robust superconductivity in magic-angle twisted trilayer graphene [1,2]. The lattice symmetry-breaking in vdW materials has also been identified as one of the key ingredients for realizing a variety of exotic quantum phenomena such as valley Hall and non-linear Hall effects [3,4]. Furthermore, the lattice symmetry breaking, when combined with time-reversal symmetry (TRS) breaking in vdW materials, is also expected to generate novel exotic phenomena, such as second-order non-reciprocal optical effect and valley Zeeman effect [5,6]. However, the coexistence of TRS breaking and lattice symmetry breaking in vdW materials is rare. In this talk, we report the growth of a ferromagnetic vdW material with such a characteristic, VAgP$_2$Se$_6$. This material crystallizes in a non-centrosymmetric, chiral structure with the space group of $C\overline{2}$ and shows a ferromagnetic transition at about 20K. Prior theoretical studies predicted that this material may realize a quantum anomalous Hall effect and show coupled spin-valley physics [7,8]. We succeeded in synthesizing single crystals of this material using a horizontal flux method and characterized its microstructures using scanning transmission electron microscopy (STEM). We have observed two types of domain structures in the STEM images, characterized by 120° in-plane rotations and 180° domains along the $z$-axis. These domains also form the superstructures along the $z$-axis. Our success in growing this material and understanding its structures pave the way for observing new exotic quantum phenomena in this promising material.

References:
GRADUATED CONCENTRATION AND HOMOGENEOUS SİGE CRYSTALS FOR OPTICAL APPLICATIONS

Presenting Author: Yasutomo Arai

Topic: Bulk Crystal Growth

Format: Poster

Session: 

Date:

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Silicon-germanium alloys are promising materials for making photodiodes, waveguides, and gradient refractive index infrared lenses. Lens system components made from them are smaller, weigh less, and are more cost-effective. Infrared lenses need to be made from highly homogeneous or graduated-concentration SiGe crystals. SiGe crystal growth experiments were carried out on the ISS in 2013 and 2014 using homogeneous and high-gradient-concentration, 2%/mm crystals, respectively. Furthermore, these crystals exhibited a characteristically high growth rate at the initial growth region that had never been observed on Earth. This will be addressed in our work. Forty-millimeter-long Si1-XGeX crystal rods 20 mm in diameter have been grown using the TLZ method on the ground with temperature gradients below 15 K/cm on earth. Infrared transmittance pictures of the grown SiGe crystals show, for example, inclusions, Ge-rich particles, cracks, and striations indicating growth interfaces. Clear images were taken of crystal disks cut from 40-mm-long crystals. The growth striations were consistently detected at thin SiGe plate cuts along the growth axis except for crystals used in about 3K/cm temperature gradient experiments. SiGe crystals with an axial concentration gradient of about 1%/mm were produced by continuously raising the growth interface temperature. The limitation on the axial concentration gradient restricted the temperature gradient on the solid side of the interface. We will describe the status of the next ISS microgravity experiments planned for 2022.
GROWTH OF STRONTIUM TETRABORATE CRYSTAL FIBERS WITH NEAR STOICHIOMETRIC COMPOSITION BY THE MICRO-PULLING-DOWN METHOD EXHIBIT THE APPEARANCE OF GROWTH RIDGES

Presenting Author: Harutoshi Asakawa

Topic: Bulk Crystal Growth

Format: Poster

Session:

Date:

Time (in MDT):

Authors: Harutoshi Asakawa, Yamaguchi University, Ube, Japan  Takaaki Machida, Yamaguchi University, Ube, Japan  Ryuichi Komatsu, Yamaguchi University, Ube, Japan

SrB$_{4-x}$O$_{7-x}$ (SBO) has recently received much attention as a wavelength-conversion material that can operate into the deepest ultraviolet wavelengths (125 nm). The utilization of SBO for semiconductor lithography and laser ablation requires fully transparent crystals. Here, we show the growth of SBO crystal fibers with near-stoichiometric composition by the μ-pulling-down method. SrB$_{2x}$O$_{3x+1}$ ceramics sintered with various values of x were evaluated by X-ray diffraction (XRD). The external form of SBO crystal fibers grown with +0.1 and -0.1 mol% SrO was opaque due to the formation of growth ridges. Also, we succeeded in obtaining transparent SBO crystal fibers by the growth with a stoichiometric composition. Then, we observed SBO crystal fibers grown with various x values by polarized optical microscopy. As a result, even when the deviation from stoichiometric composition was ±0.1 mol% SrO (x = 2 ± 0.004), SrB$_{2}$O$_{4}$/SrB$_{6}$O$_{10}$ appeared. These results demonstrate that SBO exhibits no solid-solution width. Furthermore, we found that the stoichiometric composition is equal to the congruent composition. In contrast, since growth ridges including SrB$_{2}$O$_{4}$/SrB$_{6}$O$_{10}$ were formed only on surfaces of the SBO single crystals, SBO crystal fibers grown with nonstoichiometric composition were opaque. We could explain the formation of growth ridges via compositional supercooling on rims.
INVESTIGATION OF SEEDED VERTICAL GRADIENT FREEZE (VGF) GROWTH OF CDZnte BULK CRYSTALS

Presenting Author: Özden Balbaşı

Topic: Bulk Crystal Growth

Format: Poster

Session: ,

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Cadmium Zinc Telluride (CdZnTe) has become a crucial material for X-ray and gamma ray detection due to its wide bandgap energy combined with high atomic number and high density, which offer high efficiency and sharp spectroscopic resolution at room temperatures. In addition, due to being lattice matched, CdZnTe is a suitable candidate as substrate material for the epitaxial growth of HgCdTe that can be used for infrared detection with high resolution. Hence, increasing the single crystal yield of CdZnTe from the grown ingot gained importance for the development of such detectors. Traditionally, seeded crystal growth techniques result with higher single crystal yield for bulk growth techniques since previously placed single crystal seed could act as a starting point for high area single crystal solidification process in the earlier stages of the growth. However, due to the superheating above melting point requirement for homogenization process of CdZnTe material, complete seed melting remains as a detrimental problem for the seeded VGF growth of CdZnTe. In addition, due to the typical low single crystal yields in VGF growth of CdZnTe, obtaining single crystal seed material with desired geometries could be considered as a challenge. In this study, single crystal CdZnTe seeds of cylindrical geometry with 10 mm diameter and up to 50 mm length were successfully obtained using Computer Numerical Control (CNC) cutting system with custom diamond tooling. Moreover, to avoid complete seed melting, a peculiar design of the growth crucible and support system along with radiation shielding around seed region is employed. Temperature profiling and growth experiments were conducted to observe seed melting and seeded crystal growth of CdZnTe. Initial results of seeded VGF growth using single crystal CdZnTe seeds are reported.
SINGLE CRYSTAL GROWTH OF MONOISOTOPIC GRAPHITE CRYSTALS FROM A MOLTEN FE FLUX

Presenting Author: Dylan Evans

Topic: Bulk Crystal Growth

Format: Poster

Session: ,

Date:

Time (in MDT):

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Here we report on the growth of high purity graphite crystals using an iron flux. Iron was selected as a solvent for the ability of its liquid phase solution to dissolve high concentrations of carbon. A mixture of carbon and iron powders were heated above the melting temperature of the flux, usually 1500ºC, and was left to dwell at this temperature for up to 24 hours to fully saturate the molten solution with carbon. Then the solution was slowly cooled at 4ºC/hour to 1300ºC then at 20ºC/hour to 1140ºC to precipitate graphite crystals. Nitrogen at atmospheric pressure flows continuously through the furnace during crystal growth. The dwell temperature was varied to test total graphite precipitation and average domain size. The average domain size of the graphite crystals increased from average sizes of ~150 μm to 800-1000 μm at maximum temperatures of 1300ºC and 1500ºC, respectively. The optimum concentration was around 5.3wt% C in Fe. This process was used to grow graphite crystals with controlled carbon isotope concentrations, which offers an additional parameter by which the properties of graphite and graphene can be varied. Solution growth allows for the growth of graphite crystals with different isotope concentrations by controlling the initial carbon isotope concentration in the metal flux. The quality of the crystals and the effects of isotope concentration were measured using Raman spectroscopy. The figure below shows Raman spectra obtained from three samples, ¹²C, ¹³C, and 20% ¹³C. The “G” peak positions (widths) were 1582.3 cm⁻¹ (13.5 cm⁻¹) and 1522.5 cm⁻¹ (12.4 cm⁻¹) for ¹²C and ¹³C respectively. The G peak linewidth from these two crystals are comparable to that from charge neutral single layer graphene. For a mixed composition sample of 20% ¹³C, the G peak shifted to 1571.4 cm⁻¹ (16.6 cm⁻¹). Peak broadening in the mixed sample is expected due to isotope disorder. In all samples, the “D” peak, which is usually around 1350 cm⁻¹ in ¹²C graphite, was absent. The narrow G peak and absence of the D peak both indicate high crystallinity and low defect density. These results show that the metal flux method is capable of growing high quality graphite crystals with domain sizes frequently reaching up to 1000 μm. 

<a href="http://files.abstractsonline.com/CTRL/71/S/6B7/S7F/B08/439/E8B/082/CD5/403/A40/EF/g1071_2.PNG" target='_blank' address=no > <img src="http://files.abstractsonline.com/CTRL/71/S/6B7/S7F/B08/439/E8B/082/CD5/403/A40/EF/g1071_2.PNG" alt="" border="0" width="600" height="334" /></a>
OPTIMIZATION OF BORON CONCENTRATION FOR HBN SOLUTION GROWTH FROM A MOLTEN IRON SOLVENT

Presenting Author: Eli Janzen

Topic: Bulk Crystal Growth

Format: Poster

Session: ,

Date:

Time (in MDT):

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Hexagonal boron nitride (hBN) is a wide bandgap (>6.0 eV) semiconductor that has received much research interest due to its applications in neutron detectors, 2-D heterostructures, and deep-UV LEDs among many others. Atmospheric pressure solution growth of hBN using molten metals as solvents has proven effective at growing large, high quality single crystals useful in these applications. Solubility curves could ease the optimization of this process, but these have not been used for hBN solution growth because none were available. In this work, the CALPHAD method, a semi-empirical thermodynamic method that predicts phase behavior in complex systems, was used to generate an hBN solubility curve for the Fe-B-N system. This was done by calculating the amounts of phases as a function of temperature under a constant 1 bar nitrogen atmosphere and noting the temperature at which hBN first forms. Calculating this temperature with a series of boron concentrations resulted in the solubility curve shown below. Using this curve and taking the boron concentration at 1550°C (the operating temperature optimized in previous work) to be the optimal boron concentration yields 2.3 mass% B in Fe. To verify that this concentration is optimal in practice, a series of crystal growth experiments were performed using boron concentrations between 2 and 5 mass%. Each experiment was cooled from 1550°C to 1500°C at 1°C/hr in a 1 bar N<sub>2</sub>/H<sub>2</sub> atmosphere. Between 2 and 2.5 mass% B, hBN single crystals with lateral dimensions larger than 100 µm completely covered the surface while higher concentrations did not, which supports the conclusion that 2.3 mass% B is optimal. This result demonstrates an efficient way to optimize the concentrations of components in a solution that will work with other solvents as well. Performing the same CALPHAD modeling with the eutectic Ni-Cr solvent used in past work predicts an optimal concentration of 4 mass% B in Ni/Cr, in agreement with the best experimentally determined boron concentration from that work. This greatly enhances the ability to search through the broad parameter space to predict the optimal solvent and its concentrations. As a result, research can be refocused toward studying the kinetics of the process (cooling rate, nucleation rate, mass transport, etc.), which are critical for maximizing the size and quality of the crystals grown.
YTTRBIUM DIFLUORIDE YBF$_2$: PREPARATION, STRUCTURE, PROPERTIES

Presenting Author: Denis Karimov

Topic: Bulk Crystal Growth

Format: Poster

Session: 

Date: 

Time (in MDT): 

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Yttrbium difluoride YbF$_2$: preparation, structure, properties

Karirov D.N.$^1$, Buchinskayaii I.I.$^1$, Ivanova A.G.$^1$, Zykova M. P.$^2$

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Crystals of rare earth metal difluorides (Sm, Eu, Yb), isostructural to cubic alkaline earth fluorides, represent a new class of compounds with an atypical rare earth ion oxidation state (2+). A study of the growing conditions of these crystals and their characterization is of great both fundamental and practical interest [1]. A technique for the synthesis of cubic ytterbium (II) fluoride has been developed. The reaction of YbF$_3$ and metallic Yb$_0$ taken in a stoichiometric ratio of 2:1 (according to the theoretical reaction: $2\text{YbF}_3 + \text{Yb} = 3\text{YbF}_2$) was carried out in an evacuated (∼$10^{-2}$Pa) quartz ampoule at a temperature of 950°C for a day. The inner surface of the ampoule was preliminarily subjected to graphitization by pyrolysis of acetone to prevent contact of the reagents with quartz. As a result of the reaction, small transparent yellow crystals were obtained (Figure). The samples were studied by single crystal X-ray diffraction analysis. Its have space group Fm-3m, lattice parameter = 5.5983(3) Å. Using the dependence of the lattice parameter on the composition [2]: $a(x) = 5.5994 - 0.0779x$, it was found that the resulting reaction product corresponds to the composition YbF$_{2.01}$, which is very close to stoichiometry. Preparation of transparent yellow single crystals of YbF$_2$ with the lattice parameter $a = 5.5946(16)$Å was reported earlier [3]. However, in accordance with the data [1], such a lattice parameter should be present in the YbF$_{2.06}$ composition, which is not stoichiometric. The report presents the results of a study of the physical properties of the grown YbF$_{2+x}$ single crystals. Prospects for their practical application in optics and photonics are discussed. Figure. Schematic representation of the YbF$_{2+x}$ synthesis process, images of as-grown YbF$_2$ crystals in optical and scanning electron microscopes.
Abstract Book - ACCGE-22//OMVPE-20

References:


TWINNING AT LINEAGES ACCOMPANIED WITH CRACKING IN CZOCHRALSKI-GROWN LiTaO$_3$ INGOTS

Presenting Author: Yutaka Ohno

Topic: Bulk Crystal Growth

Format: Poster

Session: ,

Date:

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There is a growing demand for high quality LiTaO$_3$ wafers used for surface acoustic wave filters. However, growth of long high quality LiTaO$_3$ ingots by the Czochralski (CZ) method is still challenging. One important issue to obtain long CZ-LiTaO$_3$ ingots is cracking during the growth. Kumaragurubaran has classified the cracking phenomena in CZ-LiTaO$_3$ ingots into four origins; 1) the crossover of macroscopic twins, 2) change in crystal geometry forming vertexes, 3) ridges, and 4) lineages composed of dislocation arrays [1]. The first three cracking phenomena can be suppressed in the present commercial CZ-LiTaO$_3$ ingots by using an appropriate growth condition. Meanwhile, cracking process at lineages is still unclear. In the present work, we have found that polycrystallization via twinning, accompanied with cracking, takes place at lineages (Fig. 1). We have examined structural properties around the lineages and discussed a possible cracking mechanism, towards the control of the generation and growth of twins so as to suppress cracking. Specimens were commercial-grade CZ-LiTaO$_3$ ingots grown from a congruent melt. The pulling direction was a so called 36º-RY direction, that is widely used for commercial wafers. Structural properties of lineages and twins were examined by x-ray topography, optical microscopy combined with etch pit techniques, and transmission electron microscopy. We have found that cracking takes place at the twin lamellae generated at lineages beneath the -Z' surface of 36º-RY CZ-LiTaO$_3$ ingots. Twin lamellae on (10-12) and (-1102) would be generated via the dissociation of the dislocations composing lineages [2], and they grow with the CZ growth towards the bottom of the ingot, forming the intersections nearly parallel to the growth direction. Cracking takes place at the intersections with developing the twin lamellae. The twinning accompanied with cracking takes place when the diameter of the ingots is suddenly decreased. It is hypothesized that radial tensile stresses needed for the generation and growth of twins would be applied via an accidental fluctuation of growth temperature due to some reason, such as the heat of solidification of LiTaO$_3$ crystals on the crucible.

twinning process at lineages beneath the -Z’ surface of 36^o\text{RY CZ-LiTaO}_3\text{ ingots. (d) Schematic view of the development of a pair of twin lamellae intersecting each other.}
THE INFLUENCE OF SYNTHESIS CONDITIONS OF YB:CAWO<sub>4</sub> SINGLE CRYSTALS ON THEIR DOWNCONVERSION LUMINESCENCE

**Presenting Author:** Kirill Subbotin

**Topic:** Bulk Crystal Growth

**Format:** Poster

**Session:** ,

**Date:**

**Time (in MDT):**

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Yb-doped Scheelite-like molybdate and tungstate single crystals possess the efficient UV to NIR quantum cutting via cooperative energy down-conversion. They can be applicable for improvement the efficiency of crystalline silicon-based solar cells, due to the conversion of blue and UV sunlight photons into twice number of secondary photons with the energy just above the silicon band gap. The mechanism for this down-conversion involves some donor centers existing in the crystal. However, the nature of these donor centers in scheelite-like crystals remains unknown. The purpose of this research was to test two versions of that nature: Yb<sup>2+</sup> ions, and the high-lying charge transfer excited states of Yb<sup>3+</sup> ions. The Yb:CaWO<sub>4</sub> crystal was selected for the research, because of the largest bandgap among all crystals of the scheelite family, 5.2 eV, as well as due to the most favorable crystallochemical conditions for Yb<sup>2+</sup> formation. The series of Yb:CaWO<sub>4</sub> and Yb,Nb:CaWO<sub>4</sub> single crystals was grown by Czochralski in air, in N<sub>2</sub>, and in extra-pure argon atmospheres. Some samples were then additionally annealed in air, in a CO / CO<sub>2</sub> atmosphere, and in a forevacuum. We studied the optical absorption spectra of the crystals, as well as the luminescence spectra under the excitation at different wavelengths of UV range. It has been determined that the additional introduction of Nb<sup>5+</sup> into Yb:CaWO<sub>4</sub> crystal raises the distribution coefficient of Yb<sup>3+</sup> in the crystal by an order of magnitude, upto almost unity. Under the UV-excitation the Yb<sup>3+</sup> downconversion luminescence was observed at ~1 µm. Increasing the oxidizing conditions of the samples fabrication and Nb<sup>5+</sup> introduction into their composition reduce the intensity of this luminescence. Based on the data obtained, it was concluded that Yb<sup>2+</sup> ions are the main donors involved into the down-conversion and the charge transfer excited states of Yb<sup>3+</sup> ions are much less efficient donors. It was also confirmed that color centers and self-
trapped excitons on tungstate complexes, do not participate in the down-conversion in Yb doped scheelite-like crystals.<br />
This work was supported by the Ministry of Science and Higher Education of Russia, project FSSM-2020-0005
EFFECT OF Li<sup>+</sup>CODOPING ON THE PROPERTIES OF YB: ZNWO<sub>4</sub> SINGLE CRYSTALS

Presenting Author: Kirill Subbotin

Topic: Bulk Crystal Growth

Format: Poster

Session: ,

Date:

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Yb: ZnWO<sub>4</sub> single crystal is promising laser material. Spectroscopic studies of this crystal have shown that, along with attractive characteristics typical for tungstates of other structural classes (high specific luminescence intensities and significant inhomogeneous broadening of spectral bands), this crystal is also characterized by significant Stark splitting of the Yb<sup>3+</sup> ground state, as well as extremely weak optical absorption in the wavelength range corresponding to the strongest luminescence band. This should facilitate the achievement of the efficient low-threshold lasing of ytterbium near 1 micron, almost insensitive to heating of the active medium during the laser operation. 

Undoped ZnWO<sub>4</sub> single crystals are well known for a long time as efficient scintillating materials, and their fabrication technology is well developed. However, as our previous studies have shown, doping the crystal by Yb<sup>3+</sup> ions without a charge compensator sharply deteriorates the crack resistance of the samples. Probably, the reason for such behavior is the formation of an increased number of cation vacancies. They serve as charge compensators for the heterovalent entrance of ytterbium into the lattice, but at the same time they should significantly worse and weaken the connection between neighboring atomic layers of the crystal structure. 

In the frame of our work the series of ZnWO<sub>4</sub> single crystals doped with various concentrations of Yb<sup>3+</sup> and Li<sup>+</sup> ions (including zero concentrations) was grown by Czochralski. Lithium was used as a charge compensator preventing the formation of the above cation vacancies. The actual dopants concentrations in the crystals and their segregation coefficients between the crystal and the melt, were determined, as well as the unit cell parameters, the melting points, and the mechanical strength characteristics of the crystals, as a function of the dopants concentrations. It has been shown that the optimal Li<sup>+</sup> amount in the initial charge for the crystal growth of doubled one, as
compared to ytterbium amount. This results in significant enhancement of heterovalent incorporation of ytterbium with into the crystal lattice, and prevents the deterioration of crack resistance of the crystal.

This work was supported by the Ministry of Science and Higher Education of Russia, project FSSM-2020-0005
CRYSTAL GROWTH OF $\text{La}_2\text{Hf}_2\text{O}_7$ BY MICRO-PULLING-DOWN METHOD USING W CRUCIBLE

Presenting Author: Takahiro Suda

Topic: Bulk Crystal Growth

Format: Poster

Session:

Date: 

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The micro-pulling-down (μ-PD) method has been used for material researches of functional single crystals because of its relatively faster growth rate than conventional melt-growth methods. Ir and Pt crucibles have been generally used for the crystal growth by the μ-PD method and various functional single crystals have been developed. On the other hand, various novel materials with high melting point have been fabricated as a sintered compact and transparent ceramic to investigate their physical properties. However, there are few reports of the crystal growth for the materials with high melting point (>2200°C) by melt growth methods because the Ir and Pt crucibles can’t be used. Therefore, we focused on the W crucible (melting point 3400°C) with higher melting point than Ir and Pt, and La$_2$Hf$_2$O$_7$ single crystal could be grown by the μ-PD method using the W crucible. In this study, we tried to grow La$_2$Hf$_2$O$_7$ single crystal by the μ-PD method using a W crucible. Starting materials, La$_2$O$_3$ (5N) and HfO$_2$ (3N) powders, were mixed as the nominal composition of La$_2$Hf$_2$O$_7$. Mixed powders were sintered at 1600 °C for 24 hours in air and the crystal growth was performed under Ar using a W crucible with a φ3 mm die, deoxygenated ZrO$_2$ insulators and a W seed rod. Deoxygenated ZrO$_2$ insulators were used to prevent the crucible from being oxidized. A La$_2$Hf$_2$O$_7$ crystal was grown by the μ-PD method using a W crucible. Without any damages of the crucible, the La$_2$Hf$_2$O$_7$ sintered powder could be melted completely and the melt came out from the inside of the crucible through the hole of the die. The W rod was touched to the melt on the bottom of the die and the La$_2$Hf$_2$O$_7$ crystal could be fabricated by pulling-down the melt.
As a result, the grown $\text{La}_{2}\text{Hf}_2\text{O}_7$ crystal was obtained as shown in Fig. 1. The black color of the crystal suggested that oxygen deficiency occurred during the growth. The powder XRD pattern of the grown crystal showed that it was a single phase of $\text{La}_{2}\text{Hf}_2\text{O}_7$. Details of crystal growth and properties will be reported.
INVESTIGATION OF CdZnTe INGOTS GROWN BY THM FURNACE IN METU-CGL

Presenting Author: Mustafa Ünal

Topic: Bulk Crystal Growth

Format: Poster

Session: ,

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Cadmium Zinc Telluride (Cd<sub>1-x</sub>Zn<sub>x</sub>Te) semiconductor crystals have gained attention in the field of X-ray and gamma-ray detection applications over the past years owing to developments in crystal growth and surface preparation processes. Unlike Si and Ge, CdZnTe detectors can operate at room temperature thanks to its wide band-gap, high atomic number and high density. In addition, by changing the fraction of Zn content in the crystal matrix, both mechanical and electrical properties of the crystal can be altered. %Zn is usually kept around 10% for an optimal CdZnTe crystal to be used in X-ray and gamma-ray detection systems. However, due to segregation of Zn during melt growth (segregation coefficient, k<sub>Zn</sub>=1.35), Zn concentration varies along growth axis. Additionally, melt growth techniques usually result with multi-crystalline CdZnTe ingots because of the high growth temperature which causes complete seed melting (>1100 °C). Thus, overall yield of CdZnTe crystal production decreases significantly. In order to eliminate this problem, solution-based growth is proposed, one of which is Travelling Heater Method (THM). THM enables low temperature and seeded growth with high compositional uniformity unlike high temperature growth processes. By using a single crystal seed material, resulting ingots have a high chance to be single crystalline, thus increasing the yield significantly. THM growth technique employs a melt solidus region to dissolve feed material and the growth is conducted by the translation of the melt region over the seed. During THM growth of CdZnTe crystals, melt region is formed by Cd-rich Te alloy with melting temperature between 700-900 °C. By moving heaters, feed CdZnTe material is dissolved into solidus region while CdZnTe crystallizes over the seed crystal at the opposite side of solidus region. The problem in THM growth is obtaining highly stable growth interfaces. Due to the presence of Cd-rich Te solution, interface instabilities can cause formation of secondary phases like Te inclusions with various size and shapes which degrades electrical properties of CdZnTe crystals. Additionally, progress of the growth results with change in interface shape due to low thermal conductivity of CdZnTe. In this presentation, CdZnTe ingots grown by THM furnace are examined. Obtained crystals from THM growths are investigated by IR microscope and SEM to observe and analyze secondary phases. Additionally, growth interface is inspected for micro
instabilities. Further investigations are conducted to obtain general properties of THM grown CdZnTe ingots.
MICROSTRUCTURE AND THERMOELECTRIC PROPERTIES OF LA-DOPED SRTIO$_3$/TiO$_2$ EUTECTIC CRYSTALS GROWN BY MICRO-PULLING-DOWN METHOD

Presenting Author: Yuui Yokota

Topic: Bulk Crystal Growth

Format: Poster

Session: ,

Date:

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Phase-separated eutectic structure can be self-organized by unidirectional solidification of melt with an eutectic composition. Recently, we developed the undoped and Nb-doped SrTiO$_3$/TiO$_2$ (STO/TO) crystals with the eutectic structure as a thermoelectric material fabricated by the unidirectional solidification. Undoped and Nb-doped STO/TO (Nb:STO/TO) eutectic crystals were composed of the uniform phase-separated eutectic structure of the STO matrix and the TO rod phases. The thermal conductivity of the Nb:STO/TO eutectic crystal was lower than that of the Nb:STO single crystal owing to the decrease of the lattice thermal conductivity by phonon scattering at the boundaries. Eutectic morphology in the eutectic crystal can be controlled by growth rate, and relationship between diameter of rod phase and the growth rate is expressed as the Jackson-Hunt model. In this study, the eutectic morphology of the La-doped STO/TO (La:STO/TO) eutectic crystal were controlled by the growth rate to investigate the effects of eutectic structure on the thermoelectric properties of the La:STO. La-doped SrTiO$_3$/TiO$_2$ (La:STO/TO) eutectic crystal was grown by a micro-pulling-down method at various growth rates to control the eutectic morphology and the thermoelectric properties were investigated. The La:STO/TO eutectic crystal was composed of the TiO$_2$ rod phase in the SrTiO$_3$ matrix phase for all growth rates. Diameter of the TiO$_2$ rod phase systematically decreased with increasing the growth rate according to the Jackson-Hunt model and reached to approximately 1 mm. La:STO/TO eutectic crystals indicated the lower thermal conductivity than the Nb:STO single crystal owing to decrease of the lattice thermal conductivity by phonon scattering at boundaries in eutectic morphology. The figure of merit $ZT’s$ of the La:STO/TO eutectic crystals grown at 0.02 and 0.5 mm/min growth rates were 0.015 and 0.025, respectively.
IN-SITU INTERFACE OBSERVATION OF SOLUTION GROWTH OF 4H-SiC AT THE INITIAL GROWTH STAGE

Presenting Author: Takeshi Yoshikawa

Topic: Characterization techniques for bulk and epitaxial crystallization

Format: Invited

Session: 2, 1

Date: 8/2/2021

Time (in MDT): 10:30:00 AM

Authors: Takeshi Yoshikawa, The University of Tokyo, Tokyo, Japan Sakiko Kawanishi, Tohoku University, Sendai, Japan

4H-SiC is a key material for energy-saving power devices. Solution growth technique is a promising process to obtain high quality bulk single crystals because of its growth close to the thermal equilibrium. The growth rate has been greatly improved by selecting the alloy solvents composed by transition metals and silicon to increase the carbon solubility, and the reduction of the dislocation density of grown crystal has been realized. However, the interface control under the moderate growth condition is needed to avoid the polytype transition and solvent inclusions. To effectively control the growth front with understanding the interfacial phenomena during the solution growth process, we established a real-time observation technique of SiC/solution interface at high temperature using an optical microscope. We have performed the interface observation of solution growth of 4H-SiC at different growth temperatures and from different solvents such as Si, Fe-Si and Si-Cr solvents. We will discuss the observed growth phenomena of SiC at the initial growth stage.
IN-SITU STUDIES OF DOUBLE SHOCKLEY STACKING FAULT EXPANSION/SHRINKAGE IN NITROGEN-DOPED 4H-SIC BY SYNCHROTRON X-RAY TOPOGRAPHY

Presenting Author: Fumihiro Fujie

Topic: Characterization techniques for bulk and epitaxial crystallization

Format: Invited

Session: 2, 3

Date: 8/2/2021

Time (in MDT): 11:00:00 AM

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Silicon carbide (SiC) is a very promising material for power devices because of its excellent physical properties. However, many crystal defects still exist in the crystal, and these are known to degrade the device performance. Especially in the case of nitrogen-doped n-type SiC substrates, the formation of double Shockley-type stacking faults (DSFs) has been observed to occur at typical device processing temperatures. To elucidate the formation/expansion mechanism of the DSFs, we have developed an in-situ observation system of dislocation motion using synchrotron X-ray topography [1]. We studied the temperature and nitrogen concentration dependence [2]. Fig. 1 shows the in-situ system, which is composed of an electric furnace and a goniometer. This system allows us to observe the glide motion of partials in the basal plane with the expansion of DSFs at high temperatures up to about 2000 K. Fig. 2 shows an example of the in-situ observation, 000,16 reflection images at 1580-1710 K (Figs. 2(a)-(c)) and −1−120 reflection images at 1730-1910 K (Figs. 2(e)-(g)) of a 4H-SiC with nitrogen concentration of 1.0×10^{-19} cm^{-3}. Si-core partials bounding DSFs appear as white and black line contrasts for each diffraction condition. One can see that the DSFs expand up to 1610 K but rather shrink above 1730 K. It has been suggested that the driving force for DSF expansion is attributed to the local energy levels associated with the DSFs which can be regarded as the presence of 3C-SiC (small bandgap: 2.4 eV) structures. The electronic energy gain induced by the electron trapping by the local levels varies depending on temperature, which induces a change in the driving force for DSF expansion. This means that at low temperatures, the electronic energy gain exceeds the structural formation energy and the net stacking fault energy becomes negative, but at high temperatures above 1730 K, the relationship between the two terms is reversed and the stacking fault energy is considered to have turned positive. Additional in-situ studies for nitrogen concentration dependence of DSF behavior revealed the driving force for DSF expansion increased with increasing nitrogen concentration. We identified the temperature range where the stacking fault energy becomes positive for each nitrogen concentration and suppression of DSF expansion is suggested to be achieved by optimized heat treatment. [1] F. Fujie et al., Appl. Phys. Lett. 113(1) (2018). [2] F. Fujie et al., Acta Mater. 194 (2020) 387-393. <p><a href="http://files.abstractsonline.com/CTRL/C1/2/24C/737/1F0/48E/18C/005/CFB/9F0/67A/30/g1252_3.jpg" target='_blank' address=no >
DISLOCATION CONTRAST ON X-RAY TOPOGRAPHS UNDER WEAK DIFFRACTION CONDITIONS

Presenting Author: Hongyu Peng

Topic: Characterization techniques for bulk and epitaxial crystallization

Format: Contributed

Session: 2, 5

Date: 8/2/2021

Time (in MDT): 11:30:00 AM

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X-ray topography (XRT) based on modern synchrotron light sources is a diffraction imaging technique similar to transmission electron microscopy (TEM), but XRT has much larger view fields, up to a few square inches. Another advantage of XRT is that it is a non-destructive method and thus can image bulk crystals, epitaxial films, and wafers fabricated with electronic devices. In comparison to white-beam X-ray topography that is dominated by integrated Bragg-peak diffraction, the contrast of dislocations in 4H-SiC crystals shows distinctive features on monochromatic topographs and it can dramatically vary on different points of the same rocking curve. These features can reveal the detailed and comprehensive atomic structures of the dislocations. Instead of using the conventional Takagi-Taupin theory that is extremely complicated with many limitations and drawbacks, we demonstrate that the simple geometric-diffraction-based ray-tracing method together with a simplified effective rocking curve can accurately simulate the contrast of all kinds of dislocations on any point of the rocking curve. Successful applications of this method reveal that the dislocation contrast in weak-beam diffraction is more sensitive to local lattice distortion (strain fields), consequently enabling unambiguous determination of the dislocation senses not obtainable from white-beam topography. Of more importance is that this method is an extremely simple and straightforward geometrical method that can be easily implemented even by non-specialists for quantitatively interpreting monochromatic topographs.
X-RAY CHARACTERIZATION OF DEFECT STRUCTURES IN PVT-GROWN ZNSE CRYSTALS WITH DIFFERENT SEEDING CONDITIONS AND GROWTH CONFIGURATIONS

Presenting Author: Qianyu Cheng

Topic: Characterization techniques for bulk and epitaxial crystallization

Format: Contributed

Session: 2, 6

Date: 8/2/2021

Time (in MDT): 11:45:00 AM

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Zinc Selenide (ZnSe) as a II-VI semiconductor is notable for its superior properties such as wide bandgap, low optical absorption in the visible and infrared spectral region, and intense edge luminescence in the short-wavelength spectral region. Those excellent features realize its utilization on high efficiency electronic and optoelectronic devices including blue light-emitting diodes, lasers, and blue/ultraviolet-light-sensitive photodetectors, which are of considerable interest for applications in optical storage, lighting and illumination, biomedical sensing, etc. However, structural defects within the bulk ZnSe crystal are hampering the overall device performance. To continuously improve the device reliability, obtaining a comprehensive understanding on ZnSe crystallographic structure and defect formation mechanism is crucial. In this study, characterization techniques including synchrotron white beam X-ray topography (SWBXT), optical microscopy and high-resolution triple X-ray diffraction (HRTXD) were conducted on seeded and self-seeded ZnSe crystals grown by physical vapor transport (PVT) method in horizontal and vertical growth configurations. The effect of seeding condition and gravity vector orientation with respect to growth geometry on crystalline quality and defect structures is investigated. The presence of grains and the occurrence of twinning is revealed and analyzed. This study provides a clear understanding of factors that causes ZnSe crystal quality variation during the growth process, which contributes to achieving the routine production of high-quality ZnSe crystal and modern device enhancement.
GAN WAFERS AND EPITAXIAL FILMS WITH DRAMATICALLY IMPROVED CRYSTALLINE AND ELECTRICAL PROPERTIES

Presenting Author: Jaime Freitas, Jr.

Topic: Characterization techniques for bulk and epitaxial crystallization

Format: Invited

Session: 3, 1

Date: 8/2/2021

Time (in MDT): 1:00:00 PM

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Gallium Nitride (GaN, with room temperature Eg ~ 3.4 eV) and its alloys with Indium and Aluminum, part of third semiconductors generation, are revolutionizing both the optoelectronic and electronic device industries. Despite a previous lack of native substrates, a number of devices exceeding the performance of those fabricated from well-developed semiconductors were realized. However, the fabrication of higher performance devices with higher yields requires higher crystalline quality substrates with fully controlled electronic transport properties. Bulk ammonothermal GaN substrates, recently developed and commercialized, are characterized by low dislocation density, a single crystal nature, and high flatness; but they lack full control of the electrical properties. It is expected that films deposited by vapor transport techniques, typically with low impurities background, would allow the growth of materials with high crystalline quality and improved electrical properties. More recently, it was demonstrated that thick GaN films deposited by Hydride Vapor Phase Epitaxy (HVPE, a fast deposition process) on ammonothermal GaN substrates reproduce the high crystalline quality of those substrates, and have free carrier concentrations that are several orders of magnitude lower that of the substrates [1,2]. We have verified that such HVPE GaN wafers can be used for further homoepitaxial growth. This is extremely important, because it demonstrates the usefulness of this new type of substrate to fabricate highly efficient optoelectronic and electronic devices. The development of high quality GaN substrates and device grade films will be reviewed, and the challenges encountered in the realization of GaN devices will be compared to those facing the development of UWBG materials and devices. Finally, a brief overview of the intrinsic properties of the WBG and UWBG semiconductors will be presented. This work was supported by the Office of Naval Research. [1] T. Sochacki, et al., J.J. Appl. Phys., 53 (2014) 05FA04. [2] J.A. Freitas, Jr., et al., J. Crystal Growth 456 (2016) 113. [3] J. A. Freitas, Jr., et al., J. Crystal Growth 500 (2018) 104.
ACCELERATED DISCOVERY OF NEW NITRIDE SEMICONDUCTORS: FROM COMPUTATIONAL DISCOVERY TO EXPERIMENTAL REALIZATION TO EPITAXIAL INTEGRATION

Presenting Author: Sage Bauers

Topic: Characterization techniques for bulk and epitaxial crystallization

Format: Invited

Session: 3, 3

Date: 8/2/2021

Time (in MDT): 1:30:00 PM

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Coupling high-throughput experimental and computational tools allows for accelerated discovery of new functional materials in underexplored chemistries. Nitrides represent one such chemical space: despite nitrogen being approximately four times more prevalent than oxygen in the Earth’s atmosphere, the stability of dinitrogen leads to an order of magnitude more oxides than nitrides in the Inorganic Crystal Structure Database (ICSD). At the same time, many of the known nitrides—and nitride semiconductors in particular—are important technological materials, motivating the discovery of new nitride materials. Our team has developed a nitride discovery workflow utilizing a combination of data-mined ionic substitution algorithms, unconstrained structure prediction calculations, combinatorial thin film screening, and targeted growth of compelling candidates. This work has resulted in computational identification of 91 chemical spaces containing stable ternary nitrides, but which have no entries in the ICSD. Thus-far we have experimentally synthesized new nitrides in over 15 of these spaces, representing a 100% success rate.

One family of compounds discovered using this approach is Mg-TM-N (TM=Ti, Zr, Hf, Nb). These compounds form in a rocksalt-derived crystal structure over a broad metal composition range. Whereas inorganic nitrides usually belong to one of two primary families—hexagonal main-group metal nitride semiconductors or cubic transition-metal nitride superconductors—these materials represent a rare class of semiconducting nitrides which adopt the rocksalt crystal structure. Ab-initio calculations on this family of mid-gap (0.8-2.1 eV) semiconductors reveal extremely large dielectric constants (up to 80 &lt;math&glt;epsilon&glt;/sub&gt;0&ltnosub&gt;), and a striking tolerance to structural defects relative to other ternary nitrides. The ternary composition space also allows for tunable properties. For example, transport properties can be radically tuned with Mg:TM ratio from metallic (TM-rich) to non-degenerately doped (Mg-rich). Furthermore, TM identity can be used to tune the visible-range optical absorption onset between (0.9-2.4 eV). Finally, the lattice parameters of these Mg-TM-N materials are compatible with multiple families of technologically important nitrides, suggesting the possibility for epitaxial integration of these materials into functional nitride devices. For example, our data show that epitaxial alignment can be readily achieved during sputter-deposition of MgZrN<sub>2</sub> and
Mg$_2$NbN$_2$ thin films on MgO, GaN, and Al$_2$O$_3$ templates, as well as onto the various transition metal nitride superconductors. The combination of elemental abundance, compelling properties, and structural compatibility highlights the potential of these materials for integration with known nitrides.
APPLICATION OF SYNCHROTRON X-RAY ROCKING CURVE TOPOGRAPHY TO GAN SUBSTRATES AND EPITAXIAL LAYERS USED FOR POWER ELECTRONIC DEVICES

Presenting Author: Yafei Liu

Topic: Characterization techniques for bulk and epitaxial crystallization

Format: Contributed

Session: 3, 5

Date: 8/2/2021

Time (in MDT): 2:00:00 PM

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GaN, together with other wide band gap semiconductor materials such as SiC and AlN, are being developed rapidly to replace silicon materials in the applications to power electronic devices. In the fabrication processes of GaN-based power electronic devices, microstructures, including dislocations and lattice strain, are key factors that can affect the performance of the products. Previous work [1-4] has adopted synchrotron monochromatic beam X-ray topography [5] to characterize the microstructures of various types of GaN substrates. In this study, synchrotron X-ray rocking curve topography, a very highly strain-sensitive technique, is used to analyze the strain and tilt distribution. It has been successfully adopted to estimate the strain levels in different single crystals such as Si, GaAs, Nb, CdZnTe, InP, diamond and SiC [6]. Recently Kim et, al. [7] used similar technology to characterize the lattice plane bending effect of GaN epilayers. In this method, a high-resolution CCD camera is used to record the data of rocking curves for all pixels under both +g and -g reflections, giving possibility to calculate the strain and tilt values for each pixel points and enabling one-to-one correlation between dislocations and lattice strain maps as well (Figure 1). The difference in strain and tilt distribution between different types of GaN substrates and under different processing stages of device fabrication such as etch/regrowth and ion implantation will be discussed.
PRISMATIC SLIP IN PVT-GROWN ALN CRYSTALS

Presenting Author: Shanshan Hu

Topic: Characterization techniques for bulk and epitaxial crystallization

Format: Contributed

Session: 3, 6

Date: 8/2/2021

Time (in MDT): 2:15:00 PM

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Aluminum nitride (AlN) single crystals are desirable as substrates for nitride based electronic and optoelectronic applications. To grow high-quality heteroepitaxial epilayers, a low density of dislocations and other structural defects in bulk AlN substrates is demanded. AlN crystals grown by physical vapor transport (PVT) possess a low density of dislocations and other structural defects. Basal plane slip is the most frequently observed deformation mechanism in AlN crystals grown by PVT. However, prismatic slip takes place as well in such crystals. As the diameter of AlN wafers expands to 50 mm and larger, it becomes critical to manage the thermal gradients in the PVT growth chamber, in order to minimize thermal stresses that cause deformation. Recent synchrotron X-ray topography studies of 50 mm diameter AlN wafers showed that while most wafers contained few to no basal plane dislocations (BPDs), some wafers possessed a 6-fold BPD dislocation pattern which was aligned along the <11-20> directions. This configuration indicated that prismatic slip had likely occurred, such that screw dislocations from the prismatic plane cross slipped onto the basal plane, where they underwent basal plane slip, leading to dislocation multiplication. To investigate the origins of prismatic slip, a radial thermal gradient model was developed showing the resolved shear stress across the entire area of the crystal boule during growth. The results from the model were correlated with experimental observations to investigate the role of radial thermal gradients in the nucleation of prismatic slip in AlN during bulk growth. This insight will help guide efforts to reduce structural defects in PVT AlN.
COMPLIMENTARY INVESTIGATION OF EXTENDED DEFECTS IN THICK SIC EPITAXIAL LAYERS USING UVPL AND X-RAY TOPOGRAPHY.

Presenting Author: Nadeemullah Mahadik

Topic: Characterization techniques for bulk and epitaxial crystallization

Format: Invited

Session: 4, 1

Date: 8/2/2021

Time (in MDT): 3:00:00 PM

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Silicon carbide (4H-SiC) devices are commercially available for voltage class up to 3.3kV due to availability of low defect epitaxial layers. However, for higher voltage applications beyond 6.5kV, thicker epitaxial layers are required, which are prone to extended defects. Investigation of these defects is key for their mitigation. In this work, we perform investigation of extended defects using ultraviolet photoluminescence (UVPL) imaging and X-ray topography (XRT). For this work, we used commercially grown, 125μm thick, 5x10<sup>14</sup> cm<sup>-3</sup> n-type doped, 4H-SiC epitaxial layers with a 20μm highly doped buffer layer grown on n-type 4H-SiC substrates. UVPL imaging of the 150mm diameter wafer was performed on a custom setup with 355nm laser excitation. The 660-1000nm luminescence was collected using a cooled CCD detector. XRT was performed on the Rigaku XRTmicron system using reflection, transmission and section topography. Section topography was performed on selected sample regions to investigate defect evolution and propagation with depth. Multiple Bragg conditions were used in each geometry to analyze defect types and Burgers vectors. Extended defects including basal plane dislocations (BPD), slip planes, in-grown stacking faults, inclusions, half loop arrays, dislocation pile-up, double half loop arrays, etc. were examined. Few BPDs propagated from the substrate to the epitaxial layer due to implementation of widely known mitigation strategies. However, new sources of BPDs are introduced during epitaxial growth such as inclusions, as seen in Fig. 1. The inclusion generates BPDs that glide perpendicular (up/down) to the step flow direction. These BPDs remain within the epitaxial layer, and are observed in both XRT images with <i>g</i>=11-20 and <i>g</i>=2-202, indicating their Burgers vector is not in the step flow direction. Additionally, BPD lines emanate from the inclusion gliding left towards the substrate. These BPDs propagate into the substrate and form dislocation loops as seen in the transmission XRT image with <i>g</i>=11-20. The BPD loops were generated ~40μm after the inclusion was created. Hence, in thick epitaxial layers, significant stress at inclusions can cause BPD propagation from the epitaxial layer into the substrate. The BPD loops extended ~200 μm into the substrate. These BPDs have Burgers vector, <i>b</i>=1/3<11-20> since they are not observed in the image with <i>g</i>=2-202. Analysis of other extended defects including dislocation pile-ups and double half loop array generation with depth resolution will be also be presented.
X RAY NANOBEAMS TO MEASURE LIGHT, COMPOSITION AND STRUCTURE IN NITRIDES

Presenting Author: Joel EYMERY

Topic: Characterization techniques for bulk and epitaxial crystallization

Format: Contributed

Session: 4, 3

Date: 8/2/2021

Time (in MDT): 3:30:00 PM

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The emergence of disruptive functionalities in nitrides is strongly related to the growth and technology controls, but also to the development of advanced characterization techniques with high spatial resolution. Focused X-ray beams provide innovative solutions to analyse quantitatively the morphology, defects, strain and composition of these materials. We will present here some recent breakthroughs obtained at the European Synchrotron Radiation Facility on nitride wires grown by MOVPE and etched µLEDs.

MOVPE GaN wires with GaN/InGaN Multiple Quantum Well (MQW) core-shell heterostructure deposited on m-plane sidewalls [1] are first measured by scanning and transmission electron microscopy and then by X-ray excited optical luminescence (XEOL) & X-ray Fluorescence (XRF) with hard X-ray nanoprobe at the ESRF ID16 beamline [2]. We show that (i) the optical luminescence of the near band edge of the GaN core is directly related to differential Si incorporation in N- and Ga-polar parts of thick wires (silane addition being used in the process to favour 1D growth, see left of Fig. 1), and that (ii) core-shell and top axial MQW luminescence can be imaged (see middle of Fig. 1).

The simultaneous XEOL and µLaue diffraction mapping has been performed with the unique setup developed at the French BM32@ESRF beamline. With a polychromatic beam, the sample does not need to be orientated at specific Bragg diffraction conditions as it is the case for monochromatic techniques. XEOL spectra and µLaue diffraction patterns (~0.3 µm beam size) are recorded simultaneously to link the optical properties to the strain and misorientation resulting from the MOVPE growth. This will be quantitatively illustrated with the measurements of GaN wire heterostructures dispersed on glass with only 1s of counting time per point (see Figure 1 right) and with µLED samples obtained by etching of planar MOVPE heterostructures (see Fig. 2).
SAMPLE ENVIRONMENT EFFECTS ON SYNCHROTRON-MEASURED TEMPERATURE PROFILES WITHIN A FURNACE APPROXIMATING OPTICAL FLOATING ZONE CRYSTAL GROWTH

Presenting Author: Yusu Wang

Topic: Characterization techniques for bulk and epitaxial crystallization

Format: Contributed

Session: 4, 4

Date: 8/2/2021

Time (in MDT): 3:45:00 PM

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The optical floating zone (FZ) crystal growth method has had an immense scientific impact due to its many advantages, including crucible-free crystal growth, rapid growth speeds, and suitability for a wide variety of emerging complex materials. However, the implementation of this method remains more of an art than a science because of the difficulties of obtaining quantitative information of the crystal growth process. Building on recent work demonstrating that in-situ synchrotron method can be used to map sample rod temperature profiles (a key factor that strongly affects crystal growth outcomes) during heating, investigations were carried out to better understand how the sample environment affects the sample temperature profile within a customized synchrotron-compatible miniature FZ furnace. Through a combination of experimental studies and modeling efforts, it is shown that the environment within the furnace can strongly influence the sample temperature at the lamp focus, the steepness of the vertical temperature gradient, and the timescale required for sample heating and cooling - effects which can combine to produce a strong history-dependence to sample temperature profiles. It is demonstrated that the furnace effects can be effectively included into thermal models, allowing both the steady-state and time-dependent behavior of the sample to be accurately reproduced with predictive models, and providing a launching point for improved furnace designs that can more readily deliver desired thermal profiles.
MORE INSIGHTS IN SEMICONDUCTOR MATERIAL QUALITY WITH ADVANCED X-RAY TOPOGRAPHY IMAGING

Presenting Author: Christian Reimann

Topic: Characterization techniques for bulk and epitaxial crystallization

Format: Invited

Session: 4, 5

Date: 8/2/2021

Time (in MDT): 4:00:00 PM

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Characterization of structural defects in semiconductor materials is an important task to understand the influence of the production conditions on the material quality of substrates and epilayers and to correlate the impact of structural defects on the performance and reliability of devices manufactured out of the substrates and epilayers. State of the art characterization of structural defects in single crystalline material like dislocations, dislocation networks, and slip lines is done by defect selective etching (DSE), Cathodoluminescence (CL), Photoluminescence (PL) or by X-ray topography (XRT). Unfortunately DSE is a destructive method and leads to a significant yield loss, especially important for expensive substrate materials. CL could be used only on small samples and needs a high sample preparation effort. CL and PL are applicable only for electrically active defects. PL is not easily available for semiconductors with high band gaps like AlN. XRT measurements were done in the past mostly at synchrotron radiation sources, are highly complex and the accessibility is not satisfying. Meanwhile advanced X-ray topography tools for use in a laboratory are on the market like the XRTmicron, which allows high quality 2D and 3D topograms due to the usage of a novel highly focusing anode. The availability of such advanced tools gives the possibility to investigate crystallographic defects such as the amount and different types of dislocations, slip lines, dislocation networks, (small angle) grain boundaries, inclusions, precipitates, pits, scratches, etc. with high speed and high resolution on full wafer scale on bare wafers, wafers with epilayers, partially processed wafers as well as bonded wafers. At first an overview of the principle of the XRTmicron tool will be given. Furthermore it will be shown how XRTmicron measurements can support R&D, production and quality assurance to analyze e.g. slip line formation in 300mm silicon wafers, different kinds of dislocation types (threading screw, threading etch and basal plane dislocations) in 4H-SiC substrates and epilayers and their quantification, the quality of sapphire substrate and grown AlGaN layers on top.
NUCLEATION, COALESCENCE AND STRUCTURAL TRANSITION DURING THE EARLY GROWTH STAGES OF ZIF-8 PROBED BY NONLINEAR OPTICAL LIGHT SCATTERING

Presenting Author: Stijn Van Cleuvenbergen

Topic: Characterization techniques for bulk and epitaxial crystallization

Format: Contributed

Session: 4, 7

Date: 8/2/2021

Time (in MDT): 4:30:00 PM


STRUCTURAL EVOLUTION IN PHASE CHANGE STRONTIUM FERRITE THIN FILMS

Presenting Author: Yingge Du

Topic: Characterization techniques for bulk and epitaxial crystallization

Format: Contributed

Session: 4, 8

Date: 8/2/2021

Time (in MDT): 4:45:00 PM

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Facile cation diffusion can give rise to new material structures that can in turn generate novel and useful functionalities. For example, an oxygen diffusion-induced phase transition between the vacancy-ordered, brownmillerite phase of \( \text{SrFeO}_{2.5} \) and its stoichiometric perovskite counterpart \( \text{SrFeO}_3 \) has been extensively studied for its intriguing electronic and magnetic transitions. These transitions are of considerable interest in microelectronics and energy storage. In particular, the insulator-to-metal transition that accompanies the phase transition has enabled the fabrication of thin film memristor devices needed for neuromorphic computing. However, the atomic-scale mechanism remains elusive due to the lack of control over oxygen vacancy channel (OVC) alignment with respect to the substrates. In this talk, I will present our effort in tuning the orientation of OVCs by adjusting synthesis and processing parameters during epitaxial growth, which allows the systematic testing of working hypotheses; We characterize the structural evolution and defect formation in the films as a response to external stimuli (e.g., strain, oxygen chemical potential, and electrical field), and highlight the advantage and disadvantage of using such materials for memory devices.
HIGH-RESOLUTION NUCLEAR RADIATION DETECTORS ON 4H-SiC EPITAXIAL LAYERS

**Presenting Author:** Krishna Mandal

**Topic:** Detector Materials: Scintillators and Semiconductors

**Format:** Invited

**Session:** 2, 1

**Date:** 8/3/2021

**Time (in MDT):** 10:30:00 AM

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Silicon carbide (SiC) is one of the most promising wide-bandgap (3.27 eV) semiconductors due to its high radiation hardness, high breakdown voltage, high electron saturation velocity, and high thermal conductivity. These appealing features make SiC, especially 4H polytype, a suitable candidate for harsh-environment-compatible nuclear radiation detectors where conventional semiconductors (e.g. Si, Ge, CdZnTe (CZT)) are inadequate. In this work, high-resolution radiation detectors have been fabricated on 20-250 μm thick n-type 4H-SiC epitaxial layers. Current-voltage measurements revealed a near ideal Schottky barrier device with an ideality factor of ~1.1, high barrier height (~1.72 eV), and very low leakage current of <1 nA at an operating reverse bias of ~350 V. Capacitance-voltage measurements revealed low doping concentration (~10^{14} cm^{-3}), and electron beam induced current (EBIC) characterization showed low micropipe density (< 0.1 cm^{-2}) in the epilayers. Pulse-height spectroscopy (PHS) was carried out using a 0.9 μCi <sup>241</sup>Am radiation source for detecting alpha particles and using U3C and X8A beam lines for sub-keV to 10 keV x-rays at National Synchrotron Light Source (NSLS), Brookhaven National Laboratory (BNL). PHS exhibited highest reported energy resolution of ~0.29 % full-width half maxima (FWHM) for alpha particles at 5486 keV with a detector area of ~11 mm<sup>2</sup>. Deep level transient spectroscopy (DLTS) was carried out to investigate defect levels and capture cross sections. Using a drift-diffusion model, a diffusion length of ~18.2 μm for holes (minority carriers) has been determined. Detailed electronic noise analysis in terms of equivalent noise charge (ENC) was carried out to study the effect of various noise components that contribute to the total electronic noise in the detection system. These 4H-SiC multi-purpose complete radiation detection systems are capable of monitoring neutrons, x-rays, and alpha particles at very high temperature and extreme radiation background, can be used for nuclear material control, accounting, and safeguards.
HIGH-PURITY GERMANIUM CRYSTAL GROWTH AND ITS SPECIFIC USE-CASE APPLICATION FOR HIGH-SENSITIVE DETECTION OF NEUTRINOLESS $\beta\beta$-DECAY

**Presenting Author:** R. Radhakrishnan Sumathi

**Topic:** Detector Materials: Scintillators and Semiconductors

**Format:** Invited

**Session:** 2, 3

**Date:** 8/3/2021

**Time (in MDT):** 11:00:00 AM

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High-purity (HP) crystals are utilized to address fundamental questions like, why matter is much more abundant than anti-matter in today’s Universe. A positive detection of a very rare neutrinoless $\beta\beta$-decay (0ν$\beta\beta$) process would manifest the observation of a matter-creating process, without the balancing emission of antimatter. A 0ν$\beta\beta$-decay transforms in a nucleus with a given mass number and atomic number, two neutrons simultaneously into two protons, along the emission of two electrons but, without the emission of two neutrinos. These two electrons carry the available decay energy, and the resulting mono-energetic signal is the prime experimental signature. GERDA/LEGEND experiment at the Gran Sasso, Italy, underground laboratory is operating background-free with detectors made-up of HP germanium (HPGe) single crystals, enriched in $^{76}$Ge isotope. Czochralski technique is employed to grow such HPGe single crystals because of the freedom for the required diameter, purity ($n < 10^{10}$ cm$^{-3}$), and the possibility to tailor the structural defects. Nonetheless, growing “detector-grade” crystalline material with controlled properties and uniformity, throughout the crystal, is still a challenge. At IKZ-Berlin, as an active member of the multinational consortium for GERDA/LEGEND research, the fore-end (FE) process steps for detector fabrication, namely: (i) reduction of GeO$_2$ to Ge for preparing poly-crystalline Ge bars, (ii) multi-zone-refining of the starting Ge metal bars up to ultra-high purity (12N); (iii) Cz growth of single crystals, have been established and are operational. All these and also other related following steps, viz., crystal machining, metrology, characterisation, for the detector block preparation could be performed, all “in-house” under a single roof. We have scaled-up and are optimising the process for growing 3-inch crystals. The 3-inch diameter crystals were grown along both the [100] and [111] orientations and the dislocation densities in these crystals are relatively high ($\approx 10^{4}$ cm$^{-2}$), but uniform along the crystals. Further, this presentation will discuss main results reached in each of the FE process steps, reduction and ZR of enriched Ge, recycling of this critical raw material and crystal growth. As benchmark for future crystal production, we summarize recently published performance of detectors produced by commercial companies in collaboration with the GERDA and the LEGEND collaborations.

**Acknowledgments:** Authors thankfully acknowledge the IKZ colleagues (Jörg Fischer, Uta Juda, Mike Pietsch, Klaus Irmscher) and this work would not have been possible without their dedicated support and involvement.
Financial support from the German Federal Ministry for Education and Research (BMBF) is also gratefully acknowledged.
UNDERSTANDING THE 3D CDZNTET DRIFT STRIP DETECTORS

Presenting Author: Irfan Kuvvetli

Topic: Detector Materials: Scintillators and Semiconductors

Format: Invited

Session: 2, 5

Date: 8/3/2021

Time (in MDT): 11:30:00 AM

Authors: Irfan Kuvvetli, Technical University of Denmark, Kgs Lyngby, Denmark Carl Budtz-Jørgensen, Technical University of Denmark, Kgs Lyngby, Denmark Selina Howalt Owe, Technical University of Denmark, Kgs Lyngby, Denmark

Although CdZnTe material has many desirable properties for use as room temperature semiconductor detector material, it has also some drawbacks. The mobility-lifetime (µτh) product for holes is much lower than the mobility-lifetime (µτe) product for electrons in the CdZnTe crystals, which can result in poor charge collection and degraded energy resolution. In order to solve the problem with inefficient hole collection in a CdZnTe (CZT) detector and knowing that the electrons are being efficiently collected, one can modify the electrode design with geometrically weighted contacts and can make the induced signal on collecting electrodes dependent primarily on the electrons drift only. At DTU Space, detector research resulted in a number of methods to improve considerably the spectral and spatial resolution of this type of compound semiconductor detectors. The so-called drift strip method (DSM) [1], leads to a considerable improvement of the achievable energy resolution even for poor quality crystals. Figure 1 shows electrical diagram of the 3D CZT drift strip detector and image of a full illumination in xy-plan. The drift strip electrodes and the cathode electrodes are biased in such a way that the electrons drift and collected by the anode strips. The DSM enabled us to develop CZT detectors having both excellent energy resolutions, close to that of classical Ge detectors [2] and also excellent sub-mm position resolution in 3D [3 and 4]. Figure 2 shows result that DSM can achieve energy resolutions which are within a factor of 2 to 3 of the CdZnTe Fano-limited resolution. Moreover, the accurate 3D interaction position determination together with excellent energy determination allow us to perform 3D mapping of carrier lifetime and mobility of the CdZnTe detector material. These quantities are of critical importance for the performance of the drift strip detector. The 3D CZT drift strip detector has demonstrated excellent performance and open up new possibilities for compact new generation high resolution gamma-ray imaging sensors[5] for wide range of application. In this paper, the drift strip method will be explained in detail and advantages of the method will be explained with experimental results.

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MERCUROUS BROMINE Hg$_2$Br$_2$ AS THE NEXT GENERATION SCINTILLATOR FOR SPACE MISSION, HIGH ENERGY PHYSICS, DEFENSE, AND SECURITY APPLICATIONS

Presenting Author: Henry Chen

Topic: Detector Materials: Scintillators and Semiconductors

Format: Invited

Session: 3, 1

Date: 8/3/2021

Time (in MDT): 1:00:00 PM

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Undoped mercurous bromine Hg$_2$Br$_2$ is a semiconductor material that can also fluoresce due to its excellent optical properties. The material has been grown in-house at Brimrose and used in LWIR imaging and Acousto-optic devices. Previously, we have also been able to demonstrate the radiation detection capability of undoped Hg$_2$Br$_2$ via direct charge collection mode, as a room temperature semiconductor detector. In general, mercury-based compounds have been known to be radiation hard and mercurous bromine’s cousin, mercuric iodine HgI$_2$ has also been well known to be a good room temperature semiconductor detector but Hg$_2$Br$_2$ has more advantages due to the fact that it is not a layer compound so there is no problem with crystal cutting and processing. It is also non-hygroscopic and non-toxic. In fact, we are the only company in the world currently capable of growing large sized single crystals (50 mm diameter X 60 mm length) of this material. Our recent R&D efforts have shown that by doping with proper activators, we can enhance the light emission capability of Hg$_2$X$_2$ (X = Br, Cl) in the visible to near-IR range, making them great scintillators as well. Scintillator form of doped Hg$_2$X$_2$ totally eliminates the stability issue associated with electrode contacts of undoped Hg$_2$X$_2$. Encountered in direct detection form, Doped-Hg$_2$X$_2$ scintillators have shown encouraging results on detection of gamma and alpha particle using SSPM. The responses have been stable and very repeatable after several months. In this presentation, we will present and discuss why Hg$_2$Br$_2$ is the next generation scintillator for space mission, high energy physics, defense, and security applications, specifically, with its many advantages over existing COTS semiconductors and scintillators such as being high density, bright, fast, good energy resolution, no intrinsic radiation, and cost-effective.
SOLUTION GROWTH OF CENTIMETER-SCALE MAPbBr\textsubscript{3} CRYSTALS FOR HIGH-ENERGY RADIATION DETECTION

Presenting Author: Bianca Boschetti

Topic: Detector Materials: Scintillators and Semiconductors

Format: Contributed

Session: 3, 3

Date: 8/3/2021

Time (in MDT): 1:30:00 PM

Authors: Bianca Boschetti, CapeSym, Inc., Natick, Massachusetts, United States  Reyhaneh Toufanian, CapeSym, Inc., Natick, Massachusetts, United States  Amlan Datta, CapeSym, Inc., Natick, Massachusetts, United States  Shariar Motakef, CapeSym, Inc., Natick, Massachusetts, United States

Organic-inorganic lead halide perovskites have shown to be promising materials for radiation detection applications. Such perovskites contain the High-Z element Pb, which results in a high stopping power for higher energy radiation. Among the methylammonium lead halide perovskites, methylammonium lead bromide (MAPbBr\textsubscript{3}) shows the best environmental stability. MAPbBr\textsubscript{3} also has a long carrier lifetime, enabling good energy resolution for gamma-rays. In addition, MAPbBr\textsubscript{3} single crystals can be grown using a low capital-cost solution technique without the use of expensive equipment required by the melt growth processes that are generally used for other semiconductor radiation detectors such as CZT. However, a drawback of solution-grown MAPbBr\textsubscript{3} compared to other conventional melt-grown semiconductors is that the attainable single crystal size is limited to a few millimeters. We were able to overcome this limitation by utilizing a modified inverse temperature crystallization (ITC) process, growing centimeter-scale MAPbBr\textsubscript{3} crystals through sequential seeded growths at low temperatures. We investigated the solution growth parameters for successfully growing large MAPbBr\textsubscript{3} crystals and their high-energy radiation detection capabilities. In this presentation, the crystal growth process and the detection performance of MAPbBr\textsubscript{3} crystals will be discussed.
PRECIOUS METAL CRUCIBLE-FREE BULK CRYSTAL GROWTH OF CE DOPED GD<sub>3</sub>(Ga,Al)<sub>5</sub>O<sub>12</sub> SINGLE CRYSTAL FROM THE MELT AND ITS SCINTILLATION PROPERTIES

Presenting Author: Akira Yoshikawa

Topic: Detector Materials: Scintillators and Semiconductors

Format: Contributed

Session: 3, 4

Date: 8/3/2021

Time (in MDT): 1:45:00 PM

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Ce doped Gd<sub>3</sub>(Ga,Al)<sub>5</sub>O<sub>12</sub> (GAGG:Ce) has increased the light yield and accelerated scintillation decay. These effects need further systematic study for full understanding. The detailed discussion is being carried out based on the influence of co-doping itself, induced host defects, and cerium charge state. As a suitable co-dopant, we proposed Mg and Li, which allow GAGG faster decay time. In this report, bulk crystal growth of up to 4 inch GAGG and co-doped GAGG will be shown and discussed taking segregation phenomena into account. So far, the GAGG-based crystals are grown under the Ar or N<sub>2</sub> atmosphere to protect Ir crucible. This atmosphere generates large amount of oxygen vacancies and Ga vacancies in the crystal. Such a growth atmosphere is necessary to protect the iridium crucible from oxidation. During many years there is the well-known crystal growth technique called “Skull melting” or “Cold container”. This technique uses the fact that many oxides have enough high electric conductivity melts at high temperature and can be thus heated directly by the high frequency electric field without the use of a metal crucible. So far, the majority of the functional single crystalline materials including scintillator are fabricated as bulk crystals using the Czochralski (Cz) or Bridgeman (BS) methods. Therefore, we need extensive machining process such as cutting, slicing, polishing and so on. Moreover, the atmosphere is limited as we use Ir crucible, which is easily oxidized by oxygen (above 2% of partial pressure) in high temperature. This low oxygen partial pressure induces the oxygen vacancy, which can be the origin of slow component or non-radiative transition. We investigated the opportunity to use scull melting technique for the formation and keeping GAGG melt without a crucible. The growth process itself was performed with the use of rotated seed by slow pulling up like at ordinary Czochralski technique. Such combined technique allows to solve both mentioned problems of conventional Cz process for GAGG. Due to the absence of Ir crucible there is no growth limitation caused by Ir crucible deformation. Also, the absence of Ir crucible gives the opportunity to apply any growth atmosphere (including air or even pure Oxygen). As a result, melt
overheating needed for gas bubbles removing can be realized easily without beta-
$\text{Ga}_2\text{O}_3$ evaporation. GAGG crystals were grown in air without use of Ir crucible
using pulling up from the cold container. Such technique gives the opportunity to avoid growth
problems typical for traditional Czochralski method.
ENHANCING THE GRAIN SIZE OF HIGH SENSITIVITY PEROVSKITE X-RAY DETECTORS FOR MEDICAL AND SYNCHROTRON IMAGING

Presenting Author: Katherine Hansen

Topic: Detector Materials: Scintillators and Semiconductors

Format: Contributed

Session: 3, 5

Date: 8/3/2021

Time (in MDT): 2:00:00 PM

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Metal halide perovskites, such as methylammonium lead iodide (MAPbI$_3$), are excellent candidates for room-temperature X-ray detection due to strong X-ray absorption afforded by the presence of High-Z elements like Pb, high defect tolerance, low trap density, and long carrier lifetime, as well as low-temperature solution processing. Although there have been many studies with this class of materials for various applications, significant challenges specific to X-ray imaging and practical application remain. While single crystal perovskites exhibit significantly lower trap density, the preparation is limited for large-area devices. Due to the low bandgap of MAPbI$_3$ (1.6 eV), thick polycrystalline films of MAPbI$_3$ show high leakage current and baseline noise. Improving crystallinity and increasing the grain size can reduce charge recombination at the grain boundaries, thereby increasing the X-ray sensitivity. It also can significantly minimize the ion migration that causes dark current drift and degrades the signal-to-noise ratio. In this study, we have implemented a two-step thick film fabrication process that includes an innovative MAPbI$_3$ crystallite seed layer preparation. This layer promotes large grains in the subsequent doctor-bladed polycrystalline film. We also investigated the growth of these crystallites using a low-cost technique to form compact MAPbI$_3$ films with high X-ray sensitivity. These films can be deposited over large areas to fabricate X-ray detectors with low dark currents and excellent X-ray sensitivity. In this presentation, the details of the MAPbI$_3$ crystal growth processes and the X-ray detection performance enhancements will be discussed.
SUCCESSES AND CHALLENGES IN CRYSTAL GROWTH OF THE NEW GENERATION OF HALIDE SCINTILLATORS

Presenting Author: Shariar Motakef

Topic: Detector Materials: Scintillators and Semiconductors

Format: Invited

Session: 4, 1

Date: 8/3/2021

Time (in MDT): 3:00:00 PM

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Over the past two decades a large number of halide scintillators with varying levels of compositional complexity have been developed, primarily driven by the need to achieve higher sensitivity and higher energy resolution for nuclear threat detection and non-proliferation monitoring. Of these a few have become commercially available and have been slowly incorporated into radiation detection instruments. In this presentation we will discuss challenges and successes in obtaining high-performance large-volume halide scintillator for gamma and neutron detection, focusing on binary to quartenary compounds with single and mixed halides. We will also discuss the current state of theoretical frameworks needed for efficient charting of the course for further advances in the field.
LARGE-SIZE GD<sub>3</sub>(GA,AL)<sub>5</sub>O<sub>12</sub> BASED TRANSPARENT CERAMICS PREPARED BY THE SPARK PLASMA SINTERING PROCESS

Presenting Author: Shunsuke Kurosawa

Topic: Detector Materials: Scintillators and Semiconductors

Format: Contributed

Session: 4, 3

Date: 8/3/2021

Time (in MDT): 3:30:00 PM

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Transparency is required for material search of optical materials such as laser or scintillator, and we have investigated their optical properties for transparent single-crystals as scintillators or other optical materials grown by the Czochralski growth, micro-pulling down method [1]. From around 2010, transparent ceramic scintillators have been studied [2] using Vacuum sintering process or/and Hot Isostatic Pressing (HIP). Spark Plasma Sintering (SPS) Process is much simpler and shorter sintering time than other methods, and we have investigated the scintillation properties for the transparent ceramics (i.e. Ce:SrHfO<sub>3</sub>, Nd:Lu<sub>2</sub>O<sub>3</sub>) prepared by SPS process [3,4]. However, such materials had high-melting temperature, and preparation of single crystals (good transparent materials) is hard. In this time, we prepared Gd<sub>3</sub>(Ga,Al)<sub>5</sub>O<sub>12</sub>-based materials with a diameter of 20 mm by SPS process as shown in Fig. 1, and compared the optical and scintillation properties for the same materials by Czochralski growth and other techniques. Photo-lumineence (PL) and radio-lumineence peaks were located at around 550 nm excited by 420-nm photons, X-ray and 5.5 MeV alpha-rays, and this is the same results as the single crystal and ceramics by HIP. Up to now, the SPS sample had a transparency of around 10-20% which is smaller than HIP sample (~50%) and single crystal (~80%). The light output was around 13,000 photons/MeV, while HIP and single crystals had that of ~ 55,000 photons/MeV. The small light output for the SPS sample might be due to low transparency and some defects. Although the SPS sample had light output and transparency, as a material search technique, this process is also effective, especially for high melting temperature samples. In this paper, we show the above results and compare the defects to a single crystal sample using Thermo-luminescence measurement. 

Fig. 1 photograph of Gd<sub>3</sub>(Ga,Al)<sub>5</sub>O<sub>12</sub>-based scintillator prepared by SPS.
References

GROWTH AND SCINTILLATION PROPERTIES OF DIRECTIONALLY SOLIDIFIED EUTECTIC SCINTILLATORS

Presenting Author: Kyoung Jin Kim

Topic: Detector Materials: Scintillators and Semiconductors

Format: Contributed

Session: 4, 4

Date: 8/3/2021

Time (in MDT): 3:45:00 PM

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Scintillators coupled with photodetectors have been widely used in radiation imaging applications such as medical imaging, security, high energy physics, astrophysics, oil well logging, etc. In X-ray imaging applications, radiation detectors composed of scintillators and photodetectors such as CCD are generally used. Columnar grown Tl:CsI scintillator plate is a common material for X-ray imaging application. In the case of columnar grown Tl:CsI scintillator plates, scintillation light scattering occurs in the micrometer size Tl:CsI fiber crystals and light cross talk occurs between the fibers. As a result of the scattering and crosstalk, spatial resolution degrades. In addition, light diffusion through scintillator material on the photodetector degrades the resolution of the radiation imaging sensors and limits the sensitivity. Further improvement of the spatial resolution is required in this application. In this investigation, submicron-diameter phase-separated scintillator fibers (PSSFs) were designed. The PSSFs can be fabricated by a directionally solidified eutectic (DSE) growth at the eutectic points. In the PSSFs, the scintillation lights propagate in the scintillator fibers phase by a total reflection mode against to the matrix phase, so that light cross talk is limited, and spatial resolution can be improved. In order to find a suitable combination of eutectic structure with PSSFs and matrix, choice of scintillator materials is important. The Ce:LaCl$_3$ scintillator has attracted attention for this purpose due to its high light yield of above 50,000 photons/MeV and fast decay time of 28 ns with enough density of 3.85 g/cm$^3$ for low energy X-ray detection even it is hygroscopic. Ce doped LaCl$_3$/AECl$_2$ (AE=Mg, Ca, Sr) system eutectics were explored. Ce doped LaCl$_3$/AECl$_2$ eutectics were grown using the Bridgman-Stockbarger (BS) method in quartz ampoules. In the case of AE=Mg, Ca, eutectic with submicron-diameter phase-separated scintillator fibers (PSSFs) structures were observed. In the case of AE=Sr sample, solid state La$_{0.708}$Sr$_{0.292}$Cl$_{2.708}$ was observed. The eutectics displayed optical transparency like bundle optical fibers. The grown eutectic structure showed a mixture of rods and plates shape. This mixed structure was aligned with a length of around 300-400 µm. The Ce:LaCl$_3$/CaCl$_2$ eutectic showed 345 nm emission ascribed to
Ce$^{3+}$ 4f-5d transition under X-ray excitation. The Ce:LaCl$_3$/CaCl$_2$ sample resulted in the highest light yield of 9,000 photon/MeV, which is around 28% of the LYSO standard. Scintillation decay time of the Ce:LaCl$_3$/CaCl$_2$ sample under 662 keV gamma-ray was 26.8 ns (26%) and 282 ns (74%).
Abstract Book - ACCGE-22//OMVPE-20

LATEST DEVELOPMENT ON ADVANCED TL-BASED SCINTILLATOR CRYSTALS FOR RADIATION DETECTION AND MEDICAL IMAGING

Presenting Author: Rastgo Hawrami

Topic: Detector Materials: Scintillators and Semiconductors

Format: Invited

Session: 4, 5

Date: 8/3/2021

Time (in MDT): 4:00:00 PM

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Scintillator crystals, starting from classic scintillators such as NaI:Tl and CsI:Tl to the most latest advanced compounds, play an important role in various technologies and applications ranging from medical imaging, security inspection, to space explorations. Because photo detection efficiency is directly proportional to density, recently discovered Tl-based scintillators, such as Tl-halide and Tl-elpasolite scintillator crystals, have been proven to be very important materials for X-ray and dual-mode γ-ray and neutron detection applications. In this paper we will present a comprehensive study on the development of the latest advanced high-density Tl-based halide and elpasolite scintillator crystals for radiation detection and medical imaging.

Acknowledgements: This work is partly supported by U.S. Department of Defense DTRA Contract # HDTRA1-20-C-0051 and DTRA-IIRM URA Cooperative Agreement # HDTRA1-20-2-0002
ANALYSIS OF THE DYNAMICS OF THE BRIDGMAN GROWTH OF SCINTILLATOR CRYSTALS VIA FINITE-ELEMENT MODELING AND NEUTRON IMAGING

Presenting Author: Swanand Pawar

Topic: Detector Materials: Scintillators and Semiconductors

Format: Contributed

Session: 2, 1

Date: 8/4/2021

Time (in MDT): 10:30:00 AM

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We have developed groundbreaking diagnostics that employ spallation neutrons to visualize, in situ, the compositional field that is developed during the growth of scintillator crystals by the Bridgman method. In conjunction with the development of these powerful, new measurements, we have developed rigorous finite-element computational models that faithfully represent heat transfer, fluid flow, segregation of species, and phase-change phenomena. Together, these tools provide, for the very first time, a means to directly observe and analyze the physical phenomena occurring during the growth of bulk crystals from the melt. In this presentation, finite-element modeling and energy-resolved neutron imaging are employed to analyze the dynamics of a scintillator crystal, cesium iodide doped with europium, CsI:Eu, in a Bridgman growth system. The synergy between rigorous modeling and direct, in-situ observations allows for unambiguous interpretation of growth behaviors. We present results from a growth experiment in which two step changes are applied to the ampoule translation rate, each step doubling the speed. A step change from 1 mm/hr to 2 mm/hr produced a smooth transition to a new quasi-steady growth state. The second increase to 4 mm/hr resulted in a more dramatic outcome, with the neutron image becoming hazy and the interface no longer clearly visible. We apply computational studies to understand how the combination of latent heat release, flow changes, and species accumulation near the interface gave rise to these time-dependent behaviors. We use the model to assess a postulated growth instability caused by constitutional supercooling after the second step increase in growth velocity.<br />
This research was supported in part by NASA NNX10AR70G, DOE/NNSA DE-NA0002514, DOE/NNSA/DNN R&D (LBNL subcontract AC0205CH11231) and a University of Minnesota Grant-in-Aid award; no official endorsement should be inferred.
DETECTING NEUTRONS. SCINTILLATOR CRYSTALS AND SEMICONDUCTORS FOR THERMAL NEUTRON DETECTION, AND THEIR TRADEOFFS WITH COMPETING TECHNOLOGIES

Presenting Author: Kevin Pritchard

Topic: Detector Materials: Scintillators and Semiconductors

Format: Invited

Session: 2, 2

Date: 8/4/2021

Time (in MDT): 10:45:00 AM

Authors: Kevin Pritchard, National Institute of Standards and Technology, Gaithersburg, Maryland, United States

Neutron detectors are most prevalently used for simple detection of fissile material at ports of entry and security checkpoints. But, there are a large and growing number of science facilities and national laboratories which provide thermal and cold neutrons for basic materials research. These research techniques include neutron scattering (akin to X-ray crystallography), neutron imaging, and prompt gamma spectroscopy. A neutron detector for scientific research not only detects the presence of a neutron, but it also pinpoints the time and location of this event. A material’s ability to quickly absorb weakly interacting neutrons dictates the detector’s efficiency and its location precision. In addition, the material must generate a distinct signal in response to neutron absorption. Current and emerging neutron detectors are reviewed, as well as newly proposed research.
GROWTH OF P-TERPHENYL AND CARBAZOLE CRYSTALS AS FAST NEUTRON SCINTILLATOR

Presenting Author: Shunsuke Kurosawa

Topic: Detector Materials: Scintillators and Semiconductors

Format: Contributed

Session: 2, 4

Date: 8/4/2021

Time (in MDT): 11:15:00 AM

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Scintillation and fluorescent properties of organic crystals, carbazole and p-terphenyl, were measured and compared to the conventional material, trans-stilbene. Although trans-stilbene is well-known as a neutron scintillator, trans-stilbene cannot be applied at high-temperature conditions such as in the monitoring of the nuclear fusion due to its lower melting point (124deg.C). On the other hand, carbazole and p-terphenyl have high melting points of 246 and 213deg.C, respectively. In this paper, we investigated the luminescence and scintillation properties in the high-temperature range for the carbazole and p-terphenyl crystals grown by the self-seeding vertical Bridgman method. Each crystal size had a diameter of around 5 mm. The carbazole crystal had the high light yield and decay time of ~11,000 photons/(5.5-MeV α-rays) and ~14.6 ns (primary component), respectively, and p-terphenyl had those of ~9,000 photons/(5.5-MeV α-rays) and ~7.1 ns, respectively, at room temperature. The photoluminescence quantum yield was almost constant up to 150deg.C for p-terphenyl. Although the yield of carbazole decreased between 25-150deg.C gradually, carbazole was found to be available under high temperature. Additionally, we succeeded in obtaining the novel organic crystal scintillator which can operate even at higher temperatures up to 150deg.C. Besides, we grew 2-inch diameter p-terphenyl as shown in Fig. (a) and assembled pixel scintillation array to obtain fast neutron imaging as shown in Fig. (b). The pixel array was coupled with a multi-anode PMT (H8500, Hamamatsu Photonics), and the 64 channel anodes were digitized with an amp unit manufactured by ClearPulse. In this presentation, we show the crystal growth of the above materials and scintillation properties for these samples excited by neutron and gamma-rays. Moreover, we report pulse-shaped discrimination test to remove gamma-ray events and imaging test.
GROWTH AND SCINTILLATION PROPERTIES OF (LI,CA)I₂ SOLID SOLUTION

Presenting Author: Masao Yoshino

Topic: Detector Materials: Scintillators and Semiconductors

Format: Contributed

Session: 2, 5

Date: 8/4/2021

Time (in MDT): 11:30:00 AM

Authors: Masao Yoshino, Institute for Materials Research, Tohoku University, Sendai, Japan Kei Kamada, New Industry Creation Hatchery Center, Tohoku University, Sendai, Japan Yuui Takizawa, Institute for Materials Research, Tohoku University, Sendai, Japan Akira Yoshikawa, Institute for Materials Research, Tohoku University, Sendai, Japan

Scintillators are used as radiation detectors in many fields, such as high-energy physics, medical imaging, and homeland security. Homeland security applications often require the detection of both neutron and gamma-ray. In the case of scintillators, Li-containing materials have good thermal neutron detection efficiency through the \((\text{Li}(n, \beta') \text{H})\) capture reaction, and gamma rejection from neutron signal may be accomplished by pulse shape discrimination (PSD). CaI₂ scintillator crystals were discovered by Hofstadter et al. in the 1960s [1] and high light yield - double those of Tl doped NaI - was reported. Since 2016, we have been developing CaI₂ scintillators using the vertical Bridgeman-Stockbarger (VB) method. We reported the high light yield (~107,000 ph/MeV) [2] and excellent particle identification (PI) capability between alpha and gamma even using a simple pulse shape ratio analysis [3]. In this study, to apply this excellent PI capability of CaI₂ to gamma/neutron separation, we grew solid solution of \((\text{Li}_{x} \text{Ca}_{1-x})\text{I}_2\) as a neutron scintillators. Starting materials were CaI₂ and LiI beads with 4N purity. The starting materials were enclosed in a quartz tube with 3.8 mm inner diameter under a high vacuum (~10⁻⁴ Pa). The crystal growth was performed by the VB method. An example picture of grown LiₐI₀.₁Ca₀.₉ crystal was shown in Fig. 1. In this presentation, the phase diagram of LiI/CaI₂ systems, crystal phase analysis, and these scintillation properties will also be discussed.

CRYSTAL GROWTH OF KSR\(_2\)I\(_5\) AND LI\(_2\)Sr\(_2\)I\(_5\) SCINTILLATOR FOR GAMMA AND NEUTRON DETECTION

Presenting Author: Luis Stand

Topic: Detector Materials: Scintillators and Semiconductors

Format: Invited

Session: 3, 1

Date: 8/4/2021

Time (in MDT): 1:00:00 PM

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High performance single crystal scintillators are the materials of choice for radiation detection instrumentation due to their detection versatility and their ability to distinguish gamma rays and neutron signatures of dangerous radioactive sources from non-threat radioactive sources. The main challenge when developing high performance scintillators is scale-up, taking the crystal from laboratory-scale (millimeter size) to device-scale (a few cubic centimeters) while maintaining the ultimate performance achieved with the smaller crystals. At the Scintillation Materials Research Center significant effort has been made to develop the growth processes for new single crystal scintillators that could replace NaI:Tl in the next generation of radiation detection devices. In this presentation we will discuss the development of the recently discovered high performance scintillators KSR\(_2\)I\(_5\) and LI\(_2\)Sr\(_2\)I\(_5\) doped with Eu\(^{2+}\) and Ce\(^{3+}\). Growth parameters and dopant concentrations for these materials have been optimized, allowing the growth of excellent quality single crystals measuring up to 25 mm in diameter via the vertical Bridgman technique, at translation rates between 0.2 and 5 mm/hour. Codoping and composition optimization strategies were used to obtain the highest achievable light yield and energy resolution from each compound.
CRYSTAL GROWTH AND SCINTILLATION PROPERTIES OF THALLIUM-BASED PEROVSKITE SCINTILLATORS

Presenting Author: Edgar van Loef

Topic: Detector Materials: Scintillators and Semiconductors

Format: Contributed

Session: 3, 3

Date: 8/4/2021

Time (in MDT): 1:30:00 PM

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High energy X-ray radiography of cross-border shipments such as shipping containers and multi-combination cargo trucks is vital to the mission of the Office of Countering Weapons of Mass Destruction (CWMD, Department of Homeland Security). Typically, X-ray energies in the range from 0.5 to 9 MeV are used which are detected by inorganic scintillators such as CdWO₄ and CsI:Tl. Unfortunately, CdWO₄ crystals are expensive and have relatively low light output (15,000 photons/MeV), which affects their signal to noise ratio. CsI:Tl crystals on the other hand are inexpensive but have moderate density and effective Z (Zₑffective), which leads to lower detection efficiency.<br />

Recently, organic and inorganic Perovskite materials (and hybrids thereof) have become popular in a multitude of applications due to their high quantum efficiencies and efficient photon conversion. For example, tetraalkylammonium metal halides applied in Perovskite Solar Cells, which in tandem with silicon have an efficiency of up to 30%, exceed the efficiency achieved in single-junction silicon solar cells. Also, for radiation detection the novel Perovskite materials are of interest. For example, CsSrI₃:Eu, which has been investigated at RMD for dual mode gamma-neutron detection, has a light yield of 45,000 photons/MeV (3x higher than CdWO₄). Although bright and showing excellent energy resolution, these Perovskite scintillators still suffer from low density and Zₑffective, which limits their use in high energy X-ray radiography.<br />

In this paper, we report on the crystal growth and scintillation properties of thallium-based Perovskite scintillators. We will show that substitution of the monovalent cation (e.g., Cs, Li, or K) in the base Perovskite with the heavier isovalent thallium ions leads to high density and Zₑffective scintillators, while retaining and often even improving the scintillation properties. This material is based upon work supported by the U.S. Department of Homeland Security under Grant Award Number 20CWDAR100036-01-00. The views and conclusions contained in this document are those of the authors and should not be interpreted as necessarily representing the official policies, either expressed or implied, of the U.S. Department of Homeland Security.
In this work, compounds of the type $\text{Cs}_2\text{ZnX}_4$ and $\text{Cs}_3\text{ZnX}_5$ ($X = \text{Cl, Br, I}$) were explored for their potential use in radiation detection applications. The primary objective was to find a suitable dopant, or activator, that could provide optimal scintillation properties such as high light yield and fast decay time. Single crystals, both doped and undoped, were grown in 7 mm diameter quartz ampoules using the vertical Bridgman technique. Luminescence properties were evaluated for both melt-synthesized samples (polycrystalline) as well as the grown single crystals. Despite promising properties from the melt-synthesized samples (intense photoluminescence and radioluminescence emission), incorporating the dopant into the grown crystals proved to be a difficult task. Most of the dopants appear to be rejected from the host matrix during growth, regardless of ionic radius and/or valence state. The most promising activator evaluated was $\text{Tl}^{+}$, which resulted in a light yield increase of ~11% (from 740 ph/MeV to 820 ph/MeV) for $\text{Cs}_3\text{ZnCl}_5$:Tl compared to the undoped crystal. Physical properties of the undoped crystals were characterized using dynamic vapor sorption, differential scanning calorimetry, and powder X-ray diffraction. All samples are non-hygrosopic. Congruent melting was observed for all $\text{Cs}_2\text{ZnX}_4$ crystals, as well as $\text{Cs}_3\text{ZnCl}_5$, with melting points ranging from 495 °C to 597 °C. All $\text{Cs}_2\text{ZnX}_4$ compounds were single phase and adopt the orthorhombic structure with space group $\text{Pnma}$. $\text{Cs}_3\text{ZnCl}_5$ and $\text{Cs}_3\text{ZnBr}_5$ were also single phase and adopt the tetragonal structure with space group $\text{I}_{4}/\text{mcm}$. Band gap calculations were performed using the PBE0 hybrid functional and are in close agreement with optical absorbance measurements.
ADVANCED INORGANIC HALIDE CERAMIC SCINTILLATORS

Presenting Author: Elsa Ariesanti

Topic: Detector Materials: Scintillators and Semiconductors

Format: Invited

Session: 3, 5

Date: 8/4/2021

Time (in MDT): 2:00:00 PM

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Development of low-cost ceramic scintillators has steadily progressed alongside the research in bulk single crystal scintillator growth. Increasing interest in faster scintillation material production with lower cost necessitates more research on ceramic scintillator fabrication. Research on optically transparent and dense ceramic scintillators is underway at Xtallized Intelligence, Inc. (XI, Inc.). The objective of this research is to produce ceramic scintillators that can rival the performance of bulk-grown single crystal scintillators, while reducing production cost, increasing production yield, and eliminating material waste. Ceramic compounds of interest are those that are bright (> 40,000 ph/MeV), with less moisture sensitivity for ease of handling, high density (> 5 gm/cm$^3$), and high effective atomic number (Z > 60).<br/>

Acknowledgement: This work was supported by U.S. Department of Energy Office of Science Grant # DE-SC0020816.
BULK CRYSTAL GROWTH OF CESIUM LEAD BROMIDE FOR GAMMA DETECTION

Presenting Author: Santosh Swain

Topic: Detector Materials: Scintillators and Semiconductors

Format: Contributed

Session: 4, 1

Date: 8/4/2021

Time (in MDT): 3:00:00 PM

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Cesium lead bromide (CPB) is an inorganic perovskite wide gap semiconductor that has a high intrinsic defect tolerance, with CPB detectors shown to detect gamma radiation at 662keV with close to 2% energy resolution. CPB detectors promise to be an alternative to CZT detectors that are expensive due to slow crystal growth rates and the presence of extended defects. Production of single crystals with high quality and yield is key to advancing the CPB technology. In this paper, we describe the production and scale-up of bulk single crystal CPB from 16 to 64mm diameter by the vertical Bridgman technique. The as grown crystals show high resistivity up to 10^{-9}-10^{-10} ohm.cm, and hole lifetime-mobility product of mid-10^{-4} cm^{2}/V.s.
DEEP LEVEL TRANSIENT SPECTROSCOPY AND MINORITY CARRIER TRAPS IN AU/SIO$_2$/N-4H-SiC MOS STRUCTURE ON THICK 4H-SiC EPILAYERS

**Presenting Author:** OmerFaruk Karadavut

**Topic:** Detector Materials: Scintillators and Semiconductors

**Format:** Contributed

**Session:** 4, 2

**Date:** 8/4/2021

**Time (in MDT):** 3:15:00 PM

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Oxide passivation layer inserted between the contact electrode and the epilayer surface significantly improves the performance of 4H-SiC epitaxial layer radiation detectors in terms of energy resolution. The choice of thickness of the oxide layer is crucial as it also determines the onset of the inversion mode or the threshold bias voltage. In case the detector operating bias exceeds the threshold bias, it essentially operates in the deep inversion mode and consequently minority carrier trap centers play an important role in defining the channel mobility. Electrically active defects in Au/SiO$_2$/n-4H-SiC metal-oxide-semiconductor (MOS) structures with various oxide thickness have been studied using deep level transient spectroscopy. In one of the MOS structures with 200 nm thick SiO$_2$ layer grown on a 20 μm thick 4H-SiC epilayer, both majority and minority carrier trap levels have been observed using capacitance deep level transient spectroscopy (C-DLTS) with the device operated in depletion and deep inversion mode, respectively. The structure of the defects has been identified using ab-initio calculations based on density functional theory (DFT). Three electron trap centers were identified including titanium impurities in substitutional sites (Ti(h) and Ti(c)) and carbon vacancy complexes ($Z_{1/2}$) and one hole trap situated 1.35 eV above the valence band edge, which is also a derivative of carbon vacancies, has been identified in the C-DLTS scans in the temperature range 84 - 800 K. Radiation detection measurements using the Au/SiO$_2$/n-4H-SiC MOS detectors will be presented. Additionally, results from similar studies on MOS capacitor radiation detector with 4H-SiC epilayer thickness as large as 150 and 250 μm will also be presented.
SUGGESTED MATERIAL AND SEMICONDUCTOR RESEARCH FOR IMPROVING DETECTORS FOR NATIONAL SECURITY AND CIVIL DEFENSE

Presenting Author: Mark Derzon

Topic: Detector Materials: Scintillators and Semiconductors

Format: Invited

Session: 4, 3

Date: 8/4/2021

Time (in MDT): 3:30:00 PM

Authors: Mark Derzon, Gold Standard Radiation Detection, Albuquerque, New Mexico, United States

It is not an overstatement to say that Single events such as Hiroshima, 9/11, Chernobyl, the Covid-pandemic caused worldwide havoc and devastation. The effects of those disasters will likely be small compared to the consequences of a nuclear bomb or terrorist nuclear event. That the members of this organization can contribute sensors that improve our ability to finding nuclear materials, as well as Chemical weapons, explosive and biological this research is critical. These developments will also lead to improvements in sensors for medicine and other applications. This talk will start with features of radiation in abnormal environments and some unmet needs. We’ll then segue into materials improvements that can respond to these unmet needs. Research into intense radiation following a criticality accident rises and falls rapidly. It is difficult to detect and monitor these burst events and the details determine the potential for survival. The electromagnetic pulse will travel farther than the ionizing radiation and both can destroy the equipment we use to understand what is happening and which is used to protect civilians, and first responders. We will show how this may affect an event response as well as discuss research that may result in improved sensors for prompt and delayed event diagnosis and actionable information to help save lives. Our viscera, and preferred response is to try and interdict or stop nuclear terror events. We will show data that that we (and others worldwide) are developing fast, safe and portable means of finding CBRNE (Chemical, Biological, Radiation Nuclear and Explosive) materials. We will discuss how material developments can be applied to these needs and methods to improve performance.
GROWTH DIFFICULTIES AND GROWTH OF CRACK FREE EU\(^{2+}\) ACTIVATED KSR\(_2\)I\(_5\) SCINTILLATOR SINGLE CRYSTAL BY VERTICAL BRIDGMAN-STOCKBARGER TECHNIQUE FOR RADIATION DETECTION APPLICATIONS

Presenting Author: Raja Arumugam

Topic: Detector Materials: Scintillators and Semiconductors

Format: Poster

Session: ,

Date:

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The parent compound of Strontium Iodide (SrI\(_2\)), Potassium Iodide (KI) and Europium Iodide (EuI\(_2\)) was purified by homemade Zone-refinement experimental set-up. Insoluble impurities were filtered by specially designed dual chamber quartz ampoule with frit filter method. The Europium activated potassium strontium iodide (KSR\(_2\)I\(_5\):Eu\(^{2+}\)) compound melt was filtered by frit filtering method. Steep temperature profile of this growth furnace is also measured to growth a quality single crystal of KSR\(_2\)I\(_5\):Eu\(^{2+}\). The KSR\(_2\)I\(_5\):Eu\(^{2+}\) single crystal was grown by homemade vertical transparent Bridgman-Stockbarger technique. The photoluminescence excitation and emission spectra indicated the typical 4f 5d - 4f transition. The broad emission peak was at 443 nm. The X-ray excited radioluminescence broad emission was observed at 452 nm. The scintillation properties of the grown crystal were tested by gamma ray spectrometer. The energy resolution of the KSR\(_2\)I\(_5\):Eu\(^{2+}\) crystal was found to be 4.1% at 662 KeV under \(^{137}\)Cs sealed gamma source and scintillation decay time was also determined and calculated value is 1.25 μs.
GROWTH AND SCINTILLATION PROPERTIES OF 
Li₂SrCl₄/LiSr₂Cl₅ EUTECTIC SCINTILLATOR

Presenting Author: Kei Kamada

Topic: Detector Materials: Scintillators and Semiconductors

Format: Poster

Session:

Date:

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Today, demand for neutron detection is increasing for medical imaging, security system, astrophysics, and well logging applications etc. In neutron detection applications, it is important to distinguish between gamma rays and neutron rays, and it is essential to develop a detector that has high sensitivity to neutron rays and low sensitivity to gamma rays. The current candidates for neutron detection were detectors include boron-coated straws, plastic and liquid scintillators, and inorganic scintillators containing high thermal neutron capture cross-section elements such as Li and B. While the scintillator for gamma-ray detection needs to be composed of heavy elements, the scintillator for neutron detection needs to have a high Li density in the scintillator to have high neutron detection efficiency. In this study, we focus novel neutron scintillator as Li₂SrCl₄/LiSr₂Cl₅ with higher Li concentration. Crystal growth of Eu doped Li₂SrCl₄/LiSr₂Cl₅ with higher Li concentration. Eutectic and evaluation of scintillation properties were performed. The starting materials were prepared using LiCl, SrCl₂, EuCl₂, powders (4N). LiCl and SrCl₂ based eutectics were grown by the Bridgman-Stockbarger (BS) method in a quartz ampoule with 4 mm inner diameter under various pulling rate. Mixed powders were induced into the ampoule under high purity Ar atmosphere in a glove box. Growth rate was 0.05~0.5 mm/min. Circular samples of with 1-mm thickness were obtained from the grown eutectics. Fig.1 shows photograph and BEI of the polished eutectic sample. Grown eutectic showed optical transparency due to close refractive index of the observed two phases. Two phases of Sr lich and less were observed by EDX. Eu emission peaking at 400 nm was observed under X-ray excitation. Details about growth, crystal structures and evaluation of scintillation properties will be showed in my presentation.
ROLE OF CARRIER TRAP CENTERS IN NI/N-4H-SIC EPITAXIAL SCHOTTKY RADIATION DETECTORS WITH VARYING EPILAYER THICKNESS UP TO 250 µM

Presenting Author: Joshua Kleppinger

Topic: Detector Materials: Scintillators and Semiconductors

Format: Poster

Session: ,

Date: 

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Semiconductor devices based on 4H-SiC epitaxial layer are most suited for high-resolution radiation detection and front-end electronics in harsh environments such as high-energy astroparticle physics experiments, nuclear reactor cores, laser-generated plasma environments and nuclear material storage environments. Advances in the growth processes of 4H-SiC epitaxial layers has led to the continued expansion of epilayer thickness allowing for the detection of more penetrative radioactive particles. Growth of thick epilayers, while maintaining the crystallinity and formation of intrinsic defects, is of high scientific and industrial interest. In this presentation we discuss the fabrication and characterization of high-resolution Ni/n-4H-SiC Schottky barrier detectors (SBDs) with epilayer thicknesses ranging from 20 µm to 250 µm and discuss the prospect of thick epilayers as radiation detectors. The epitaxial layers used for the detector fabrication were grown on bulk conductive 4H-SiC substrates of 100 mm diameter with micropipe densities <0.1 cm⁻². Schottky barrier detectors were fabricated by depositing circular nickel contacts (~11 mm²) on 8×8 mm² 4H-SiC epilayers. Capacitance-voltage (C-V) measurements showed that all the epilayers had comparable effective carrier concentrations of 1.5 × 10¹⁴ cm⁻³ which are low enough to obtain full depletion at bias voltages that are much lower than the breakdown potential. Current-voltage (I-V) revealed extremely low leakage currents (30 pA at 300 V reverse bias), high barrier heights (1.30 eV), and ideality factor close to unity even for the thickest epilayer SBDs. The radiation detection performance with a Am alpha source exhibited an energy resolution of 0.47% FWHM for 5486 keV alpha particles for a 250 µm epilayer SBD which is comparable to that obtained for thin epilayer SBDs. Capacitance deep level transient spectroscopy (C-DLTS) studies revealed the presence of similar intrinsic trap centers viz. Ti(c), Z₁/₂, and EH₆/₇ in all the epilayers albeit with different concentrations and capture cross-sections. Comparison of the defect parameters obtained from the C-DLTS studies with epilayer thickness will be presented along with the correlation of the defect parameters with the device performance. Results from DFT calculations to identify the structure of the above-mentioned trap centers will also be presented.
MODIFIED VERTICAL BRIDGMAN GROWTH OF Cd₀.₉Zn₀.₁Te₁₋ₓSeₓY (CZTS) SINGLE CRYSTALS FOR RADIATION DETECTION WITH RECORD HIGH BULK-RESISTIVITY AND ELECTRON-MOBILITY

Presenting Author: Joshua Kleppinger

Topic: Detector Materials: Scintillators and Semiconductors

Format: Poster

Session: ,

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Cd₀.₉Zn₀.₁Te₁₋ₓSeₓY (CZTS) single crystal is a recently discovered wide bandgap and high-Z semiconductor for room temperature detection of high energy gamma photons. CZTS, like its ternary predecessor CdₓZn₁₋ₓTe (CZT) has all the physical properties that are required for field applications such as gamma-ray medical imaging, monitoring and safeguarding of special nuclear materials, Homeland security applications such as nuclear non-proliferation etc. In addition, CZTS has major advantages of having crystal growth yield of 90% and above and manifestation of very low macroscopic and microscopic defects. These deleterious defects include cracks, twin/grain boundary networks and microstructural defects such as mosaic structures, tilt boundaries, dislocations, point defects, impurities, and tellurium inclusions/precipitates which act as hole trapping centers. Low defect concentration, especially tellurium inclusions in CZTS help to obtain unparalleled transport properties among high-Z room temperature gamma detectors with large crystal volumes. We present the growth conditions of detector grade Cd₀.₉Zn₀.₁Te₁₋ₓSeₓY single crystals with excellent charge transport properties using a modified vertical Bridgman method. We report a record-high bulk resistivity on the order of 10¹¹ Ω-cm measured from the current-voltage (I-V) characteristics and electron drift-mobility of 1330 cm²/Vs measured using a digital time-of-flight method. The single crystals also exhibited very high electron mobility-lifetime product (μτₑ) of 2.2 × 10⁻³ cm²/Vs measured through alpha spectroscopy. We will present high energy gamma radiation detection studies using these grown crystals and discuss the role of charge carrier trapping in defining the energy resolution of these fabricated detectors.
THE EFFECT OF DOPING WITH HALOGENS ON THE HARDNESS OF VAPOR GROWN CdTe SINGLE CRYSTALS

Presenting Author: Volodymyr Popovych

Topic: Detector Materials: Scintillators and Semiconductors

Format: Poster

Session: ,

Date:

Time (in MDT):

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Yuri V. Pavlovskyy, Ivan Franko Drogobytsk State Pedagogical University, Drogobytsk, Ukraine

Compensating doping of CdTe crystals with chlorine is a typical approach to obtain semi-insulating material, which has been industrially used in the last few decades for production of uncooled X- and γ-rays detectors. The identification of mechanical properties of this compound is of great practical importance to select the optimal technology of detectors fabrication and to understand their behaviour in a hostile condition of long-time high-energy irradiation. Despite the fact that a number of hardness studies of CdTe has been carried out, data about the effect of doping on this characteristic is very limited, and, besides, the studies have been mostly performed using the crystals grown from liquid phase. In the present study, thorough measurements of microhardness variations of vapour grown CdTe single crystals in results of their doping with halogens were performed for the first time. CdTe single crystals, grown by the modified PVT method [1], undoped and doped with Cl and I in a wide range of concentrations, were investigated. Vickers microhardness experiments were undertaken on {110}- and {111}-oriented surfaces of the samples, both cleaved and chemo-mechanically polished. The dependences of hardness on the doping level (Fig. 1) were explained within the framework of the model of heavily doped and compensated inhomogeneous semiconductors. It was found that in the range of low dopant concentrations for CdTe:Cl and in the whole doping range for CdTe:I, the hardness of the material is determined by the motion of dislocations in the Peierls-Nabarro potential relief and by their interaction with the doping-induced charged point defects. For the case of heavily doped CdTe:Cl, the decisive effect becomes the decreasing of yield stress due to the development of dopant-enriched second phases in the CdTe host matrix when exceeding of Cl solubility limit in this compound. <p><a href="http://files.abstractsonline.com/CTRL/BB/A/306/5D4/F35/4A2/BB7/820/609/878/785/39/g1266_2.jpg" target="_blank" address=no >img src="http://files.abstractsonline.com/CTRL/BB/A/306/5D4/F35/4A2/BB7/820/609/878/785/39/g1266_2.jpg" alt="" border="0" width="600" height="424" /"></a></p><br />Fig. 1. Vickers microhardness as a function of dopant concentration (in the initial charges), measured on {110}-oriented CdTe surfaces at a load of 30 g. A tight correlation was revealed between the microhardness and the defect structure (dislocation density, presence of second phase inclusions), optical (IR-transmission) and electrical (resistivity, charge carriers mobility) properties of halogen-doped CdTe crystals, which demonstrates the effectiveness of the microhardness measurement technique for testing the alteration of the physical properties of CdTe-based semiconductors in consequence of their doping.<br />[1] V.D. Popovych, et al. J. Cryst. Growth, 2007, 308, 63-70.
CRYSTAL GROWTH AND SCINTILLATION PROPERTIES OF TUBE SHAPE-CONTROLLED CE-DOPED
Y$_3$Al$_5$O$_{12}$ AND Lu$_3$Al$_5$O$_{12}$ SINGLE CRYSTALS GROWN BY MICRO-PULLING-DOWN METHOD WITH MO CRUCIBLES

Presenting Author: Masao Yoshino

Topic: Detector Materials: Scintillators and Semiconductors

Format: Poster

Session: ,

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Scintillator materials are fluorescent substances that have been used as radiation detectors in combination with photodetectors. Recently, simultaneous multi-RI imaging with a wide range of energy could be achieved, which was a significant challenge for such imaging methods [1]. For simultaneous imaging, imaging methods where a scintillator array serves as a collimator have been developed. There has been a strong demand for tube-shaped single-crystal scintillators to realize further improvements in imaging performance. In our group's latest research, tube-shaped Ce-doped Y$_3$Al$_5$O$_{12}$ single-crystal scintillators were successfully grown by micro-pulling-down method with a specially-designed Ir crucible [2]. However, the crystal growth using a lower-cost crucible such as Mo would be preferable and the Ce:YAG single crystal grown by the Mo crucible was reported recently. In this research, tube-shaped Ce:YAG and Ce:LuAG single-crystal scintillators were grown using specially-designed Mo crucibles (Fig. 1, 2). In addition, Mo crucibles with 4 and 8 capillaries were used to investigate effects of capirally number on Ce’s segregation and scintillation properties in the grown single crystals. The crystal growth was performed under Ar + 3% H$_2$ atmosphere. The Mo crucibles made possible the growth of Ce:YAG and Ce:LuAG single crystal tube as small as 0.2 mm in inner diameter and 0.4 mm in outer diameter. In this presentation, we will talk about crystal growth, Ce’s segregation and the scintillation properties of the Ce-doped Y$_3$Al$_5$O$_{12}$ single crystals grown by micro-pulling-down method, Appl Phys Express. 13 (2020) 125503.

INTERFACIAL DRIVERS FOR NON-CLASSICAL CRYSTALLIZATION

Presenting Author: Maria Sushko

Topic: Fundamentals of Crystal Growth

Format: Invited

Session: 2, 1

Date: 8/2/2021

Time (in MDT): 10:30:00 AM

Authors: Maria Sushko, Pacific Northwest National Laboratory, Richland, Washington, United States

Crystallization often does not follow the monomer-by-monomer addition pathway described by classical nucleation theory. Instead, the initial steps may involve the formation of larger building blocks, such as crystalline or amorphous nanoparticles, droplets, clusters, complexes, or oligomers, that subsequently undergo assembly into a crystal. These multistep crystallization processes are ubiquitous in mineral formation. The creation of intermediate phases in solution introduces a number of interfacial interactions that profoundly change local speciation and forces and affect nucleation and growth pathways. To elucidate the link between the structure and chemistry of the surface and the interfacial gradients in solution speciation and facet specific-forces that alter nucleation and growth pathways and select for attachment faces, we developed a theoretical framework based on coupled plane-wave and classical density functional theory and applied it to aqueous solutions of iron salts. The approach, which separates contributions to the total chemical potential describing entropy of mixing (ideal chemical potential) and all interfacial interactions (potential of mean force, PMF), revealed that the interfacial potential of mean force for precursor species is the predictor of nucleation and growth pathways. Specifically, repulsive PMFs indicate that the surface is stable and precursor species form a highly correlated double layer at the interface. Under these conditions, growth via monomer addition is unlikely, leaving, however, the possibility for the growth via particle-based crystallization. When the PMF has a minimum at the interface and is dominated by short-range precursor/surface interactions, the classical monomer-addition mechanism is favored. Finally, in the presence of ligands that create a layer of charged, discrete sites on the surface, the potential of mean force is dominated by entropic ion correlation interactions, which stabilize the interfacial diffuse layer of solvated precursor ions, hindering diffusion and deposition on the surface and driving nucleation of new particles approximately a nanometer away from the surface and leads to formation of mesocrystals or random aggregates. These studies furnish a generalized approach for predicting nucleation and growth pathways based on the nature of interfacial structure and forces.
INTERFACIAL STRUCTURE, INTERPARTICLE FORCES AND ASSEMBLY DYNAMICS DURING NANOCRYSTAL FORMATION VIA ORIENTED ATTACHMENT

Presenting Author: James De Yoreo

Topic: Fundamentals of Crystal Growth

Format: Invited

Session: 2, 3

Date: 8/2/2021

Time (in MDT): 11:00:00 AM


Assembly of inorganic nanocrystals to form hierarchical structures is a common approach to creating functional materials. This process exhibits diverse styles ranging from oriented attachment (OA) of like phases to mis-oriented aggregation of disparate phases followed by coarsening to ordered structures. While descriptions of these systems must share a commonality with continuum-based DLVO-type theories for simple colloids, nanocrystals present additional complexities, including face-specificity of properties, inherent diopolar interactions, structured nanoscale interfaces, and solvent-responses at length scales comparable to particle size. To understand the relationship between interfacial structure, interparticle forces and assembly dynamics, we are investigating colloidal assembly of titanium-, iron- and zinc-oxides. AFM-based force mapping shows that solution structure exhibits sub-nm heterogeneities both along and perpendicular to crystal surfaces, reflecting gradients in speciation and water density that mediate interparticle forces. 

<i>In situ</i> TEM demonstrates that direction-specific forces attract and align diffusing ZnO nanoparticles at distances far in excess of expectations based on DLVO theory. Particles start their approach from beyond 10 nm and undergo OA unopposed by significant energy barriers. MD simulations on numerous systems predict that solvation forces drive coalignment by creating orientation dependent solvent-separated minima. However, no attractive interactions are predicted beyond ~1 nm and minima are separated by barriers of 100 kT or more, making it unclear why particles are attracted from long range and how contact is ultimately achieved. Classical density functional theory predicts that ion correlation effects decrease barriers, enabling attachment, but does not predict long range attraction nor coalignment. We find that, in ZnO, the long range of the forces and torques and high degree of coalignment are consequences of an inherent dipole moment. Dipole-dipole interactions enforce alignment even in the absence of solvation-defined forces and drive attraction at large separations. Similar studies on iron-oxide/sodium-oxalate and gold/sodium-citrate show that addition of the organics produces a dramatically different assembly pathway and outcome. The first particles to appear, either through seeding or nucleation, become covered with the organic ligand, which creates interfacial gradients that drive all new particles to nucleate about 1 nm.
away from existing ones, to which they attach without a barrier. Consequently, aggregates of coaligned particles form with a shape reflecting differences in nucleation rate along distinct crystallographic directions. Thus, the random assembly process that dominates in many systems is replaced by a deterministic process giving rise to self-similar nanoparticle assemblies.
NONCLASSICAL PATHWAYS OF CHOLESTEROL CRYSTALLIZATION THROUGH THE ATTACHMENT OF CLUSTERS ON THE SURFACE

Presenting Author: Wenchuan Ma

Topic: Fundamentals of Crystal Growth

Format: Contributed

Session: 2, 5

Date: 8/2/2021

Time (in MDT): 11:30:00 AM

Authors: Wenchuan Ma, U of H, Houston, Texas, United States

Nonclassical pathways of cholesterol crystallization thought the attachment of clusters on the surface. Approximately twenty percent of adults have gallstones making gallstone disease is one of the most common biliary tract diseases caused by a combination of genetic and environmental factors. Gallstones occur when the chemical constituents of bile become imbalance. Precipitation of solid cholesterol crystals from supersaturated bile plays an essential role in gallstone formation. Gallstones can cause various problems: biliary colic/cholecystitis; Jaundice; ascending cholangitis; pancreatitis; Bouveret’s syndrome and gallstone ileus and Gallbladder cancer. The most common treatments for gallstone disease are drug dissolution therapy and open surgery. The understanding of the mechanism behind cholesterol crystallization will provide insights for designing more effective therapeutic drugs to prevent or remove gallstones. Previous studies forced on investigating the role of hepatic secretion of biliary cholesterol, phospholipids and bile salts that may govern the crucial steps of formation of gallbladder. Those results unveiled pathways to modify or stop the formation of cholesterol crystals from controlling the precipitation, growth or agglomeration. However, Difficulties built in the nature of cholesterol crystallization build a wall that barricade a deep understanding of molecular mechanisms. The extreme fast nucleation and growth rate outrun the rate that we can catch. We establish a system mimicking the environment in where cholesterol crystal forms while regulating the rate of crystal growth within a rage that can be monitored by atomic force microscopy. We develop an improved understanding of cholesterol crystallization with an emphasis on the assembly and role of clusters. This research will predominantly employ in situ AFM to elucidate layer generation and spreading at physiologically-relevant conditions. We conducted preliminary studies revealing cholesterol crystal growth occurs by a combination of classical and nonclassical pathways involving the addition of monomer and precursors, respectively. In situ AFM confirmed the addition of clusters while dynamic light scattering indicated their presence over a range of temperatures and solute concentrations. It was found that growth at high supersaturation leads to layered surfaces populated with step bunches and double steps that grow at reduced rates. At low supersaturation, we observe highly unusual step advancement mediated by the presence of protrusions. Collectively, our preliminary data indicates that cholesterol grows by pathways that are distinct compared with other pathological crystals.
INVESTIGATION OF VATERITE GROWTH UNDER CONTROLLED CONSTANT COMPOSITION CONDITIONS

Presenting Author: Lijuan Wang

Topic: Fundamentals of Crystal Growth

Format: Contributed

Session: 2, 6

Date: 8/2/2021

Time (in MDT): 11:45:00 AM

Authors: Lijuan Wang, Norwegian University of Science and Technology, Trondheim, Norway; Jens-Petter Andreassen, Norwegian University of Science and Technology, Trondheim, Norway; Seniz Ucar, Norwegian University of Science and Technology, Trondheim, Norway

Observations of complex, non-equilibrium morphologies and polycrystallinity of calcium carbonate can be explained within the classical crystallization theory, via kinetic roughening and interface instability induced at high thermodynamic driving forces. To investigate the effects of solution supersaturation and temperature on morphology development of vaterite crystals, seeded growth experiments at a constant composition setup is utilized in this work. Spherulitic vaterite particles were used as seeds for crystal growth experiments in aqueous solutions at a supersaturation range of $S_{\text{vaterite}}=1.5-5$ and at temperature values between 10-60°C. The constant composition conditions were fulfilled by automated titrant addition to compensate for ion consumption, changing ionic strength and alkalinity in the reaction media. The overall growth rate, growth rate constant and the apparent growth order were calculated by using the titration curves. The overall growth rate constant increased with increasing supersaturation and higher temperature, while the growth order decreased from 2.11 to 1.40 as temperature increased from 10°C to 40°C. The new layers of growth developed from the equator of the seed vaterite particles, indicating the anisotropy of the inner structure of the vaterite spherulites. The effects of temperature and supersaturation on the growth morphology were decoupled in a matrix of experiments. At 10°C, the subunit size of the new growing layer was smaller at high $S$ ($S_{\text{vaterite}}=5$) than at low $S$ ($S_{\text{vaterite}}=1.5$), which was consistent with the results of a phase field modelling and our previous findings. High supersaturation gives rise to high rate of the growth front nucleation, leading to a high extent of non-crystalline branching, small grain size and compact morphology. By fixing the supersaturation at low value ($S_{\text{vaterite}}=1.5$) and allowing for 50 w% growth, with increasing temperature from 10°C to 40°C, the shape of the subunits changed from long and thin needle-like to short and thick rectangular. When particles were grown to higher extents (200 w% or higher), at low supersaturation ($S_{\text{vaterite}}=1.5-2.5$), the subunit size increased drastically and produced a morphology with hexagonal plates stacked perpendicularly from equator to poles. On the contrary, at high supersaturation ($S_{\text{vaterite}}=5$), the subunit size did not show a significant change due to high rates of growth front nucleation. Our results demonstrate the strong correlation of particle morphology with thermodynamic driving force for growth, which is elucidated within the framework of classical crystal growth theory.

The nucleation of hematin crystals can be suppressed and fine-tuned via the properties of a population of nucleation precursors extant in the solution. Hematin crystals form in the digestive vacuoles of malaria parasite, where they sequester toxic hematin released as the parasite catabolizes hemoglobin from the host’s erythrocytes. Suppression of hematin crystallizations is the most productive pathway to kill the parasites and fight malaria. The addition of four antimalarial drugs, heme-artesunate adduct (H-ARS), mefloquine (MQ), chloroquine (CQ), and pyronaridine (PY), known to control hematin crystallization, invokes one of three outcomes: accelerated nucleation (H-ART), suppressed nucleation (PY), or no effect (CQ and MQ). The nucleation enhancement and the passivity of two modifiers can be understood within CNT. The nucleation suppression falls outside of the realm of CNT and suggests that hematin crystal nucleation may follow a nonclassical pathway. Transmission electron microscopy (TEM) characterization of supersaturated hematin solutions reveal the presence of amorphous particles with diameters ranging from 70 to 250 nm that host and assist the nucleation of elongated hematin crystals. Oblique illumination microscopy reveals the presence in the solution of mesoscopic hematin-rich clusters with size similar to those measured by TEM. The addition of the modifiers CQ, MQ, PY, and H-ARS does not affect the clusters size. These additives, however, invoke disparate responses of the cluster concentration $<\!\!N\!\!>$ $. Remarkably, the responses of the cluster population to the four modifiers run parallel to the responses of crystal nucleation, coherently with the role of clusters as crystal nucleation sites. Collectively, the TEM observation of cluster-assisted nucleation and the parallel trends of additive activity on the cluster population and crystal nucleation support a mechanism of nucleation control employing additives that modulate the nucleation precursors.
UNIQUE MECHANISMS OF MOLECULAR MODIFIERS IN CRYSTAL NUCLEATION AND GROWTH

Presenting Author: Jeffrey Rimer

Topic: Fundamentals of Crystal Growth

Format: Invited

Session: 2, 3

Date: 8/3/2021

Time (in MDT): 11:00:00 AM

Authors: Jeffrey D. Rimer, University of Houston, Houston, Texas, United States

Crystals are commonly implicated in deleterious processes, such as human diseases (e.g. kidney stones, malaria, atherosclerosis, etc.) and the formation of scale in water treatment and oil/gas pipelines. A common method of crystal prevention or treatment is the use of modifiers, which are molecules (or macromolecules) that preferentially bind to crystal surfaces and reduce the rate of solute attachment. This talk will highlight several unique modes of modifier action that include mechanisms of nucleation suppression, strain-induced layer inhibition (leading to surface dissolution), alterations in surface termination (promoting intergrowths), irreversible growth suppression (involving the formation of disordered interfaces), and cooperative action (synergism or antagonism) of binary molecule combinations. When designing new modifiers, such as drugs for debilitating human diseases, it is important to consider the underlying fundamental physical interactions of modifiers with crystal surfaces. Here, we will describe the results of collaborative projects involving bulk crystallization, in situ characterization, microfluidic assays, and computational studies that are collectively aimed to better understand the mechanisms of crystal growth modification, and determine to what extent molecule-crystal interactions can be tailored to reduce (or prevent) crystallization. Understanding the interactions between growth modifiers and crystal interfaces requires a combination of experimental techniques capable of probing a wide range of length and time scales. Analysis of macroscopic properties (bulk crystal growth) provides information on modifier changes to crystal size and habit. To gain molecular insights, in situ atomic force microscopy (AFM) is used to observe time-resolved dynamics of surface growth in the presence of modifiers. The culmination of these studies provide insight on how we can potentially engineer modifiers with tailored properties to take advantage of specific modifier-crystal interactions to suppress growth or induce crystal dissolution. To this end, we will present our discoveries of viable candidates to replace commercial modifiers as effective inhibitors of crystallization in pathological diseases and other applications.
AN INTERMEDIATE COMPLEX REGULATES THE INCORPORATION OF MOLECULES INTO KINKS ON GROWING CRYSTALS

Presenting Author: Rajshree Chakrabarti

Topic: Fundamentals of Crystal Growth

Format: Contributed

Session: 2, 5

Date: 8/3/2021

Time (in MDT): 11:30:00 AM

Authors: Rajshree Chakrabarti, University of Houston, Houston, Texas, United States Lakshmanji Verma, University of Houston, Houston, Texas, United States Jeremy C. Palmer, University of Houston, Houston, Texas, United States Peter G. Vekilov, University of Houston, Houston, Texas, United States

Molecular crystallization is an essential step in many biological, geological, and engineered materials. Classical theories posit that the crystallization rates and pathways are largely dictated by the slow ingress of solute molecules into specifically structured growth sites, the kinks, but the interactions and structures that administer the access to a kink remain elusive. Here we show that \textit{en route} to a kink an incoming solute molecule forms an intermediate complex, in which the solute binds, but only partially, to the molecules that comprise the kink; the disruption of the solute-solute and solute-solvent contacts that uphold this complex constitutes the transition state for incorporation. We combine time-resolved \textit{in situ} atomic force microscopy with all-atom molecular dynamics simulations to examine the crystal growth of etioporphyrin I, which represents a class of materials with appealing optico-electronic properties. Violating the classical models of solution crystallization, the measured activation barriers for crystallization disconnect from the strengths of the interactions of the solute with the four solvents and imply that a structure comprised of both solute and solvent molecules controls the access to a kink. MD simulations reveal that in this structure an incoming solute molecule forms a fraction of the crystal contacts whereas the remaining contacts are open to solvent molecules. The spatial constraints on the solvent access to the open contacts rank how much the distinct solvents stabilize this complex and set the height of the barrier to be surmounted for incorporation. The proposed two-step scheme of molecular incorporation presents an alternative paradigm that may expedite the selection of solutes and solvents in the crystallization process design of numerous organic electronic and solar materials.
TAUTOMERISM UNVEILS A SELF-INHIBITION MECHANISM OF PATHOLOGICAL CRYSTAL GROWTH

Presenting Author: Weiwei Tang

Topic: Fundamentals of Crystal Growth

Format: Contributed

Session: 2, 6

Date: 8/3/2021

Time (in MDT): 11:45:00 AM

Authors: Weiwei Tang, University of Houston, Houston, Texas, United States Cristian A. Morales Rivera, University of Pittsburgh, Pittsburgh, Pennsylvania, United States Francisco C. Robles Hernandez, University of Houston, Houston, Texas, United States Giannis Mpourmpakis, University of Pittsburgh, Pittsburgh, Pennsylvania, United States Jeffrey D. Rimer, University of Houston, Houston, Texas, United States

Crystallization is driven by excess Gibbs free energy of supersaturated solutions relative to its saturated state, which conventionally leads to monotonic increases in growth rates with increasing solute concentration. In the absence of crystal growth modifiers (or impurities), trends in growth rates for most systems follow classical mechanisms without disruption of solute attachment to crystal surfaces. In this presentation, we will discuss mechanisms for the crystallization of ammonium hydrogen urate, a pathological component of dolphin kidney stones. Using a combination of high resolution experimental techniques and density functional theory (DFT) calculations, we show that keto-enol tautomers of urate, which constitute a minor fraction of solute, function as natural inhibitors of crystal growth. Measurements over a range of supersaturation reveal concentration dependencies where growth inhibition completely suppresses ammonium urate formation. Time-resolved scanning probe microscopy measurements are used to monitor crystal surface growth wherein we demonstrate that the presence of tautomers impede layer nucleation and spreading at lower supersaturation; and at higher supersaturation we observe layered growth involving step bunches, which is qualitatively consistent with bulk crystallization assays revealing the formation of dendrite-like crystal aggregates where high-resolution electron microscopy indicates a higher percentage of defects owing to tautomer occlusion. Our study also shows that tautomer concentration is dramatically reduced in growth media prepared at higher alkalinity, as confirmed by a combination of DFT calculations and spectroscopy measurements. Under these conditions, ammonium urate surfaces grow via a more traditional mechanism of single layer birth and spreading, leading to bulk crystals with needle-like morphology and fewer defects. To our knowledge, this is the first identification of tautomers acting as natural inhibitors of their parent crystals wherein their unique modes of action lead to deleterious effects, such as growth suppression and defect incorporation.
MODELING THE ENGULFMENT OF BUBBLES DURING SAPPHIRE CRYSTAL GROWTH

Presenting Author: Jeffrey Derby

Topic: Fundamentals of Crystal Growth

Format: Contributed

Session: 1, 3

Date: 8/4/2021

Time (in MDT): 9:00:00 AM

Authors: Jeffrey J. Derby, University of Minnesota, Minneapolis, Minnesota, United States  Swanand Pawar, University of Minnesota, Minneapolis, Minnesota, United States

Bubbles of 10-100 microns in size are often observed in sapphire crystals grown from the melt. Bubbles act as defects, ruining the precise uniformity of large-surface-area wafers, reducing the yield of high-quality material, and increasing costs. A better understanding of the fundamentals of bubble engulfment will provide a basis for improved material quality, increased process yields, and reduced costs.

The engulfment of bubbles during solidification is determined by a balance of repulsive van der Waals forces between the bubble and the solidification interface and drag forces arising from the flow around the bubble and into a thin liquid gap between particle and interface, typically on the order of 10-100 nanometers in thickness. When drag forces overcome repulsive forces, the bubble is engulfed, otherwise it is steadily pushed ahead of the advancing interface. Since drag increases with bubble size and velocity, there exists a critical velocity at which a bubble of a certain size is engulfed. However, drag forces are strongly dependent upon the nature of flows along the bubble surface (which may include thermocapillary effects) and shape of the solid-liquid interface as the bubble approaches. Thus, the critical velocity is affected by significant and nonlinear interactions involving heat transfer, premelting, and Gibbs-Thomson phenomena.

We present our initial efforts to develop and apply computational models to elucidate the mechanisms of bubble engulfment during crystal growth. We describe finite-element, moving-boundary analyses to assess bubble dynamics near moving solidification fronts. This numerical approach allows for an accurate representation of forces and dynamics previously inaccessible by approaches using analytical approximations.

Our bubble engulfment analysis builds upon prior steady-state and dynamic models at the continuum level that have been developed to study the pushing or engulfment of a solid particle at a moving, solid-liquid interface. Prior results have revealed new mechanisms that impact the engulfment of silicon carbide particles engulfed during the growth of multi-crystalline silicon. We present initial computations for the case of bubble engulfment in a model sapphire growth system and highlight the differences in behavior compared to the engulfment of solid particles.

This research was supported in part by the U.S. National Science Foundation, CMMI-1760689; no official endorsement should be inferred.
WHAT AFFECTS THE SHAPE OF LEADING EDGE IN HORIZONTAL RIBBON GROWTH SOLIDIFICATION PROCESS?

Presenting Author: Alireza Pirnia

Topic: Fundamentals of Crystal Growth

Format: Contributed

Session: 1, 4

Date: 8/4/2021

Time (in MDT): 9:15:00 AM

Authors: Alireza Pirnia, Clarkson University, Potsdam, New York, United States  Brian T. Helenbrook, Clarkson University, Potsdam, New York, United States

Horizontal ribbon growth (HRG) is an efficient alternative for traditional techniques for silicon wafer production. In this method, thin ribbons (sheets) solidify on the surface of a molten pool with the help of a cooling source and are horizontally pulled from the pool. Continuous operation of this process and the maximum ribbon pulling speed depend on the stability of the ribbon leading edge (LE), where the crystallization initiates and propagates. In this study, the multi-physics interactions that occur during the HRG process are analyzed both theoretically and numerically with an emphasis on the ribbon LE. The heat balance equation is solved theoretically in the vicinity of the LE, and the temperature distribution and gradients are obtained as a function of the material properties, pulling speed, and the cooling heat flux. It is shown that different LE shapes, specifically single and double facet formations, result in varying temperature profiles in the vicinity of LE that affect the rate of solidification and the amount of liquid supercooling. Linking the temperature distributions with empirical solidification kinetics for silicon, the variations of the misalignment angle along the facets and the rate of solidification in the vicinity of LE are obtained and the constraints they may impose on the ribbon pulling speed are discussed. The problem is also studied numerically using an hp-finite element model that benefits from a moving and adapting mesh algorithm. With the numerical model, a more accurate solution can be obtained that accounts for the convective liquid flow, conductive and convective heat transfer, and directional solidification kinetics. It is shown that by increasing the grid resolution near the triple junction point (TJP), where the liquid, solid, and gas phases meet, and the under-hanging nose (UHN), in case of a double facet formation, the numerical temperature profiles match the theoretical predictions. This means that the simplified theoretical formulations are able to predict the ribbon LE behavior and the conditions leading to its instability.
CHARACTERIZATION OF SURFACE FEATURES AT A THREE-PHASE BOUNDARY FROM GROWTH OF HEAVILY DOPED DISLOCATION-FREE SINGLE CRYSTAL SILICON

Presenting Author: Joel Kearns

Topic: Fundamentals of Crystal Growth

Format: Contributed

Session: 1, 5

Date: 8/4/2021

Time (in MDT): 9:30:00 AM

Authors: Joel K. Kearns, NASA Glenn Research Center, Cleveland, Ohio, United States

Single crystal dislocation-free silicon, heavily doped with electronic impurities such as arsenic or antimony, is used as starting material to make the lowest power-consumption electronics for cars, laptops and cell phones. The crystals are grown by Czochralski pulling technique, which is a normal freezing process. The dopant concentration in the liquid at the solid-liquid interface during crystal growth is elevated, due to dopant partitioning during solidification. This can lead to a condition known as constitutional supercooling, where the planar solid-liquid interface shape deforms, generating channels of impurity enriched-melt bounded by solid silicon. Constitutional supercooling can occur if the ratio of temperature gradient to solidification rate exceeds a material- and dopant concentration-specific parameter. Dislocations can nucleate near the locations of the channels, but the cause of dislocation nucleation is not understood. Once dislocations are present, the crystal is not usable for devices. Constitutional supercooling can take place at the three-phase boundary as the crystal diameter is increased from the small seed and neck to the full wafer sized crystal body. This crystal geometry makes the channels visible at the crystal-vapor surface after solidification. Corrugated features on the surface of an initially dislocation-free silicon crystal were examined by optical microscopy, scanning electron microscopy, energy dispersive x-ray spectroscopy and electron backscatter diffraction. The measured characteristics are compared to criteria for constitutional supercooling and accepted theories for dislocation nucleation.
CRYSTALLOGRAPHIC ORIENTATION OF COLUMNAR ICES FORMED ON MATERIAL SURFACES

Presenting Author: Emily AsenathSmith

Topic: Fundamentals of Crystal Growth

Format: Contributed

Session: 2, 1

Date: 8/4/2021

Time (in MDT): 10:30:00 AM

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The hexagonal lattice of ice is elegantly translated to snowflake forms, revealing the c-axis to be normal to the radial features with six-fold symmetry. Many bulk ices formed in nature exhibit prismatic grains, with pseudo-hexagonal cross-sections, that exhibit a range of length scales; however, the orientation of the c-axis is not always collinear with the axis of six-fold symmetry. Years ago, A.J. Gow discovered that ice which had spontaneously nucleated, in the absence seeding, on lake surfaces was composed of elongated ice grains (S1) which did have the underlying c-axis predominantly oriented along the length of the grains. In contrast, he also observed ice formed on water surfaces that had been seeded by meteorological events favored the formation of columnar S2 ice, wherein the c-axis is oriented perpendicular to the axis of the elongated (pseudo-hexagonal) grains. The versatility of ice covers formed in nature to exhibit columnar microstructures with variable c-axis orientations begs the question of how substrate materials with variable compositions and properties affect the crystallographic orientation of adhered ice laminates. This presentation will report on the crystallographic orientation of columnar ice grown on surfaces by a crystallization-from-the-melt technique. Etching and optical microscopy are used to identify the underlying orientation(s) of the ice lattice within the ice laminates. With a focus on how surface properties affect the orientation of the c-axis within microstructure of the ice laminates, substrate materials with variable roughness, thermal properties, and wettability will be discussed. The results will be presented in the context of ice adhesion and the relevance of ice crystallographic orientation to mechanical and chemical removal techniques associated with ice mitigation.
WHAT DO ALL-ATOM MOLECULAR SIMULATION OF ORGANIC CRYSTAL GROWTH REVEAL?

Presenting Author: Lakshmanji Verma

Topic: Fundamentals of Crystal Growth

Format: Contributed

Session: 2, 2

Date: 8/4/2021

Time (in MDT): 10:45:00 AM

Authors: Lakshmanji Verma, University of Houston, Houston, Texas, United States  Rajshree Chakrabarti, University of Houston, Houston, Texas, United States  Jeremy C. Palmer, University of Houston, Houston, Texas, United States  Peter G. Vekilov, University of Houston, Houston, Texas, United States

Crystallization from solution is ubiquitous. Solvents play a crucial role in the determination of the crystal habit and solvent-surface interactions lead to distinct morphologies for a crystal. During crystallization, solvents structured on the solute as well as growth sites are removed. Therefore, solvent structure and dynamics at the crystal-solvent interface, which depends on crystal-surface interactions, become essential for understanding the growth mechanisms. Experiments have been crucial in understanding the crystal growth from the solution, but the molecular perspective of the fundamental thermodynamics and kinetics which drive these growth mechanisms still evade the community. We employ atomistic molecular dynamic (MD) simulations and advanced sampling techniques to investigate the structure, dynamics, and energetics that determine the growth mechanism of the molecular crystals. We studied the crystallization of organic crystals from the organic solvents which recently attracted a lot of attention to obtain better crystals for pharmaceutical and fine chemicals. We also addressed the growth mechanism of etioporphyrin-I, an organic semiconductor candidate, from pure organic solvents. We found that irrespective of the solvents used the incorporation of the etioporphyrin-I happens in two steps through an intermediate state and this intermediate state is stabilized by the solvent-solute as well as solvent-crystal interaction. The proposed two-step scheme of molecular incorporation presents a new paradigm for solution crystallization that may contribute to understanding crystallization in nature and expedite the selection of solutes and solvents in the crystallization process design of organic pharmaceuticals and advanced materials.
MODELING THE EFFECTS OF OPTICAL ASYMMETRY AND HIGH PRESSURE ON CRYSTAL GROWTH IN AN OPTICAL FLOATING ZONE SYSTEM

Presenting Author: Scott Dossa

Topic: Fundamentals of Crystal Growth

Format: Contributed

Session: 2, 3

Date: 8/4/2021

Time (in MDT): 11:00:00 AM

Authors: Scott S. Dossa, University of Minnesota, Minneapolis, Minnesota, United States

Jeffrey J. Derby, University of Minnesota, Minneapolis, Minnesota, United States

Optical floating zone (OFZ) crystal growth furnaces are powerful tools to grow single-crystal samples of materials that have never before been synthesized, a necessary step in the discovery of new materials with novel properties. However, full utilization of these novel crystal growth systems is hindered by operational challenges brought on by nonlinear, strongly coupled phenomena and a lack of understanding of their underlying physical interactions. Indeed, a skilled operator is often an essential element for the successful growth of a new material in a reasonable time frame. These problems are further compounded by the new generation of high-pressure furnaces.

In this presentation, we focus on single-lamp, two-mirror optical floating zone systems that have been designed to operate under very high pressures, up to 300 bar (such as the HKZ system from Scientific Instruments Dresden, GmbH). Our models demonstrate the strong influence in growth behavior caused by the vertically asymmetric heating profiles with sharp cut-offs that are produced by the optics of the two-mirror configuration. We also investigate the effects of high pressure in the gas/fluid region surrounding the sample. We show how buoyant flows in this region dramatically strengthen with pressure, leading to increased heat transfer from the zone and vertical asymmetry. We discuss the impact of pressure on volatilization from the melt. Additionally, we discuss probable instabilities that arise as these gas/fluid flows become turbulent at very high pressures.
SELF-ASSEMBLY AND CRYSTALLIZATION OF CONJUGATED POLYTHIOPHENES STUDIED BY NONLINEAR OPTICAL LIGHT SCATTERING

Presenting Author: Stijn Van Cleuvenbergen

Topic: Fundamentals of Crystal Growth

Format: Contributed

Session: 2, 4

Date: 8/4/2021

Time (in MDT): 11:15:00 AM


A growing body of research demonstrates that crystallization commonly involves complex nonclassical pathways or transitions through metastable polymorphic states. In our work we use a novel approach based on a combination of second- and third harmonic light scattering to study the internal structure of relevant species in situ. These nonlinear optical light scattering techniques are inherently sensitive to symmetry and ideally suited to probe the structure of molecules, aggregates, and crystals. By combining nonlinear light scattering with standard scattering and electronic spectroscopy, we were able to study the nucleation of a regioregular polythiophene microcrystalline phase, and provide experimental evidence for the role of structured pre-nucleation clusters in the supramolecular organization of these systems. We studied the evolution of the supramolecular organization in different solvent/nonsolvent systems and upon cooling. We found markedly different assembly mechanisms for these different regimes. Moreover we found that the final structure of the assemblies is strongly influenced by the crystallization procedure.

5 Moris, M. et al. Macromolecules 0c01232 (2020)
COARSE-GRAINED MODEL FOR THE HYDROTHERMAL SYNTHESIS OF ZEOLITES

Presenting Author: Debdas Dhabal

Topic: Fundamentals of Crystal Growth

Format: Contributed

Session: 2, 5

Date: 8/4/2021

Time (in MDT): 11:30:00 AM

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Zeolites are crystalline microporous silicates or alumino-silicates extensively used as catalysts, cation exchange membranes, molecular sieves, and in petrochemistry. The synthesis of new zeolites with superior properties is a highly active field. The molecular mechanism of the formation of zeolitic crystals from its amorphous precursors is not yet fully understood. Molecular simulation can play an important role in understanding these processes microscopically but are limited by the lack of models that can represent the different steps and structures associated to hydrothermal synthesis with feasible computational costs. Herein, we present a simple coarse-grained model of zeolite nucleation in presence of water which takes care of the three phase transitions -de-mixing, crystallization and dehydration- that occur in the hydrothermal synthesis of zeolites. Our parameterization is built upon structural and thermodynamic data of common pure-silica zeolites as well as experimental phase behavior observed in hydrothermal zeolite synthesis. The simplified model is able to capture effectively the structural evolution of amorphous precursor to the crystal with homogeneous nucleation occurring inside the intermediate amorphous phase. With the help of this model, we show that zeolites can be crystallized from a spherical amorphous aggregate of size as small as 5 nm. Furthermore, we investigate the effect of zeolite size on their thermodynamics and the results suggests that both freezing and melting temperature decreases with the decrease in the nanoparticle size and follow the Gibbs-Thomson equation quite well. We also probe the role of nanoparticle size, phase (amorphous or crystalline) and temperature on the mechanism and outcome of zeolite growth by oriented attachment process.
A FACETED-ROUGH SURFACE IN A NUCLEATION-LIMITED GROWTH

Presenting Author: Noriko Akutsu

Topic: Fundamentals of Crystal Growth

Format: Poster

Session: ,

Date: 

Time (in MDT):

Authors: Noriko Akutsu, Osaka Electro-Communication University, Neyagawa, Japan

Surface roughness is a key property of the surface to control the growth velocity. When the surface is smooth, it grows in the manner of a two-dimensional nucleation process; whereas when the surface is rough, it grows continuously. At equilibrium, the roughening transitions of surfaces are connected to the faceting transitions on the equilibrium crystal shape (ECS). The ECS is the shape of a crystal droplet with the least surface free-energy at equilibrium. When a surface is smooth, the surface becomes flat to form a facet on the ECS. When a surface is rough, the surface forms a curved area on the ECS. Hence, in the non-equilibrium state, a faceted surface has been considered to be smooth, as well. However, our Monte Carlo study shows that a vicinal surface with faceted macrosteps can have a self-affine-rough structure in nucleation-limited crystal growth (Fig. 1) [1-3]. We call the surface a faceted-rough surface [3]. The faceted-rough surface grows continuously. Therefore, facets on the growing surface at long length scales can no longer be considered evidence that the surface is smooth. In the presentation, we will also show criteria on the length and the time scales for continuous growth. [1] N. Akutsu, <i>Phys. Rev. Mat.</i> 2, 023603 (2018). [2] N. Akutsu, <i>Cryst. Growth and Des.</i> 19, 2970--2978 (2019). [3] N. Akutsu, <i>Sci. Rep.</i> 11, 3711, 1--11 (2021).
ROUGHNESS EXPONENTS AND A SCALING FUNCTION FOR A FACETED-ROUGH SURFACE WITH A MACROSTEP-DISASSEMBLING

**Presenting Author:** Noriko Akutsu

**Topic:** Fundamentals of Crystal Growth

**Format:** Poster

**Session:** ,

**Date:**

**Time (in MDT):**

**Authors:** Noriko Akutsu, Osaka Electro-Communication University, Neyagawa, Japan

In the other presentation titled "A FACETED-ROUGH SURFACE IN A NUCLEATION-LIMITED GROWTH", we showed that a vicinal surface with faceted macrosteps can have a self-affine-rough structure in nucleation-limited crystal growth using the Monte-Carlo method [1]. We call this surface a faceted-rough surface. In this presentation, we will show that the roughening of the faceted-rough surface is connected to the macrostep-disassembling [1-3]. It is known that the faceted macrosteps disassemble to locally merged steps for a larger driving force for crystal growth than a characteristic driving force, the step-disassembling point [2,3]. At less driving force than the step-disassembling point, we found that the variance of the surface height [4] increases as the size of the system increases with provisional roughness exponents being 0.58 ~ 0.78 (Fig. 1 (a)). Around the step-disassembling point, we also found a scaling function for the variance of the surface height (Fig. 1 (b)). Therefore, the provisional roughness exponents converge to the roughness exponent 0.602 in the large system size limit [1].

FERROELECTRIC, PYROELECTRIC AND MECHANICAL PROPERTIES OF TRI-GLYCYNE SULPHO PHOSPHITE (TGSP) SINGLE CRYSTALS

Presenting Author: Senthil Kumar

Topic: Fundamentals of Crystal Growth

Format: Poster

Session: ,

Date:

Time (in MDT):


FERROELECTRIC, PYROELECTRIC AND MECHANICAL PROPERTIES OF TRI-GLYCYNE SULPHO PHOSPHITE (TGSP) SINGLE CRYSTALS


Abstract: Single crystals of triglycine sulpho phosphite were grown by solvent evaporation method using aqueous medium. Triglycine with different ratio of sulphuric and phosphorous acid (1: 0.8 + 0.2, 1:0.5+0.5 & 1:0.2+0.8) were used to grow the crystals in ferroelectric phase. Single crystal and powder X-ray diffraction analyses were carried out for the as grown crystals to understand the structural properties and the crystallinity. Optical properties of the as grown crystals were identified by UV-Visible spectral analysis. Functional groups as well as different vibrational modes present in the crystal were identified by FTIR and Raman spectral analyses. Ferroelectric P-E hysteresis loop was measured in different planes of the crystals to analyse the ferroelectric properties. The determined ferroelectric parameters were used to calculate the pyroelectric co-efficient to reveal the pyroelectric properties of the material. Vickers Micro hardness analysis was made to identify the mechanical properties of material. Defect density and growth mechanism were identified with chemical etching results. Based on the results and analyses, the suitable ratio of the precursors for the crystal was identified towards the device applications. The results were compared with pure, doped and admixture TGS crystals and reason for the enhancement of properties was discussed.
INVESTIGATIONS ON NUCLEATION KINETICS AND DIELECTRIC BEHAVIOR OF POTASSIUM DL-MALATO BORATE HYDRATE (C₈H₁₀BKO₁₁) SINGLE CRYSTAL

Presenting Author: Ezhil Vizhi

Topic: Fundamentals of Crystal Growth

Format: Poster

Session: ,

Date: 

Time (in MDT):

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A transparent single crystal of potassium DL-malato borate was grown with the help of solvent evaporation technique. The lattice parameters, a = 11.3571 Å, b = 5.3225 Å, c = 21.2348 Å and α = β = γ = 90° with Pna2₁ space group of the grown crystal was confirmed by using the single crystal XRD analysis. Solubility and metastable zone width of the compound was measured for various temperature by adopting the gravimetric analysis and polythermal methods. The solubility curve indicates that the material was exhibiting a positive temperature gradient of solubility. The induction period of the grown material was measured with the help of the isothermal method and was found to decrease with increasing the supersaturation ratio and temperature. Various nucleation parameters were calculated with the help of the classical theory of nucleation which was required for optimizing the growth condition for the growth of good quality crystal. The low value of the dielectric loss and constant value for high applied frequency ensure the application of this material in device fabrication. The SHG efficiency of the grown material was measured by Kurtz-Perry method and was found to be 0.85 times that of KDP material, which indicates the NLO application of the grown material.<br />

Keywords: Slow evaporation technique, Nucleation kinetics, single crystal XRD, Dielectric analysis<br />

GA(AS,BI) GA(N,AS) W-TYPE LASER STRUCTURES FOR LONG-WAVELENGTH EMISSION ON GAAS SUBSTRATES

**Presenting Author:** Kerstin Volz

**Topic:** III-V Epitaxial Growth for Devices

**Format:** Invited

**Session:** 2, 1

**Date:** 8/2/2021

**Time (in MDT):** 10:30:00 AM

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Energy efficiency, superior performance, and long-term reliability are crucial advantages of GaAs-based semiconductor laser diodes featuring strained type-I quantum wells as active regions. This class of semiconductor structures provides very good performance in the near-infrared spectral range. Achieving longer wavelength emission on GaAs substrates has proven to be difficult so far. Alloys including N and Bi promise active materials with the possibility to push this accessible emission wavelength range towards the telecommunication bands. The alloys show a drastic decrease of the band-gap energies already for small fractions of the respective elements. However, the strong nonequilibrium nature of such multinary alloys has rendered sufficient incorporation with reasonable material quality impossible so far mandating alternate approaches. Here, we embed a Ga(As,Bi) quantum well (QW) between two Ga(N,As) QWs in a so-called W-type quantum well structure (WQW). This approach has the potential to achieve significant optical gain due to sufficient wave-function overlap, which is much better than for asymmetric type-II quantum wells. In particular, we realize WQWs with emission wavelengths around 1.1 µm, 1.3 µm and 1.5 µm by drastically altering the growth conditions compared to type-I quantum well materials, especially at the interfaces in the structure. We report on the growth challenges of the different interface sequences as well as issues occurring due to the Bi segregation and their solutions. The resulting recipes enable the future growth of tailored WQWs for even longer emission wavelength, e.g., extending into the fingerprint region in the mid-infrared.
Analysis of Interface Roughness in Strained InGaAs/AlInAs QCL Structures (λ~4.6 μM) by Atom Probe Tomography

Presenting Author: Benjamin Knipfer

Topic: III–V Epitaxial Growth for Devices

Format: Contributed

Session: 2, 3

Date: 8/2/2021

Time (in MDT): 11:00:00 AM

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Characterizing the interface roughness (IFR) of the layers comprising the QCL-superlattice (SL) active region is necessary to further optimize device performance and potentially achieve higher wall-plug efficiencies. Recent atom probe tomography (APT) studies [1] have shown the need for compositionally graded models as well as group–III gas flow overshoots in thin wells and barriers to achieve the desired composition and avoid red-shifted emission wavelengths [2]. A typical QCL structure has 30 to 50 stages; each stage containing ~20 interfaces. These interfaces play a direct role in carrier lifetimes. Scattering due to IFR dominates the lower-laser level lifetime and carrier leakage from the upper-laser level in QCLs [3]. Thus, it is a critical parameter that directly impacts the threshold-current density and the slope efficiency. Recent studies have characterized the roughness properties of interfaces via APT for Si/SiGe SL’s [4]. Employing APT, we have analyzed the IFR of strained InGaAs/AlInAs active-region QCLs grown by OMVPE. The individual stages were probed using isoconcentration surfaces between the peak InGaAs-layer composition and peak AlInAs-layer composition to best represent the center of the compositionally graded region. This was done for layers of different aluminum and gallium concentrations across multiple stages. Using a height-height correlation function (HHCF) we were able to extract the amplitudes (Δ) and in-plane correlation lengths (Λ). Our preliminary findings show a large discrepancy in the roughness of interfaces with different peak aluminum concentrations and in turn, strain. The current models for IFR use two parameters for the entire structure, assuming constant roughness. High-power designs employ a step-tapered active region with varying layer compositions. We show the roughness of interfaces varies for different compositions in a full QCL structure, thus more complex models are required to properly account for the impact of IFR scattering on state lifetimes and carrier leakage.

Abstract Book - ACCGE-22//OMVPE-20

HOMOEPITAXIAL GROWTH ON NANOPATTERNED GAAS SUBSTRATES: EFFICIENTLY DEBUGGING DEFECTS USING ELECTRON CHANNELING CONTRAST IMAGING

Presenting Author: John Mangum

Topic: III-V Epitaxial Growth for Devices

Format: Contributed

Session: 2, 4

Date: 8/2/2021

Time (in MDT): 11:15:00 AM

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Nanopatterned substrates provide opportunities for reducing costs of high-efficiency III-V devices by incorporating mechanically weak layers beneficial for substrate reuse. However, devices grown on these nanopatterned substrates must remain comparable to those grown on pristine wafers and not suffer from defects brought on by patterning or coalescence. Electron channeling contrast imaging (ECCI) is a scanning electron microscopy technique ideal for simultaneously observing crystalline defects at high resolution over large areas and quantitatively determining defect densities ranging from 10\(^5\) to 10\(^9\) cm\(^{-2}\). Because ECCI does not require any specific device architectures or sample processing, it can be used to efficiently study crystalline material quality at many points throughout the growth process. In this work, ECCI is used as a vital tool for developing the process of growing high-efficiency III-V solar cells on nanopatterned GaAs substrates. Crystalline defects arise at various stages of epilayer growth starting with initial nucleation, then as neighboring crystalline regions coalesce, and finally during growth of the device structure. By stopping the growth at each of these stages and observing defect formation with ECCI, we can begin to pick apart and understand how each type of defect forms and the proper actions needed to eliminate or mitigate them. Stacking faults were found in material prior to coalescence, indicating a poor initial growth surface and the need for a surface preparation step prior to growth. After lightly etching the nanopatterned substrates in a 1 NH\(_4\)OH : 1 H\(_2\)O\(_2\) : 50 H\(_2\)O solution, stacking faults were no longer observed. Growth of 1 \(\mu\)m thick coalesced epilayers initially produced samples with many macroscale defects spanning the regions grown over nanopatterned areas. However, ECCI revealed that the coalesced material between macroscale imperfections was free from any crystallographic defects such as stackings faults and threading dislocations. With this knowledge, we focused on refining the nanopatterning process to eliminate the macroscale defects. Solar cells were then grown on the optimized nanopatterned substrates and exhibited device structures with defect densities less than 8 x 10\(^5\) cm\(^{-2}\). Device results will be discussed; however, the emphasis of the conference presentation will be on how ECCI guided this process development and can be applied to similar situations.

Considerable attention has been drawn to the design of heterostructures on GaAs substrates emitting at 1.3 µm for replacing InP injection lasers in medium range fiber-optic communication links. Leaving out considerations related to scaling, the enhanced electronic confinement in GaAs-based devices is expected to reduce carrier leakage at high temperatures, thereby overcoming one of the limiting factors associated with InP-based technologies. InGaAs metamorphic buffer heterostructures are an alternative to the conventional routes relying on quantum dots or dilute nitride approaches, all with their own technical challenges and drawbacks. Metamorphic growth techniques provide compositionally graded buffer layers where the dislocations caused by strain relaxation are confined to the graded layers. However, when growing by metal-organic vapour phase epitaxy (MOVPE), achieving ~1.3 µm emission in InGaAs metamorphic quantum well (QW) lasers (on GaAs substrate) has been shown to be extremely challenging due to a variety of growth-related issues. In this contribution we demonstrate a new "recipe" for a working and reproducible laser device emitting at > 1.3 µm, grown by MOVPE on an engineered metamorphic parabolic graded In<sub>x</sub>Ga<sub>1-x</sub>As buffer. We explored and controlled the correlation between epilayer thickness and defect generation and we importantly demonstrated that the limiting factors introduced by surface instabilities during epitaxy can be managed by combining in the cladding layers both AlInGaAs and InGaP alloys in a superlattice (SL) structure. The improved quality of the material was confirmed, for example, by extensive Atomic Force Microscopy (AFM) analyses, showing low roughness (and no direct evidence of defect lines). The compressive strain in QWs and in the metamorphic buffer layer (in combination with the surface step bunched ordering) promoted three dimensional (3D) features formation under certain growth temperatures (T<sub>gr</sub>) and for certain percentages of indium in the QWs. To avoid and control the 3D nanostructuring we proposed the insertion of a GaAs layer deposited before the QW as a possible solution. Moreover, we individuated a range of T<sub>gr</sub> and indium content in the QWs 3D nanostructures that grants defects free growth and achieves the emission of interest. We describe a number of alternative strategies to achieve smooth surface morphology to obtain efficient compressively strained In<sub>0.4</sub>Ga<sub>0.6</sub>As quantum wells in the active layer. The
resulting lasers exhibited low lasing threshold with total slope efficiency of 0.34 W/A for a 500 µm long ridge waveguide device. The emission wavelength is extended as far as 1360 nm.
QUANTUM CASCADE LASER GROWN ON GaAS WITH STRAINED QW-BASED DISLOCATION FILTERS

Presenting Author: Shining Xu

Topic: III-V Epitaxial Growth for Devices

Format: Contributed

Session: 4, 1

Date: 8/2/2021

Time (in MDT): 3:00:00 PM

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Recently, quantum cascade lasers (QCLs) grown on mismatched substrates such as GaAs [1] or Si [2] have been demonstrated only by molecular beam epitaxy. However, the high density of threading dislocations (TDs), originating from a large lattice mismatch, has been a challenging factor limiting the devices’ performances. Thus, understanding the underlying mechanisms behind how TDs affect the performance of unipolar devices such as QCLs needs further investigation. Therefore, the growth of a metamorphic buffer layer (MBL) with a low residual threading-dislocation density (TDD) is essential for realizing high performance devices grown on the mismatched substrates. Here, we report on the characteristics of MOVPE-grown InP buffer layers on GaAs substrates, using In$_{x}$Ga$_{1-x}$As strained QW-based dislocation filters (DFs) with varying In content, that have been employed for achieving a reduced TDD [3]. Furthermore, the impact of strain within these DFs on the subsequently grown full QCL structure will be discussed together with experimental data from <i>in situ</i> reflectance measurement, HR-XRD, atom probe tomography (APT), and device characterization. 6-QW structures employing either InAs or In$_{0.7}$Ga$_{0.3}$As DFs were grown, while utilizing a thermal-cycling approach [3]. An improved root mean square roughness by AFM (~6 vs ~22 Å) as well as a narrower FWHM (206 vs. 401 arcsec) of the (004) InP peak in the XRD rocking curve were obtained from the InP buffer layer grown with the higher strain InAs DFs. The degree of relaxation of the InP buffer layer in both cases was as high as 97%. HR-XRD measurements, as shown in Fig. 1, indicate a degraded peak-to-valley contrast in the superlattice XRD fringes from the sample with In$_{0.7}$Ga$_{0.3}$As DFs, which is correlated to a higher RMS roughness on the InP buffer layer and subsequent roughing during the growth of QCL active region. 20-stage QCL active-region devices, grown on GaAs substrate with InAs dislocation filter, show an EL linewidth of 23meV at 80K. Preliminary APT data analysis, using heigh-height correlation function, shows low RMS roughness on isoconcentration interfaces between InGaAs/AlInAs layers for 20-stage QCL structures grown on InP-buffer with QW-based dislocation filters.

References:
TOWARDS INCREASED INDIUM CONTENT IN\textsubscript{Y}Ga\textsubscript{1-Y}N TEMPLATES FOR USE IN LONG WAVELENGTH IN\textsubscript{X}Ga\textsubscript{1-X}N/GaN DEVICES

**Presenting Author:** Evyn Routh

**Topic:** III-V Epitaxial Growth for Devices

**Format:** Contributed

**Session:** 4, 2

**Date:** 8/2/2021

**Time (in MDT):** 3:15:00 PM

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The InGaN/GaN material system has long been employed for usage in blue LEDs. However, the challenge of shifting InGaN/GaN multiple quantum wells (MQWs) to longer wavelength emitting LEDs, such as red, has proven challenging. In order to reach red emission, the In-content in the active region must be increased; however, with increasing indium content comes a larger lattice mismatch between the well and the underlying GaN, leading to a prominent quantum-confined Stark effect (QCSE). In addition, the low temperatures necessary for higher In-content InGaN results in lower quality material. Our group has shown success in red shifting In\textsubscript{x}Ga\textsubscript{1-x}N/GaN results in lower quality material. Our group has shown success in red shifting In\textsubscript{x}Ga\textsubscript{1-x}N/GaN MQWs grown on GaN by growing them on strain-relaxed In\textsubscript{y}Ga\textsubscript{1-y}N templates using the semibulk (SB) growth approach. A SB template is created by periodically growing 15-25 nm of In\textsubscript{y}Ga\textsubscript{1-y}N, followed by a 1-4 nm GaN interlayer. Using this periodic growth we are able to slowly relax the template and enhance the indium in each successive SB period. We have successfully used this growth technique for device quality templates of y<10%. In this work, we present progress towards templates of y\sim 10-15% grown via metalorganic chemical vapor deposition (MOCVD). The SB templates In-content are quantified via secondary-ion mass-spectrometry (SIMS), photoluminescence (PL), and x-ray diffraction (XRD). In an SB sample, by correlating the PL emission of 432 nm to the XRD, we estimate the In-content to be ~11.5% with relaxation of ~81%. Using atomic force microscopy (AFM), the surface RMS roughness was measured to be approximately 3.6 nm across a (5 μm)\textsuperscript{2} area. Using SIMS, in another SB sample, we observe an indium increase of ~6.1% in the first period to ~13.4% in the topmost SB layer. AFM revealed step-flow growth, and roughness was measured to be approximately 3.57 nm. Using high resolution XRD (HRXRD) rocking curves, we have seen preliminary results of total dislocation density in the upper 10\textsuperscript{8} cm\textsuperscript{-2}. These results show that with an enhancement of In-content of nearly 2% between the two templates, comparable surface morphology can be achieved via the SB growth approach. These templates are used to improve the performance of green and yellow LEDs, as compared to those grown on GaN. In addition, we were able to shift a blue emitting MQW grown on GaN to yellow emission when grown on an SB template with In \sim 12%.
Remote Plasma Chemical Vapour Deposition of III-Nitrides for Laser Diode Applications

Presenting Author: Josh Brown

Topic: III-V Epitaxial Growth for Devices

Format: Invited

Session: 4, 3

Date: 8/2/2021

Time (in MDT): 3:30:00 PM

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InAlGaN-based laser diodes are conventionally produced using metal-organic chemical vapour deposition (MOCVD) - a process that requires high growth temperatures to effectively pyrolyse the NH$_3$. The pyrolysis of the NH$_3$ leads to high concentrations of H in the reactor that form complexes with the Mg impurity used to for p-type doping, requiring post growth activation steps to break the Mg-H complex and remove the hydrogen from the crystal to realise practically low p-type resistivities. These inherent properties of the MOCVD growth process hinder the performance of InAlGaN-based laser diodes and limit the design flexibility. In contrast, Bluglass’s remote plasma chemical vapour deposition technology (RPCVD) relies on a nitrogen plasma rather than NH$_3$ as the source of active nitrogen, and so can operate at lower temperatures with inherently low levels of hydrogen. In this paper we discuss how the unique properties of RPCVD can address some of the fundamental challenges currently limiting InAlGaN-based LD performance through improvements to intrinsic material properties as well as enabling novel design architectures.
A PATHWAY TOWARDS III-NITRIDE SUPERJUNCTIONS

Presenting Author: Dennis Szymanski

Topic: III-V Epitaxial Growth for Devices

Format: Contributed

Session: 4, 5

Date: 8/2/2021

Time (in MDT): 4:00:00 PM

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Current GaN devices show promising results, offering higher breakdown voltages and reduced on resistances compared to their silicon predecessors. However, these devices are still limited by the classical Baliga figure of merit (BFOM). To surpass the BFOM, a novel device geometry, the superjunction (SJ), is introduced (figure below). The concept of the SJ has been demonstrated in silicon, with devices having surpassed the BFOM. To date, there are no demonstrations of III-nitride SJs in the literature. To achieve III-nitride SJs, there are several research barriers to address. First, the necessity for alternating, lateral n- and p-type doping regions with zero net charge. The inherent polar doping selectivity of GaN can be used to achieve the doping scheme for a lateral GaN p/n junction. Oxygen, which unintentionally incorporates into N-polar GaN at levels >10^{19} cm^{-3}, acts as the n-type dopant, whereas Ga-polar GaN does not readily incorporate oxygen. Accordingly, lateral polarity junctions (LPJs) with alternating domains of O doped N-polar and Mg doped Ga-polar GaN have been fabricated to realize lateral p/n junctions. Second, the proper doping profiles must be attained in the N- and Ga-polar domains for SJ operation. For drift regions, the n- and p-type doping in the N- and Ga-polar domains respectively, must be reduced to ~10^{17} cm^{-3} for micron wide domains. By implementing the chemical potential control (CPC) framework, MOCVD process conditions were designed to decrease the oxygen concentration by increasing growth supersaturation. This led to a reduction in oxygen to low 10^{17} cm^{-3}. Third, due to the difficulty of making reliable Schottky contacts to the N-polar surface, the alternating Schottky/ohmic contacts on a typical superjunction are replaced with alternating p<sup>+</sup>/n<sup>-</sup>/p<sup>-</sup> (N-polar) and p<sup>+</sup>/n<sup>-</sup>/p<sup>+</sup> (Ga-polar) junctions (Ga-polar). A N-polar p/n junction with rectifying behavior was achieved. Finally, the growth of GaN LPJs must exhibit a smooth surface and equal domain growth rates. Supersaturation can be used to control the surface morphology, relative growth rates, and defect incorporation of the domains. However, the high supersaturation required for the necessary doping
profile facilitating SJ operation contradicts the intermediate supersaturation conditions required to obtain a smooth surface morphology and equal domain growth rates. To overcome these anticorrelated requirements, we demonstrate a supersaturation modulated growth (SMG), where supersaturation was modulated between low and high values via the V/III. A GaN LPJ with a smooth surface, equal domain heights, and the necessary doping profile is hence demonstrated.
UNIFORMITY IMPROVEMENT OF INGAAS AVALANCHE PHOTODIODES USING OMVPE SELECTIVE AREA GROWTH AND ZN DIFFUSION

Presenting Author: Oliver Pitts

Topic: III-V Epitaxial Growth for Devices

Format: Contributed

Session: 4, 6

Date: 8/2/2021

Time (in MDT): 4:15:00 PM

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Fabrication of InGaAs planar avalanche photodiodes (APDs) commonly involves a single or double Zn diffusion process. Control over the Zn diffusion depth is a strict requirement to improve the device yield and manufacturability. In this work, the contributions of lateral precursor transport to mask edge enhancement of Zn diffusion in an organometallic vapor phase epitaxy (OMVPE) reactor are investigated. The contributions of this phenomenon to device characteristics, including cross wafer variations of the breakdown voltage, and active area photocurrent distribution in planar InGaAs avalanche photodiodes (APDs), are studied using current-voltage (I-V) curves and raster-scanned photocurrent maps. The Zn diffusion depth distribution is studied by cross-sectional and plan-view scanning electron microscopy (SEM) in combination with a selective etching technique, and compared with OMVPE Selective Area Growth (SAG) topography obtained on the same mask patterns. Additionally, numerical device simulation is employed to estimate the relative magnitude of the contributions of the junction curvature effect and junction depth enhancement at the mask edge to the photocurrent distribution. The simulation results suggest that under the conditions observed in the fabricated devices the mask edge enhancement of the Zn diffusion depth is the dominant contributor to the photocurrent non-uniformity. Further evidence supporting this conclusion is obtained from maps of the breakdown voltage across the wafer showing a distinct shift in the vicinity of features with a large masked area. Finally, an effective mitigation measure is discussed, in which a SAG growth step is used to deposit a film of varying thickness prior to the Zn diffusion. This introduces a compensating shift in the Zn diffusion depth and resulting breakdown voltage which was previously shown to improve individual device photo-response uniformity of APDs [1,2]. In this work, it is shown that in addition, by balancing the opposing shifts of the diffusion depth, this technique can improve the device-to-device breakdown voltage uniformity across the wafer. [1] O. J. Pitts, M. Hisko, W. Benyon, G. Bonneville, C. Storey, A. J. SpringThorpe, “Planar avalanche photodiodes with edge breakdown suppression using a novel selective area growth based process,” J. Cryst. Growth, vol. 470, pp. 149-153, July 2017.[2] O. Salehzadeh, G. Bonneville, O.J. Pitts, M. Hisko, A.J. SpringThorpe, "Edge Breakdown Suppression of Avalanche Photodiodes Using Zn Diffusion and Selective Area Growth", IEEE Photonics Technology Letters 31 (2019) 767-770
GROWTH AND ACOUSTO-OPTIC STUDY OF BPO<sub>4</sub> CRYSTALS

Presenting Author: Maksim Artyusenko

Topic: III-V Epitaxial Growth for Devices

Format: Poster

Session: ,

Date: 

Time (in MDT):

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Today, there are only few crystals which are perspective or have already used for manufacturing of acousto-optic modulators. The search for new acousto-optic crystals is a complex and actual task. The desired material must have a high coefficient of acousto-optical quality M2, have high optical, chemical and physical characteristics, as well as good processability of production and processing. According to the literature data, BPO<sub>4</sub> has a high laser damage threshold of 10.3 GW / cm<sup>2</sup> [1], and a high optical uniformity of 1.6×10<sup>-5</sup>/cm [2], suitable mechanical properties, and good thermal conductivity. The complex of these properties indicates the potential application of this material in acusto-optics. BPO<sub>4</sub> single crystals were obtained using a modified TSSG method [2], under conditions of low temperature gradients of no more than 1 K/cm. The growth composition was a mixture of BPO<sub>4</sub>-Li<sub>3</sub>PO<sub>4</sub>-MoO<sub>3</sub>, taken in a molar ratio of 1.6-0.7-1.3. The growth was carried out in [101] direction. To measure the propagation velocity and attenuation of elastic waves in a crystal, a standard echo-pulse method was used, supplemented by two-pulse modulation of a high-frequency signal. Based on the obtained data, the acousto-optic quality coefficient M2 was calculated.<br />


EFFECT OF V/III RATIO AND GROWTH PRESSURE ON SURFACE AND CRYSTAL QUALITY OF ALN GROWN ON SAPPHIRE BY MOCVD

Presenting Author: Isabel Streicher

Topic: III-V Epitaxial Growth for Devices

Format: Poster

Session: ,

Date:

Time (in MDT):

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High quality AlN on sapphire plays a key role in the commercialization of III-nitride devices such as UV-Photodetectors and LEDs. Large lattice and thermal mismatch between AlN and sapphire as well as low Al adatom mobility cause a high dislocation density and poor surface morphology. We investigated the effect of V/III ratio, pressure and multi growth mode on the surface morphology and crystal quality of 500 nm thick films grown on c-plane sapphire substrates by metal-organic chemical vapour deposition (MOCVD). The growth temperature was fixed at 1130°C. The sapphire substrate surface was preconditioned with a short preflow of TMAI. The absence of preconditioning, long ammonia or long TMAI preflow caused 3D growth, incomplete coalescence and thus high surface roughness. A 50 nm thick AlN nucleation layer was grown at 880 °C with a very low V/III ratio for all samples. From low V/III (139) to high V/III (3842) step-flow growth mode was observed. The sample surfaces displayed defined monolayer steps (figure 1 (a)-(d)). At low V/III large pits appeared in the AlN layer. A minimum in surface mean square roughness of 0.15 nm was observed at a V/III of 2561 beyond which the surface roughness increased again. A very high V/III led to a layer roughening. Crystal quality was evaluated by HRXRD omega-scans of the 00.2 and 10.2 reflections. The FWHM of 00.2 reflections improved with increasing V/III indicating a decrease in screw or mixed dislocation density. Also the FWHM of the 10.2 reflection improved, which is due to a decrease in tilt and twist caused by screw, edge and mixed dislocations. Multi growth mode technique (i.e. alternating 2D and 3D growth modes) did not improve crystal quality or surface roughness further. Increasing the growth pressure from 50 to 95 mbar for a fixed multi growth mode structure led to a decrease in FWHM of 00.2 and 10.2. Thereby a transition from step-flow to step-bunched growth mode was observed in figure 1 (e)-(h). We propose that low pressure suppressed the diffusion of Al adatoms leading to step-flow growth while high pressure promoted it resulting in step-bunching, increasing the roughness of the layer. Best crystal quality was obtained at a growth pressure of 95 mbar and optimum surface roughness with a V/III of 2561 at 50 mbar growth pressure.

Figure 1 AFM images of AlN grown on c-plane sapphire at different (a)-(d) V/III ratios and (e)-(h) pressures.
III-NITRIDE BASED LED AND LASER DIODE

Presenting Author: Shuji Nakamura

Topic: III-V Wide Bandgap Nitride Semiconductors and Devices

Format: Plenary

Session: 1, 1

Date: 8/2/2021

Time (in MDT): 8:30:00 AM

Authors: Shuji Nakamura, University of California Santa Barbara, Santa Barbara, California, United States

As next generation displays, micron-sized light-emitting diode (µLED) displays have been researched intensively with advantages of higher wall-plug efficiency and wider color gamut compared to conventional liquid crystal displays (LCDs) and organic LED (OLED) displays. Currently, mini LED displays with a chip size of more than 100 µm are commercially available in spite of huge costs caused by a large chip size. For blue and green LEDs, InGaN-based LEDs are used, while for red, AlInGaP-based LEDs are currently used. In order to reduce the cost of µLED displays and to open a market for the application of small displays such as smart phones and AR/VR displays, each chip size has to be reduced to a micron size. When the size of µLEDs becomes small (especially smaller than 40 µm), the EQE decreases dramatically. This decrease is due to surface recombination and the sidewall damage of the mesa from the plasma-assisted dry etching, which contribute to increased Shockley-Read-Hall non-radiative recombination at small dimensions. Potassium hydroxide (KOH) has been used to improve the electrical performance of GaN based devices by removing the plasma-damaged material on the device side walls. However, there are several issues with the conventional µLEDs, such as color mixing, color purity, emission directionality, and thermal and color stability. Those problems of µLEDs could be addressed by using single mode emission InGaN-based blue, green and red microcavity light-emitting diodes (MC-LEDs). These MC-LEDs have advantages of thermal stability and spectral purity since the spectral width and shape are determined by the overlap of the InGaN quantum well (QW) emission and the cavity mode. In addition, the emission of MC-LEDs is more directional than conventional LEDs. These advantages suggest MC-LEDs could be the best fit for display applications.
SINGLE CRYSTAL ALN 2-INCH SUBSTRATES WITH SPATIALLY UNIFORM 265 NM ABSORPTION COEFFICIENTS BELOW 20 CM\(^{-1}\)

**Presenting Author:** Rafael Dalmau

**Topic:** III-V Wide Bandgap Nitride Semiconductors and Devices

**Format:** Invited

**Session:** 1, 1

**Date:** 8/4/2021

**Time (in MDT):** 8:30:00 AM

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There is an urgent demand for solid state light sources emitting at ultraviolet-C (UV-C) wavelengths (100-280 nm) for germicidal applications. UV-C emitters based on the AlGaN alloy system were developed in recent years for pathogen disinfection in areas such as water treatment. The COVID-19 pandemic has increased demand for UV-C disinfection of air systems and surfaces as well, applications where compact, efficient light emitting diodes (LEDs) are well suited, and where use of existing germicidal light sources based on mercury lamps are complicated by concerns about the use of toxic mercury. Already, LEDs based on AlGaN alloys have proven effective for inactivating the SARS-CoV-2 virus responsible for the COVID-19 pandemic. Since the performance of UV-C LEDs is negatively impacted by the presence of threading dislocations in the device active layers, methods for reducing these defects are being pursued. Growth on high-quality native substrates, where the lattice and thermal mismatches to the epitaxial layers are low, are a means of reducing the density of threading dislocations by several orders of magnitude compared to commonly used substrates such as sapphire and SiC. AlN single crystals grown by physical vapor transport (PVT) are characterized by high thermal conductivity and a low lattice mismatch to high Al composition AlGaN alloys, making them an excellent choice for growth of UV-C LEDs emitting in the 260-280 nm range. We have demonstrated 2-inch AlN substrates with average threading dislocation densities below 10\(<sup>3</sup>\) cm\(<sup>-2</sup>\). However, an unwanted absorption band around 265 nm, associated with the carbon impurity, was identified in AlN grown by PVT in carbon-containing atmospheres. Reduction of this absorption band is critical to improving performance in LEDs requiring light extraction through the substrate. In this work, we prepared 2-inch, double-side polished, c-plane AlN substrates. The structural perfection of these substrates was assessed by x-ray diffraction methods, including rocking curve analysis, x-ray topography, and reciprocal space mapping. The optical properties were studied at multiple points by transmittance and reflectance spectroscopy in the 250-400 nm range. Absorption coefficients were calculated by accurately accounting for reflection losses. Spatially uniform absorption coefficients below 20 cm\(<sup>-1</sup>\) at 265 nm were demonstrated. Structural and optical characterization of UV-C transparent, 2-inch AlN substrates will be presented.
ADVANCES IN ION IMPLANTATION OF GAN AND ALN

Presenting Author: James Tweedie

Topic: III-V Wide Bandgap Nitride Semiconductors and Devices

Format: Invited

Session: 1, 3

Date: 8/4/2021

Time (in MDT): 9:00:00 AM


Ion implantation is a basic tool for semiconductor device fabrication and ideally it should be available in any mature semiconductor system. III-nitrides do not possess a robust ion implantation toolbox that allows for reliable implantation control and activation, thus limiting the development of many advanced device architectures comparable to those in SiC. The opportunity is clear for III-nitrides for power applications, where the need for proper field managing schemes require spatially distributed doping distributions that can be achieved by ion implantation. Recent advances in ion implantation for the realization n-type AlN and p-type GaN will be discussed. AlN is considered for deep-UV optoelectronics and next generation high power devices due to its ultra wide bandgap. Achieving high conductivity in n-type AlN is still a major challenge due to self-compensation via DX and vacancy complex formation at equilibrium. This has made it necessary to consider other non-equilibrium based doping methods, such as ion implantation. In this work, doping AlN by Si implantation is considered. Although high-temperature post-implantation annealing is necessary for damage removal and activation, point defect control is required during the anneal to inhibit the formation of the vacancy-silicon complex, a compensator. We demonstrate defect quasi Fermi level (dQFL) control to reduce compensating point defects in Si-implanted AlN to achieve high n-type conductivity in AlN. GaN-based high power switches are a promising avenue towards realizing advances in power management. Controlling the selective area doping of both n- and p-type regions is necessary to realize these device structures. Although high carrier concentrations and conductivities in GaN have been reproducibly demonstrated, achieving high p-type conductivity after ion implantation remains a challenge. To prevent the surface decomposition during annealing at these elevated temperatures required for post-implantation anneals, previous efforts have focused on the use of capping layers (e.g. AlN) and/or complicated annealing procedures. In this work we demonstrate the ability to successfully...
achieve p-type conductivity in GaN films via room temperature Mg implantation and a post-implantation annealing procedure at high pressure (1 GPa) that prevents GaN decomposition without the need of a capping layer. We consider the results within the framework of a diffusion budget, which relates the electrical properties of Mg-implanted GaN to both the dopant diffusion and lattice damage recovery determined by activation annealing conditions. All these results support the possibility of realizing successful ion implantation in III-nitrides adding to the growing toolbox of capabilities for this technology.
FLEXIBLE SINGLE-CRYSTALLINE III-N THIN FILMS FOR PHYSICAL SENSORS OF PERSONAL HEALTHCARE AND SAFETY MONITORING AND MEDICAL DIAGNOSIS

Presenting Author: Nam-In Kim

Topic: III-V Wide Bandgap Nitride Semiconductors and Devices

Format: Contributed

Session: 1, 5

Date: 8/4/2021

Time (in MDT): 9:30:00 AM

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Wearable sensors are increasingly important in healthcare monitoring applications. In particular, skin-attachable sensors on human skin can effectively track the change of several physical parameters. Among them, the continuous monitoring of pulse wave velocity is very important to high-risk groups with cardiovascular diseases. Sensing of eyelid and eyeball movement is another new application. Brain disorders (e.g. Alzheimer’s, Parkinson’s disease, autism, stroke and attention deficit hyperactivity disorder (ADHD)) can involve abnormal motions from eye as early stage symptoms, such as slow movements and the long interval between eye blinking. The disorders can be diagnosed by detecting the peculiar eye movements in the early stages. For both applications, the sensors need to be highly flexible to be conformal on human bodies. Also, they are preferred to be lightweight and small size to attach on the skin of human body for comfortable and non-invasive wearing, e.g. temple area. Recently reported sensor systems based on lead zirconate titanate (PZT) and zinc oxide (ZnO) intrinsically possess shortcomings for the wearable devices. The PZT- and ZnO-based sensors show skin-poisoning problem and low performance issue, respectively. Alternatively, III-N thin films are very promising to detect the physical motion of skin sensing due to their advantages of high sensitivity and durability, rapid response time, non-toxic nature on humans, lightweight, and low power consumption. Especially, single-crystalline gallium nitride (GaN) aluminum-gallium nitride (AlGaN) and aluminum nitride (AlN) piezoelectric thin films have been reported to show excellent performances by a high electromechanical coupling factor, chemical and mechanical long-term stability, high thermal resistance, and excellent biocompatibility. In this study, we developed and demonstrated skin-attachable III-N based sensors for the detection of eyelid motion and eyeball movements on temple area. Flexible III-N thin films were designed by layer transfer method from the rigid silicon substrate. They were analyzed by X-ray diffraction to confirm its single-crystalline quality. The single sensor was firstly applied to the human face for sensing of eye-related motions. Then, the multiple sensors were utilized with a moderate distance on the identical region to detect the transverse, longitudinal, diagonal, and rotational eyeball motions, which can detect the abnormal eye movements. All the results from each sensor are distinguishable, which indicates that the sensors generated different values of output signals from each position with varied stimulates.
STRESS EVOLUTION IN THICK GAN LAYERS GROWN BY HVPE

Presenting Author: Gleb Lukin

Topic: III-V Wide Bandgap Nitride Semiconductors and Devices

Format: Contributed

Session: 1, 6

Date: 8/4/2021

Time (in MDT): 9:45:00 AM

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For the production of freestanding GaN wafers there are in principle two different approaches. On the one hand, the development of a single wafer process where a GaN layer of some hundreds of microns is removed from the seed producing a single GaN wafer as a result. On the other hand, the slicing of a bulk crystal of several millimeter thickness, which results in a charge of several freestanding wafers form one boule. However, growing a thick crystal by the Hydride Vapor Phase Epitaxy (HVPE) on a foreign seed results in a large internal stress in the crystal, leading to breakage and cracks during growth or upon cooling down from the growth temperature. In order to minimize the residual stress we observed the bowing behavior of the growing thick layer or crystal in situ. This contribution shows the evolution of internal stress in thick GaN layers grown by an HVPE process. The long-time in-situ thickness and bow measurements were performed during the deposition of 3-inch HVPE crystals by using a novel interferometric curvature measurement system. For the analysis of the obtained in-situ bow curves, we applied an analytical elastic model of a two-layer system developed by Etzkorn and Clarke. The comparison of the calculated and the experimental bow curves shows the evidence of the intrinsic tensile growth strain increasing with the layers thickness. As this pure thermomechanical model is not sufficient, we introduced an additional component to the model describing the action of dislocations. An in-plane component of the threading dislocations in GaN layers, which is always available due to their deviation from the growth direction, can act as a misfit dislocation contributing to an increasing tensile strain in the grown material. Using the threading dislocation density of the grown samples measured by means of etch pit density and cathodoluminescence dark spot counting, we can show that the inclination of threading dislocations is probably a root cause for the increasing growth strain during the HVPE growth. Another option for the development of an intrinsic strain during the growth would be the incorporation of large amounts of point defects, which is often discussed. Based on the available theoretical studies of impurities in GaN, we find that the impact of point defects on the lattice deformation seems to play a minor role for the appearance of tensile growth stress, at least for typical impurity concentrations in the HVPE environment.
DEFECT SPECTROSCOPY AND REDUCED COMPENSATION OF UV ILLUMINATED MOCVD N-TYPE GaN

Presenting Author: Anthony Rice

Topic: III-V Wide Bandgap Nitride Semiconductors and Devices

Format: Invited

Session: 2, 1

Date: 8/4/2021

Time (in MDT): 10:30:00 AM

Authors: Anthony Rice, Sandia National Labs, Albuquerque, New Mexico, United States  Mary H. Crawford, Sandia National Labs, Albuquerque, New Mexico, United States  Andrew Armstrong, Sandia National Labs, Albuquerque, New Mexico, United States  Andrew A. Allerman, Sandia National Labs, Albuquerque, New Mexico, United States  Normand A. Modine, Sandia National Labs, Albuquerque, New Mexico, United States

The C_{N} impurity acts as an acceptor-like trap in n-type GaN and presents a challenge for control of doping when low free electron concentration, n, is desired. n-type doping causes the Fermi level to shift towards the conduction band, and the formation energy of compensating acceptor-like defects decreases by an amount proportional to the defect charge and the magnitude of the dopant-driven shift away from the equilibrium Fermi level. The creation of electron-hole pairs by above-bandgap illumination in n-type GaN causes the quasi-Fermi level of holes to shift away from the conduction band, thereby increasing C_{N} formation energy. Through the combination of capacitance-voltage, Hall effect, and deep level optical spectroscopy (DLOS) measurements, we have confirmed the impact of UV illumination on carbon-related defect concentrations in n-type GaN.

GaN films were deposited by metal-organic chemical vapor deposition (MOCVD) on sapphire and GaN substrates using NH_{3}, TMGa, and SiH_{4} as precursors and illumination was produced by a 1 kW HgXe lamp. Impurity concentrations were measured by secondary ion mass spectroscopy with [C] being varied in each sample by changing deposition temperature, and [Si] being varied by SiH_{4} flow. No differences in deposition rate, crystallinity, surface morphology, or impurity concentrations (including carbon) were observed for GaN deposited with and without UV but otherwise identical conditions. For GaN films doped with [Si] = 5x10^{16} cm^{-3} <sup>16</sup> cm<sup>-3</sup>, [C] between 1-3x10^{16} cm<sup>-3</sup>, n was greater for GaN deposited with UV with the difference being proportional to 1.4 times [C], providing a link between UV illumination and reduced carbon compensation. Without UV, mobility decreased from 643 to 82 cm<sup>2</sup>/Vs with increasing [C]. In contrast, UV during deposition mitigated this mobility reduction, only decreasing from 638 to 545 cm<sup>2</sup>/Vs for samples covering the same range of [C]. DLOS shows decreased densities of acceptor-like defect levels below the conduction band at E_{c} - 3.0 eV and E_{c} - 3.28 eV for GaN deposited with UV. Defect reduction was more pronounced for GaN with greater [C] and was up to ~2x10^{16} cm<sup>-3</sup> for GaN with [C] ~2.5x10^{16} cm<sup>-3</sup>. For GaN doped with [Si] between 1-4x10^{16} cm<sup>-3</sup>, [C] = 1x10^{16} cm<sup>-3</sup>, n was uniformly greater for GaN deposited with UV by ~1x10^{16} cm<sup>-3</sup>. Our results demonstrate that UV illumination during MOCVD provides a method to reduce the detrimental compensating effects of
carbon in n-type GaN.<br />

SNL is managed and operated by NTESS under DOE NNSA contract DE-NA0003525<br />

SAND2021-4000 A
DIRECT EVIDENCE OF SINGLE ELECTRON OCCUPANCY FOR GE INSTEAD OF DX<sup>-1</sup>IN AL RICH ALGAN

**Presenting Author:** Pegah Bagheri

**Topic:** III-V Wide Bandgap Nitride Semiconductors and Devices

**Format:** Contributed

**Session:** 2, 3

**Date:** 8/4/2021

**Time (in MDT):** 11:00:00 AM

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Controllable n-type doping in AlGaN and AlN is one the building blocks for realization of all the applications in optoelectronics and power electronics. Si and recently Ge have been utilized as n-type dopants in Al<sub>x</sub>Ga<sub>1-x</sub>N with low ionization energy for x<0.8 and x<0.5, respectively. However, Si and Ge transition from the shallow donors to the deep states presenting challenges for novel applications employing Al rich AlGaN and AlN. While such a transition was previously observed in the AlGaAs system and confirmed to be an acceptor type DX<sup>-1</sup>. However, no such direct proof of the Si and Ge charge states in Al rich AlGaN and AlN exists. In this work we present direct evidence of single electron occupancy in the Ge deep state in Al<sub>x</sub>Ga<sub>1-x</sub>N (x>0.5). Co-doping with the shallow donor Si (at x < 0.8) was used as a source of free electrons in Ge doped AlGaN grown via MOCVD to follow on the charge state of Ge. The measured carrier concentration (n) in Al rich AlGaN shows whether Ge is a shallow donor (n~[Si]+[Ge]), neutral deep donor (n~[Si]) or a compensating acceptor type DX<sup>-1</sup> (n~[Si]-[Ge]). An increase in the ionization energy of Ge: AlGaN with increase in Al content was shown to occur at x>0.5. Si remained a shallow donor up to x~0.8. Possible electron compensation in Si and Ge codoped Al<sub>x</sub>Ga<sub>1-x</sub>N where Ge transitions into a deep state, would directly show the charge state of Ge, either D<sup>-1</sup> or DX<sup>-1</sup>. Carrier concentration measurements versus Al content under constant Si and Ge concentrations of 1×10<sup>19</sup> and 8×10<sup>18</sup> cm<sup>-3</sup>, respectively, were realized at RT and 600°C. Negligible compensation and a temperature independent carrier concentration are observed in Al<sub>x</sub>Ga<sub>1-x</sub>N where both Ge and Si are in their shallow states. Interestingly, a reduction in carrier concentration at x~0.65 corresponding only to the Ge concentration was observed, indicating that Ge is not providing free electrons nor compensating the free electrons provided by Si.
This is the signature of a deep donor and not of an acceptor state. Contrary to the formation of a stable DX\(-1\), which is expected to pin the Fermi level at the \((-+/+)\) thermodynamic transition, transition to a deep donor allows for the possibility of highly conducting AlN by degenerately doping the system. Hence, this work cast light on the true nature of donor related deep states in nitrides and pathways for highly conductive Al rich AlGaN.
COMPUTATIONAL STUDY OF FREE CARRIER COMPENSATION FROM POINT DEFECTS IN SI AND GE DOPED AL-RICH ALGAN

Presenting Author: Kelsey Mirrielees

Topic: III-V Wide Bandgap Nitride Semiconductors and Devices

Format: Contributed

Session: 2, 4

Date: 8/4/2021

Time (in MDT): 11:15:00 AM

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In AlN, GaN, and AlGaN, point defects control important properties such as free carrier concentration. Compensating defects are substantially responsible for depletion of free carriers introduced through doping; understanding both intentional and unintentional defect behavior is useful for achieving desired results. A major benefit of point defect research with density functional theory (DFT) simulations is the ability to study each potential defect individually. However, predictive modeling of point defects with this method is challenging due to the multitude of defects which must be considered in AlN and GaN, especially when including multi-member complexes which require simulating multiple configurations.<sup>1,2,3</sup> In AlGaN, explicit point defect simulations can quickly get out of hand due to the random occupation of Al and Ga on cation sites. This drastically increases the number of possible configurations making explicit point defect simulations in AlGaN unfeasible, especially when considering multiple AlGaN compositions. In this work, we propose an interpolation scheme for studying point defect behavior in AlGaN which utilizes extensive point defect DFT simulations with hybrid functionals in AlN and GaN, managed with the asphalt point defect simulation informatics suite.<sup>3,4</sup> Further, we use a grand canonical thermodynamics ensemble with appropriate chemical potentials to predict point defect populations and free carrier concentrations in multiple AlGaN compositions, focusing on compensating defects in Si and Ge doped Al-rich AlGaN. We find that compensating multi-donor complexes are prevalent in every AlGaN composition considered, however the onset doping concentration at which they occur becomes lower with increasing Al content. Other compensating defects, such as Si and Ge DX configurations, are also considered and have been found to contribute to compensation in low doping regimes.<br />References:<sup>1</sup>Harris, Joshua S., et al. "On compensation in Si-doped AlN." Applied Physics Letters 112.15 (2018): 152101.<sup>2</sup>Baker, Jonathon N., et al. "Complexes and compensation in degenerately donor doped GaN." Applied Physics Letters 117.10 (2020): 102109.<sup>3</sup>Baker, Jonathon N., et al. "An informatics software stack for point defect-derived opto-electronic properties: the Asphalt Project." MRS Communications 9.3 (2019): 839-845.<sup>4</sup>Mirrielees, Kelsey J., et al. "Computational approaches to point defect simulations for semiconductor solid solution alloys." The Journal of Chemical Physics 154.9 (2021): 094705.
APPLICATION OF SYNCHROTRON X-RAY TOPOGRAPHY TO CHARACTERIZATION OF SELECTIVE AREA DOPING PROCESSES FOR THE DEVELOPMENT OF VERTICAL GAN POWER DEVICES

Presenting Author: Balaji Raghothamachar

Topic: III-V Wide Bandgap Nitride Semiconductors and Devices

Format: Invited

Session: 2, 5

Date: 8/4/2021

Time (in MDT): 11:30:00 AM

Authors: Balaji Raghothamachar, Stony Brook University, Stony Brook, New York, United States

Selective area p-type doping of GaN is required for the development of vertical GaN devices that will help realize the potential of WBG semiconductor GaN in power electronics. Under the auspices of the ARPA-E PNDIODES program, approaches being investigated include implantation followed by activation annealing by different methods, selected area etching and regrowth of p-type regions, diffusion doping and neutron transmutation. Analysis and characterization of the relationship between processing and defect structures in these selectively doped p-n junctions is required to fully understand and overcome the limitations of these doping processes. We have applied synchrotron X-ray topography (white beam and monochromatic) as well as rocking curve topography to systematically analyze changes in microstructure due to processing. High resolution X-ray diffraction is also employed to provide quantitative information on the change in microstructure. First an overview of bulk GaN substrates available for selective area doping is presented. The choice of bulk GaN substrates plays an important role in the eventual extended defect configurations in the active layers. Ammonothermal-grown GaN substrate wafers show the best quality among all the wafers. These wafers, which are free of basal plane dislocations (BPDs), have low curvature and threading mixed dislocations (TMDs) dominant among the threading dislocations (TDs). Patterned HVPE GaN reveal a starkly heterogeneous distribution of dislocations with large areas containing low threading dislocation densities in between a grid of strain centers with higher threading dislocation densities and BPDs. The strain level of HVPE GaN substrates is very high, and the dislocation density is around $10^{5} - 10^{6}$ cm$^{-2}$, which is much higher than $10^{4}$ cm$^{-2}$ of ammonothermal samples and dislocation-free areas in the patterned HVPE samples. During epitaxial growth by CVD for implantation purposes, defects in substrates are shown to replicate into the epilayer and typically no new defects are observed to be introduced at the interface. On implantation, damaged layers are generated in the epilayer with the radiation fluence and energy determining the extent of damage. Depending on annealing conditions most of the damage is healed. However, the annealing temperatures greater than 1100°C can result in introduction of inhomogeneous strains and dislocation generation. While etching by TBCl is shown to be sensitive to certain types of threading dislocations, any thermal treatment is shown to introduce basal plane dislocations. Results will be discussed with implications for vertical device fabrication and expected impact on device performance.
NANOSCALE GAN VACUUM ELECTRONICS OPERATING IN AIR

Presenting Author: George Wang

Topic: III-V Wide Bandgap Nitride Semiconductors and Devices

Format: Contributed

Session: 3, 1

Date: 8/4/2021

Time (in MDT): 1:00:00 PM

Authors: George T. Wang, Keshab R. Sapkota, A. Alec Talin, Barbara A. Kazanowska, Brendan P. Gunning, Francois Leonard, Kevin S. Jones, Sandia National Laboratories, Albuquerque, New Mexico, United States


Solid-state, vacuum nanoelectronic devices have the potential to combine the advantages of vacuum electron devices (e.g. vacuum tubes), such as robustness in harsh environments and high frequency operation, together with those of solid-state devices, such as size, integrability, and low-power operation. By shrinking the vacuum channel to nanoscale dimensions well below the electron mean free path in air, these devices may also be operable at ambient pressures while maintaining the physical advantages of vacuum transport, thus potentially mitigating the need for vacuum packaging. We propose GaN as a superior materials platform compared to silicon or metals for solid-state, nanogap field emission devices based on its lower electron affinity, higher chemical stability, high breakdown voltage, and radiation hardness. In this work, we demonstrate novel GaN nanogap field emission diodes that exhibit ultra-low turn-on voltage down to ~0.25V, high field emission currents measured up to 10 µA for single emitters, and excellent on-off ratio. We present experimental and modeling results on the field emission characteristics of these devices at various nanogap sizes under 100 nm and operating pressures over an eight orders of magnitude pressure range. We also present preliminary results on the fabrication and performance of gated, lateral GaN vacuum nanogap transistors. These results provide critical new insights into the behavior of this new class of devices and point to future challenges and opportunities.
UNIFORM 6 x 6 GAN P-I-N ULTRAVIOLET AVALANCHE PHOTODIODE ARRAYS GROWN BY MOCVD ON GAN BULK SUBSTRATES

Presenting Author: Russell Dupuis

Topic: III-V Wide Bandgap Nitride Semiconductors and Devices

Format: Contributed

Session: 3, 2

Date: 8/4/2021

Time (in MDT): 1:15:00 PM

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High Resolution Single-Crystal CVD Diamond Radiation Detector: Defect studies and noise analysis

Presenting Author: Sandeep Chaudhuri

Topic: III-V Wide Bandgap Nitride Semiconductors and Devices

Format: Contributed

Session: 3, 3

Date: 8/4/2021

Time (in MDT): 1:30:00 PM

Authors: Sandeep K. Chaudhuri1, Joshua W. Kleppinger1, OmerFaruk Karadavut1 and Krishna C. Mandal1*

High resolution diamond detectors for ionizing radiation have been fabricated using chemical vapor deposition (CVD) grown 500 μm thick single crystalline (SC) electronic grade diamonds. The unannealed Ti/Pt/Au stacked metal contacts, deposited on the diamond surface, exhibited Ohmic-like symmetric current-voltage (I-V) curves with respect to bias polarity except at lower bias voltages. The detectors did not show any sign of polarization for a prolonged period of observation and exhibited very high energy resolution of 0.5% (26.77 keV) for 5486 keV alpha particles emitted by a 241Am alpha source at a very low optimized operating bias voltage of +120 V (hole transit). A similar resolution was obtained for electron transits as well, albeit at a higher bias of -350 V. All the three primary alpha energies emitted by the alpha source were resolved in the pulse height spectra including the 5389 keV which has a percentage emission rate of only 1%. Biparametric correlation studies indicated that electron trapping is predominant at lower operating bias voltage which account for the behavioral difference of the device with respect to bias polarity. Current transient spectroscopic studies revealed that a previously unreported defect level, situated 2.2 eV below the conduction band edge, might be responsible for the observed disparity between electron and hole transport.
RED SHIFTING BLUE LEDs EMISSION FROM BLUE TO YELLOW USING RELAXED INGAN TEMPLATES

Presenting Author: Mostafa Abdelhamid

Topic: III-V Wide Bandgap Nitride Semiconductors and Devices

Format: Contributed

Session: 3, 4

Date: 8/4/2021

Time (in MDT): 1:45:00 PM

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Long wavelength emission from InGaN based light emitting diodes (LEDs) is typically hindered by reduction in external quantum efficiency (EQE) as the indium content ($i>x<i$) is increased in the multiple quantum wells (MQWs) to achieve emission beyond the green part of the visible spectrum. This drop in efficiency can be attributed to the low growth temperature required for high indium content in the MQWs, and to the large lattice mismatch between the InGaN QWs and the underlying GaN template. The low temperature results in poor film quality while the lattice mismatch leads to a compressive strain in the QWs which induces a strong piezoelectric field which reduces the device performance because of the quantum confined stark effect (QCSE).

For improved long wavelength emission, a desired approach is to reduce the strain in the QWs, and to increase their growth temperature. Growing the QWs on relaxed InGaN templates can achieve both as the smaller lattice mismatch reduces the strain in the QWs and leads to an increased indium incorporation because of the lattice pulling effect, which allows for higher growth temperatures and better film quality. Our group has successfully demonstrated device quality highly relaxed InGaN templates using the semibulk (SB) approach grown by MOCVD. The technique relies on growing 20-30 periods of (InGaN/GaN) with thicknesses of ~(20nm/2nm) for each period, respectively. Different techniques were used to characterize the InGaN templates, such as photoluminescence (PL), secondary ion mass spectrometry (SIMS), atomic force microscopy (AFM), High resolution X-ray diffraction (HRXRD), and transmission electron microscopy (TEM).

We will report on the characterization of device quality InGaN templates and their effect on LED emission and performance. An LED grown on GaN with blue emission has been red shifted to green/yellow emission when the underlying GaN was replaced with an InGaN SB template with an In-content of 11% and 12%, respectively. This red shift translates to a relative increase in the In-content by around 40%. Electroluminescence (EL) and optical power measurements show that the device performance of the yellow LED is 1/3 to 1/5 that of the blue LED, which is close to the best reported values for yellow InGaN LEDs. These results show InGaN templates' potential in achieving long wavelength emission and shifting blue LEDs to yellow and even red by varying the In-content of the underlying template.
FABRICATION AND FIELD EMISSION OF ALGAN NANOSTRUCTURES FORMED VIA TOP-DOWN CHEMICAL WET ETCHING

Presenting Author: Barbara Kazanowska

Topic: III-V Wide Bandgap Nitride Semiconductors and Devices

Format: Contributed

Session: 3, 5

Date: 8/4/2021

Time (in MDT): 2:00:00 PM

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Al<sub>(X)</sub>Ga<sub>(1-X)</sub>N is a leading candidate for current and future ultra-wide bandgap electronic (e.g. power electronics and sensors) and optoelectronic (e.g. deep-UV light emitting diodes (LEDs) and lasers) applications. However, three-dimensional (3D) etch technologies for Al<sub>(X)</sub>Ga<sub>(1-X)</sub>N remain immature compared to silicon, limiting its full potential for novel devices. A more robust study is needed to fully utilize chemical wet etching as a possible processing pathway for future devices. Both KOH and H<sub>3</sub>PO<sub>4</sub> chemistries have been reported to etch GaN into varying nanostructures to be used in novel electronic and optoelectronic applications. Here, we build from the foundation of anisotropic KOH and H<sub>3</sub>PO<sub>4</sub> based wet etchants used to fabricate GaN nanostructures and explore Al<sub>(X)</sub>Ga<sub>(1-X)</sub>N alloys etched in acids and bases. We investigate the etch reactivity of Al<sub>0.14</sub>Ga<sub>0.86</sub>N, Al<sub>0.65</sub>Ga<sub>0.35</sub>N, and AlN in KOH-based chemical etchants in a macroscopic scale, where we perform some of the first non-polar etch rate measurements as a function of Al content. We present the etch evolution of GaN nanostructures as a function of 85% H<sub>3</sub>PO<sub>4</sub> and variable temperature which leads to sharp nanowires with tips less than ~10 nm. Using various characterization methods, we determine the (33-62) semi-polar planes bound the GaN nanowires etched in H<sub>3</sub>PO<sub>4</sub>, and a calculated activation energy of 0.9±0.9eV indicates a reaction based etch. The exposure of the (33-62) planes is consistent with etch barrier index (EBI) calculations. The field emission properties of the sharp, tapered nanowires were investigated via a nanoprobe in a scanning electron microscope as well as by a new vacuum field emission electron microscope, showing gap-size dependent turn-on and uniform emission across the array. Sandia National Laboratories is managed and operated by NTESS under DOE NNSA contract DE-NA0003525.
SI DOPED HOMOEPITAXIAL GAN DRIFT LAYERS ON SINGLE CRYSTAL GAN WITH VERY LOW CARBON GROWN BY METALORGANIC CHEMICAL VAPOR DEPOSITION

Presenting Author: Shashwat Rathkanthiwar

Topic: III-V Wide Bandgap Nitride Semiconductors and Devices

Format: Contributed

Session: 3, 6

Date: 8/4/2021

Time (in MDT): 2:15:00 PM

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There is a significant interest in enabling kV-class GaN vertical power devices for applications in energy storage, conversion, and transmission. Achieving a breakdown voltage of several kV necessitates the development of thick n-GaN drift layers with low carrier concentrations in the range of $10^{15}$ cm$^{-3}$ and high mobility. Carbon is the primary compensating impurity limiting the doping in the drift regions grown by metalorganic chemical vapor deposition (MOCVD). In this study, we demonstrate controllable doping in the low $10^{15}$ cm$^{-3}$ range with high mobility (>1000 cm$^{-2}$/Vs) in MOCVD-grown homoepitaxial n-GaN by chemical potential control (CPC) and defect quasi-Fermi level (dQFL) control necessary for the development of GaN power electronics. Two point-defect control schemes, CPC and dQFL control, were employed to increase the formation energy of C$\langle \text{sub} \rangle$N$\langle \text{sub} \rangle$ by altering the electrochemical potential near the growth surface, thereby minimizing C$\langle \text{sub} \rangle$N$\langle \text{sub} \rangle$-related compensation to $<10^{15}$ cm$^{-3}$. The CPC approach was used to establish a defect formation energy map of C$\langle \text{sub} \rangle$N$\langle \text{sub} \rangle$ as a function of the growth environment represented by gallium supersaturation at a given temperature. Accordingly, the supersaturation was suitably adjusted to maximize the formation energy of carbon within practical reactor and growth rate constraints. This reduced C incorporation to ~2x10$^{15}$ cm$^{-3}$. The dQFL control approach was then used to further reduce the fraction of carbon atoms with compensating (acceptor) configuration, i.e., C$\langle \text{sub} \rangle$N$\langle \text{sub} \rangle$=1 to $<1x10^{15}$ cm$^{-3}$. dQFL involves generating excess minority carriers near the growth surface in a steady-state condition by external above-bandgap illumination. This technique induces photo-voltage which performs work against C$\langle \text{sub} \rangle$N$\langle \text{sub} \rangle$ incorporation by increasing its formation energy. Theoretical calculations revealed that the efficacy of this approach is highest in the considered doping range of $10^{15}$ cm$^{-3}$. This was confirmed by growing Si-doped GaN epilayers on sapphire substrate without and with external UV illumination. The dQFLC led to a more
than two-fold reduction in $C_{N}^{-1}$ from $1 \times 10^{16}$ cm$^{-3}$ to $5 \times 10^{15}$ cm$^{-3}$ which correlated to a drastic improvement in mobility and electron concentration. Next, three Si-doped GaN samples were grown on semi-insulating GaN substrates using a combination of CPC and dQFLC. Free electron concentration in the range of $5 \times 10^{15}$ cm$^{-3}$ to $2 \times 10^{16}$ cm$^{-3}$ was controllably achieved while maintaining high mobility $>1000$ cm$^2$/Vs. Finally, temperature-dependent Hall-effect analysis and capacitance-voltage measurements confirmed a low density of compensation centers ($<1 \times 10^{15}$ cm$^{-3}$).
UNDERSTANDING AND CONTROLLING DISLOCATION EVOLUTION IN GAP/SI HETEROEPITAXY

Presenting Author: Tyler Grassman

Topic: III-Vs on Silicon

Format: Invited

Session: 1, 1

Date: 8/4/2021

Time (in MDT): 8:30:00 AM

Authors: Tyler J. Grassman, The Ohio State University, Columbus, Ohio, United States Jacob T. Boyer, The Ohio State University, Columbus, Ohio, United States Ari N. Blumer, The Ohio State University, Columbus, Ohio, United States Zak H. Blumer, The Ohio State University, Columbus, Ohio, United States Daniel L. Lepkowski, The Ohio State University, Columbus, Ohio, United States

Threaded dislocation density (TDD) is a key parameter that commonly limits the performance of lattice-mismatched (metamorphic) integrated semiconductor materials and devices, including III-V/Si systems. Even in the relatively small mismatched GaP/Si system, the misfit is non-negligible, and exacerbated by the heterovalent nature of the interface, thereby leading to difficulty in controlling and minimizing the ultimate TDD that is produced. Although compositionally simple, GaP/Si typically makes use of somewhat complex growth processes with a wide range of variables, some of which are often at odds with specific needs and/or limitations of the target device architectures under development, and all of which can have an impact on the formation and evolution of the microstructure within the GaP epilayer. Therefore, to truly enable a robust and scalable integrated materials platform, a deep understanding of dislocation evolution in GaP/Si growth is needed. To this end, we have undertaken a comprehensive and highly quantitative experimental investigation of dislocation dynamics in MOCVD-grown GaP/Si structures, with the goal to thoroughly identify and understand the complex relationships that exist between the wide range of process variables and the microstructure that results. This included examination of substrate preparation, GaP nucleation processes, early-stage growth conditions, epilayer doping, and growth temperatures, as well as trends with respect to layer thickness. Accurate, large-scale quantitative characterization of misfit dislocation networks and TDD was established through the use of electron channeling contrast imaging (ECCI) and novel image analysis and statistics extraction from which we could determine key dislocation dynamics metrics, like introduction/nucleation rates and glide velocities, in addition to TDD, for direct correlation against the different process variations. Such detailed quantitative dislocation dynamics information, employed within a robust growth process development feedback methodology, directly enables the informed design of processes and structures for truly effective dislocation control and TDD minimization. Our successful efforts toward this include, for example, two-order-of-magnitude TDD reduction (6.7×10^7 cm^-2 to 7.1×10^5 cm^-2) in thin, partially-relaxed GaP/Si template films via optimization of nucleation processes, the development of glide-enhancing superlattice structures for TDD reduction (<3×10^6 cm^-2) in thick, fully-relaxed GaP layers and subsequent graded buffers, and discovery of highly effective, but anti-intuitive growth processes that go against typical convention. This presentation will provide a wide, but detailed overview of this work, both in terms of the materials-related advances and in the methodologies behind them.
DEFECT REDUCTION IN MOCVD-GROWN III-V LAYERS PREPARED ON SI(100)

Presenting Author: Thomas Hannappel

Topic: III-Vs on Silicon

Format: Invited

Session: 1, 3

Date: 8/4/2021

Time (in MDT): 9:00:00 AM

Authors: Thomas Hannappel, TU Ilmenau, Ilmenau, Germany

Epitaxial growth of high-quality III-V materials on Si substrates can be pioneering in many regards, for instance, for the growth of solar cells and solar-to-hydrogen converting devices. For that, a thin GaP layer can be deposited as a transition layer between the non-polar Si substrates and polar III-V heterostructures, due to the close lattice-matching of GaP to Si. In recent years, significant research has been done to achieve low defect densities in the GaP buffer layers directly grown on Si(100) substrates. In particular, the preparation of the Si(100) substrates with double-layer stepped surfaces, decisive to avoid anti-phase disorder in the GaP epilayer, was shown for Si substrates with various offcut angles (from almost exactly oriented to vicinal substrates), terminations, and surface reconstructions ([1] and refs. therein). However, III-V-on-Si heteroepitaxy and the performance of resulting layer structures is still limited by the defect concentration at the III-V/Si(100) heterointerface and in III-V layers grown on top. Here, we thoroughly studied a new nucleation procedure employing a ternary AlGaP compound, which points to a promising route for a significant reduction of defects, lowering the density of threading dislocations in GaP epilayers by nearly one order of magnitude, from $3 \times 10^7$ cm$^{-2}$ to $6.5 \times 10^6$ cm$^{-2}$. In addition, the density of stacking faults and stacking fault pyramids in these buffer layers is reduced by two orders of magnitude. The average length of each misfit dislocation is more than 10 times longer and their number is as well less in buffer layers with AlGaP nucleation, which is essential for low threading dislocation densities. We confirm that a different surface morphology of the nucleation layer has an impact on the entire subsequent GaP growth, formation of stacking faults and stacking fault pyramids in the epilayer and density of threading dislocations. Hence, application of Al into the GaP nucleation process step reveals a very promising pathway for improving the performance of integrated III-V-on-Si-multijunction solar cells. [1] O. Supplie, O. Romanyuk, C. Koppka, M. Steidl, A. Nägelein, A. Paszuk, A. Dobrich, L. Winterfeld, P. Kleinschmidt, E. Runge, T. Hannappel; Metalorganic Vapor Phase Epitaxy of III-V-on-Silicon: Experiment & Theory; Progress in Crystal Growth ad Characterization of Materials 64 (2018) 103-132
PREPARATION OF V-GROOVE SI SUBSTRATES IN AN OMVPE REACTOR FOR III-V ON SI EPITAXIAL GROWTH

Presenting Author: Theresa Saenz

Topic: III-Vs on Silicon

Format: Contributed

Session: 1, 5

Date: 8/4/2021

Time (in MDT): 9:30:00 AM


The direct growth of III-V semiconductors on Si offers a promising pathway for fabricating high-performance III-V solar cells on low-cost substrates. V-groove Si, a substrate where nanopatterning and selective wet etching are used to create a surface with {111}-facetted trenches, is a particularly suitable platform for low cost III-V/Si solar cells because it enables III-V growth on Si wafers prepared with low cost polishing techniques [1]. V-groove Si has already been successfully used to produce III-V on Si lasers [2] and solar cells to a lesser extent [3]. However, the surface of V-groove Si prepared in an OMVPE (organometallic vapor phase epitaxy) reactor prior to III-V growth has only been studied in limited detail [4] compared to the extensive study of planar Si(100) surfaces [5].

In this work, we study the preparation of V-groove Si in an OMVPE reactor for III-V growth using As-based pretreatment annealing. Annealing conditions at 1000 °C for use with V-groove Si substrates with a native oxide layer and at 850 °C for use with wet-chemically deoxidized V-grooves were investigated. In addition, (001)- and (111)-oriented Si wafers were prepared in parallel with the V-groove samples for comparison. Samples were transferred under ultra-high vacuum (UHV) for the surface to be characterized with x-ray photoelectron spectroscopy (XPS) and low-energy electron diffraction (LEED).

The XPS and LEED results identified several conditions at both low and high anneal temperatures for which the Si surface is free of oxygen and other contaminants, and is therefore suitable for further III-V growth. The deoxidation process for V-grooves behaved similarly to the (001) and (111) reference samples for optimized conditions. Based on this result, a strategy for developing surface pretreatment anneals without the need for UHV transfer using optical in situ surface sensitive spectroscopy will be discussed.

PREVENTING DEGRADATION BY DISLOCATIONS IN III-V QUANTUM DOT LASERS ON SILICON

Presenting Author: Kunal Mukherjee

Topic: III-Vs on Silicon

Format: Contributed

Session: 1, 6

Date: 8/4/2021

Time (in MDT): 9:45:00 AM

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The growth of dislocations facilitated by non-radiative recombination of injected carriers leads to rapid degradation in GaAs-based lasers on silicon. Normally dislocations in GaAs only glide and climb appreciably at temperatures exceeding 400 °C, but threading dislocations arising from the GaAs/Si lattice-constant mismatch serve as starting points for very rapid dislocation glide and climb even at room temperature during minority carrier recombination in a laser or LED. This recombination-enhanced dislocation growth has frustrated decades of effort towards realizing a reliable laser on silicon by direct epitaxial growth. Recently, InAs quantum dot (QD) lasers on silicon have proved to be more resilient to recombination-enhanced dislocation growth, likely due to a combination of better carrier confinement in the dots away from dislocations as well as mechanical hardening. Yet the degradation rate continues to be high at 60-80 °C operating temperatures needed for commercial adoption even in QD lasers. In this work, we identify long misfit dislocations adjacent to the laser active region, both above and below, as the primary source of degradation. An electron microscopy-enabled study of the structure of misfit dislocation and luminescence in unaged and aged lasers reveals significant impact from dislocation climb, likely arising from vacancy expulsion into the active region. While the driving force for recombination-enhanced dislocation climb remains uncertain, we are able to identify the root cause for the formation of the misfit dislocations. The defect structure suggests that the misfit dislocations form not due to lattice-constant mismatch as is typical in heteroepitaxy, but rather form during post-growth sample cool down due to a tragic combination of thermal expansion mismatch between III-V and silicon and lattice hardening due to the InAs quantum dots. We validate our hypothesis by inserting a indium-containing ‘trapping’ layer slightly above and below the active region and find it to successfully displace a majority (>90%) of all misfit dislocations and with it bring dramatic improvement to the long-term operation of lasers even at elevated temperatures. We see that just an 80-180 nm displacement of the misfit dislocations away from the active region into the doped cladding shuts down recombination-enhanced dislocation climb by limiting the supply of minority carriers. With this insight, we look to the remaining contribution of threading dislocations in the aging behavior of InAs QD lasers on silicon and the dislocation-related challenges ahead.
HETEROEPITAXIAL GROWTH AND STUDY OF BINARY AND TERNARY MATERIALS FOR NONLINEAR FREQUENCY CONVERSION APPLICATIONS

Presenting Author: Vladimir Tassev

Topic: Lattice-mismatched epitaxy and alternative epitaxial substrates

Format: Invited

Session: 2, 1

Date: 8/4/2021

Time (in MDT): 10:30:00 AM

Authors: Vladimir Tassev, Air Force Research Laboratory, WPAFB, Ohio, United States  Shivashankar Vangala, Air Force Research Laboratory, WPAFB, Ohio, United States  Duane Brinegar, KBR, Beavercreek, Ohio, United States

Compact, high-power, tunable laser sources for the mid and long-wave infrared region are in great demand for a wide variety of commercial and military applications. Since the available direct sources in this wavelength region cannot satisfy requirements for power, tunability and frequency coverage, quasi-phase matching in orientation-patterned (OP) heteroepitaxially grown materials such as GaP, GaAs, GaAsP, and ZnSe is suggested as an alternative approach. Up to 700 µm thick high surface and crystalline quality growths of GaAsP ternaries with a chemical composition in the range of 0.32-0.93 are performed first on plain GaAs with the idea to obtain a material with optimized nonlinear optical properties, i.e. a material with higher nonlinear susceptibility than GaP but lower two-photon absorption (2PA) than GaAs, which dispersion allows pumping with shorter wavelengths through patterns with wider domains. In order to reveal the dependences of nonlinear parameters such as nonlinear coefficient, nonlinear refraction and 2PA on the composition, the chemical composition is measured by three different techniques - high resolution x-ray diffraction, room temperature photoluminescence and electron dispersion spectroscopy. The measured values are in a good agreement with each other and comparing with the available published results. They confirm that the composition, indeed, has an impact on the material properties. For example, the transmission measurements indicate that the band edge is different for samples with different composition as it moves towards the shorter wavelengths with the increase of Phosphorus content as expected. Up to 600 µm thick GaAsP was also grown on OP-GaAs templates indicating excellent domain fidelity of the pattern which propagates to the top of the layer surface. Experiments to confirm frequency conversion in OP-GaAsP are in-progress. Up to 500 µm ZnSe with good surface and crystalline quality was also grown on GaAs substrates while the growth on the OP-GaAs templates resulted in up to 100 µm thick OP-ZnSe structures with relatively good domain propagation. Heteroepitaxial growths of other promising nonlinear optical materials such as GaSe/GaP and GaSe/GaAs were also performed indicating that GaAs is the most suitable substrate/template material in all of the described cases. For example, the best layer quality and the highest growth rate was achieved in the case of GaAsP/GaAs (97 µm/h) compared to the growths of GaAsP/GaP (67 µm/h) and GaAsP/MOCVD GaP/Si (71 µm/h) that were conducted at the same growth conditions.
SYNTHESIS AND TRANSFER OF NANOSHEETS SEED LAYER ON LOW COST SUBSTRATES FOR COMPLEX OXIDES GROWTH

Presenting Author: Florent Baudouin

Topic: Lattice-mismatched epitaxy and alternative epitaxial substrates

Format: Contributed

Session: 2, 3

Date: 8/4/2021

Time (in MDT): 11:00:00 AM

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This work aims to propose a new solution for the growth of functional oxides on low-cost substrates and to develop the integration of high-quality complex oxides with multifunctional properties for large surface electronics. These materials are usually obtained by epitaxial growth on relatively expensive single crystalline substrates, which offer a limited choice of materials and crystallographic orientations commercially available. The project focuses on the replacement of these single crystalline substrates by low-cost (as silicon), amorphous (as glass) and flexible (as mica) substrates covered by a crystalline template of molecular thickness (oxide nanosheets), that can be used as seed layers to induce epitaxy of complex oxides thin films. The presentation will be focused on 2 dimensional (2D) [Ca$\text{sub}_2$$\text{Nb}_{3}$$\text{O}_{10}$]$^{\text{sup}}$ (CNO), [K$\text{sub}_2$$\text{Nb}_{6}$$\text{O}_{17}$]$^{\text{2sup}}$ (KNO) and [Cs$\text{sub}_4$$\text{W}_{11}$$\text{O}_{36}$]$^{\text{2sup}}$ (CWO) nanosheets, obtained by protonation and exfoliation of KCa$\text{sub}_2$$\text{Nb}_{3}$$\text{O}_{10}$ Dion-Jacobson perovskite, K$\text{sub}_4$$\text{W}_{11}$$\text{O}_{36}$ layered oxides. These types of nanosheets possess 2D square lattice ($i$$\langle i\rangle a$/$i$$\rangle = 3.85$ Å), rectangular lattice ($i$$\langle i\rangle a = 7.83$ Å, $i$$\langle i\rangle c = 6.46$ Å) and hexagonal lattice ($i$$\langle i\rangle a$/$i$$\rangle = 7.26$ Å) respectively. Their transfer on different substrates is performed by the Langmuir-Blodgett process and the drop casting technique, which shows a high
CNO enables the growth of complex oxide perovskites thin films on glass and silicon, such as KNbO$_3$ [1], BiFeO$_3$ [2] and La$_{0.67}$Sr$_{0.33}$MnO$_3$ [3], along their cubic [001] orientation. Significant results have also been recently obtained using CNO nanosheets, as the integration of SrVO$_3$ and CaVO$_3$ as transparent conducting film on glass substrates [4], or Pt thin films grown along their [111] direction, deposited at very low temperature [5]. Otherwise, KNO nanosheets are expected to induce a preferential orientation of perovskites along [011] and CWO nanosheets along [111] direction. The oxides and metal depositions have been achieved using different techniques as pulsed laser deposition, chemical solution deposition and sputtering. This work was carried out with the financial support of the ANR agency in the framework of the PolyNASH project (ANR-17-CE08-0012). 

ENGINEERED SUBSTRATES WITH TUNABLE LATTICE CONSTANTS BETWEEN GAAS AND INP

Presenting Author: Markus Feifel

Topic: Lattice-mismatched epitaxy and alternative epitaxial substrates

Format: Contributed

Session: 2, 4

Date: 8/4/2021

Time (in MDT): 11:15:00 AM


For high-quality low defect epitaxial growth of III-V arsenide and phosphide semiconductors there are only limited substrates and thus lattice constants available (Fig. 1). Typically, those are binary materials such as GaAs (5.653 Å) and InP (5.868 Å). However, new devices might benefit from a larger freedom of choice regarding the initial lattice constant. To bridge this gap, we develop engineered substrates with tunable lattice constants between GaAs and InP using metamorphic growth on GaAs or Ge wafers. These “pseudo-” or engineered substrates allow lattice matched, high-quality growth of materials within this lattice constant gap or can replace costly InP substrates. Various device applications such as multi-junction solar cells, LEDs, lasers, laser power converters, photodetectors, or HEMTs could in the future benefit from such substrates. The growth is performed by metal organic vapor phase epitaxy (MOVPE) in an industry-size, planetary, multi-wafer AIX2800G4-TM reactor on 4 inch Ge and GaAs substrates using standard precursors and process conditions. <i>In-situ</i> characterizations tools are used to monitor surface roughness and wafer curvature during growth. Investigations by high-resolution X-ray diffraction (HRXRD) reciprocal space maps is performed in order to determine the strain state of the metamorphic buffers as well as the target lattice constant of the engineered substrates. Further, the surface morphology and the dislocation density are investigated by atomic force microscopy (AFM) and cathodoluminescence (CL), respectively. Engineered substrates based on Ga<sub>x</sub>In<sub>1-x</sub>As buffers are graded to In-contents up to 28 % covering the lower lattice constant range between the GaAs lattice constant of 5.653 Å and 5.767 Å. These structures typically have a surface roughness below 8 nm RMS for a 10 x 10 µm<sup>2</sup> area and a threading dislocation density below 10<sup>6</sup> cm<sup>-2</sup>. Further graded substrates covering lattice constants up to 5.868 Å (InP) are realized using Ga<sub>x</sub>In<sub>1-x</sub>P step-graded buffers. Despite the increased lattice mismatch the observed RMS values are below 10 nm and threading dislocation densities below 2 x 10<sup>6</sup> cm<sup>-2</sup> are achieved. Further, we will show solar cell devices which were grown on engineered substrates.
EPITAXIAL NaCl THIN FILMS FOR WATER-SOLUBLE GAAS SUBSTRATE RECYCLING

Presenting Author: Brelon May

Topic: Lattice-mismatched epitaxy and alternative epitaxial substrates

Format: Contributed

Session: 2, 5

Date: 8/4/2021

Time (in MDT): 11:30:00 AM

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Semiconductor technologies, such as logic devices, sensors, energy harvesters, and light emitters, almost exclusively employ single crystalline substrates. However, the high cost of these substrates can inhibit widespread adoption, especially for area-scalable applications such as high efficiency photovoltaics. Therefore, it is of utmost importance to determine suitable alternative materials or ways to recycle existing substrates. Several methods of substrate removal and reuse have been demonstrated but use hazardous wet etches, limit heterostructure design, and frequently require expensive repolishing. Here we report on the investigation of water-soluble release layers consisting of thin NaCl films deposited using molecular beam epitaxy (MBE) for reuse of the GaAs (100) substrates. Reflection high energy electron diffraction (RHEED) and fast Fourier transforms of high-resolution transmission electron microscopy (TEM) images (Figs. (a, b)) show that deposited NaCl is epitaxial to the underlying GaAs substrate. In-situ deposition of subsequent semiconductor material (GaAs or Ge) on NaCl layers shows a variety of morphologies over the range of deposition conditions tested. If the deposition temperature is too high, the NaCl layer desorbs, too low and the semiconductor overlayer is amorphous. Striking the delicate balance yields an overlayer with crystallinity that is substantially impacted by the presence of the RHEED beam during the initial deposition. In areas exposed to the electron beam, electron back scatter diffraction (EBSD) maps reveal nearly single crystal material with the same orientation as the substrate (Figs. c,d). The degree of crystallinity is reduced in areas without exposure to the electron beam. The presence of a NaCl layer as thin as 3 nm results in nearly instantaneous separation of the overlayer from the parent substrate (Fig. (e)) when placed in water. The parent substrate does not show any obvious surface damage. These results on the incorporation of water-soluble ionic salts with III-V and group IV materials present an alternative avenue of rapid, non-hazardous substrate recycling with potential applications in other binary, or even tertiary III-V systems.
HIGH GROWTH RATE GaInP GRADED BUFFERS AND METAMORPHIC DEVICES GROWN BY HYDRIDE VAPOR PHASE EPITAXY

Presenting Author: Kevin Schulte

Topic: Lattice-mismatched epitaxy and alternative epitaxial substrates

Format: Contributed

Session: 2, 6

Date: 8/4/2021

Time (in MDT): 11:45:00 AM

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Compositional grading enables the growth of metamorphic devices with tunable bandgaps, including multijunction solar cells, light emitting diodes, and photodetectors. However, compositionally graded buffers (CGBs) are usually the thickest regions in metamorphic devices and represent a significant cost due to traditionally low deposition rates for ternary materials. Faster growth rates increase throughput and reduce cost but are only useful if a low defect density can be maintained as rates increase. Steady-state models of plastic strain relaxation suggest that threading dislocation density (TDD) is proportional to growth rate in the limit where the dislocation glide velocity controls the strain relaxation rate. We demonstrate Ga$_{1-x}$In$_x$P CGBs grown by hydride vapor phase epitaxy (HVPE) with varying lattice constants between GaAs and InP at growth rates up to 1 µm/min. We studied the effect of substrate offcut direction, growth rate, and strain grading rate on CGB defect structure, achieving TDD as low as 1.0 x 10$^6$ cm$^{-2}$. Substrate offcut direction was the most important factor for obtaining CGBs with low defect density. (001) GaAs substrates offcut towards (111)B yielded smoother CGBs with lower TDD compared to CGBs grown on substrates offcut towards (111)A. Transmission electron microscopy of CGBs grown on A and B-offcuts only found evidence of phase separation in A-offcut CGBs, indicating that the B offcut limits phase separation, which in turn keeps TDD low. Reduced growth rates of ~0.3 µm/min led to the appearance of CuPt-type atomic ordering, which affected the distribution of dislocations on the active glide planes but did not affect TDD. Higher growth rates led to smoother CGBs and did not appreciably increase TDD as otherwise predicted by steady-state models of plastic relaxation, indicating that glide velocity did not limit TDD in this case. We achieved TDD = 2.4 x 10$^6$ cm$^{-2}$ for a grade from GaAs to InP grown at 1 µm/min, which suggests that HVPE could be used to develop cost-effective large-area InP virtual substrates on GaAs. We also present results for metamorphic 1.0 eV Ga$_{0.7}$In$_{0.3}$As rear heterojunction solar cells grown using GaInP CGBs. We obtain open circuit voltages of up to 0.59 V, a result comparable to state-of-the-art metamorphic GaInAs solar cells grown by other methods, confirming the low defect density of the CGBs. These results show
PATHWAYS TO COST REDUCTION OF III-V MULTI-JUNCTION SOLAR CELLS

Presenting Author: David Lackner

Topic: Materials for photovoltaics and other energy technologies

Format: Invited

Session: 2, 1

Date: 8/3/2021

Time (in MDT): 10:30:00 AM

Authors: David Lackner, Fraunhofer Institute for Solar Energy Systems ISE, Freiburg, Germany

III-V multijunction solar cells show by far the highest conversion efficiencies of 39.2 (AM1.5g). However, up to now III-V solar cells play a significant role only in the space market due to high cost per watt. With the general need for decarbonization of the energy sector and an increasing percentage of battery powered cars, III-V multi-junction cells are a promising candidate for PV application on moving vehicles like passenger cars, trucks and even yachts or vessels due to the proven reliability, insensitivity to thermal cycling according to automotive standards and high power/area and power/weight ratio. However, in order to suit the cost structure of these markets, a cost reduction of more than one order of magnitude is necessary while keeping efficiency above 30% (AM1.5g). For typical III-V multi-junction space solar cells the epitaxy and the wafer cause about 60% of the cost. In this work, the recent progress at Fraunhofer ISE to overcome these drawbacks will be presented: The epitaxy costs are dominated by the process times (depreciation of equipment) and group-V material costs due to the typically high V/III ratios > 20. By employing a close coupled showerhead reactor, we have demonstrated MOVPE growth rates up to 280 μm/h for GaAs at V/III ratios as low as 3. For typical MOVPE production reactors the Ga$_{0.51}$In$_{0.49}$P growth rate is limited by the trimethylindium partial pressure in the reactor due to the low vapor pressure of trimethylindium and the use of conventional bubbler sources. To overcome this limitation, we are testing a new liquid In source in combination with direct evaporation. Substrate cost can either be reduced through epitaxy lift-off and recycling or by employing Si wafers which can also serve as the bottom subcell. After a GaP nucleation on the Si wafer, the lattice constant is increased in a metamorphic GaAsP buffer to finally reach GaAs. The growth is continued with a GaAs/GaInP tandem cell to form a triple-junction device. Despite the still relatively high threading dislocation density after the GaAsP metamorphic buffer of about 1*10$^7$/cm$^2$, we could already reach a conversion efficiency of 25.9% (AM1.5g) for such a GaInP/GaAs/Si triple-junction cell. Recently, we have demonstrated the high efficiency potential of this approach with a two terminal GaInP/GaInAsP/Si wafer bonded triple-junction cell which achieves a record conversion efficiency of 35.9% (AM1.5g).
OPTICALLY-THICK GaInAs/GaAsP SUPERLATTICE SOLAR CELLS

Presenting Author: Ryan France

Topic: Materials for photovoltaics and other energy technologies

Format: Contributed

Session: 2, 3

Date: 8/3/2021

Time (in MDT): 11:00:00 AM

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Quantum well and superlattice solar cells have been investigated for well over two decades, but have had performance limitations from either non-radiative recombination or incomplete carrier collection. Here, we investigate GaInAs/GaAsP strain-balanced solar cells with very large number of GaInAs wells, which can increase carrier collection beyond the GaAs bandedge. Careful stress-balancing and fine-tuned growth conditions are both needed to limit defect formation and non-radiative recombination. By implementing thin, highly strained GaAsP barriers, the GaInAs fraction in the GaInAs/GaAsP superlattice increases, thus increasing the amount of GaInAs for a given absorber thickness. Using optimized growth conditions, we demonstrate high performance pseudomorphic GaInAs/GaAsP solar cells grown on GaAs with over 2 μm of GaInAs. At this thickness, nearly all light above the GaInAs absorption edge and below the GaAs bandgap is collected. Using thin barriers also transitions the transport to being dominated by tunneling rather than thermionic emission, which opens new opportunities for high performance solar cell structures.
SINGLE-CRYSTAL-LIKE GAAS THIN FILMS PASSIVATED BY HYDROGEN AND SULFUR FOR SIGNIFICANT IMPROVEMENT OF CONVERSION EFFICIENCY OF FLEXIBLE III-V SOLAR CELLS

Presenting Author: Sara Pouladi

Topic: Materials for photovoltaics and other energy technologies

Format: Contributed

Session: 2, 4

Date: 8/3/2021

Time (in MDT): 11:15:00 AM

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Recently, we reported a successful demonstration of flexible GaAs solar cell devices based on nearly single-crystalline III-V thin films directly grown on inexpensive polycrystalline metal substrates using crystallinity-transformational buffer layers. This inexpensive high-quality III-V platform aims to address the technical and economic challenges of III-V multi-junction heterostructures which are the best photovoltaic (PV) materials for high conversion efficiencies. The efficiency advantages of high-quality III-V materials combined with a continuous roll-to-roll deposition process of the thin films on a low-cost tape substrate are employed to produce flexible, cost-competitive, and high-efficiency solar cells (SCs) with application versatility. A promising photon conversion efficiency of ~7.6% but lower than expected performance for GaAs SC was delivered for the first demonstration of flexible single-crystal-like GaAs SC. A 2-dimensional modeling of the SC revealed that the presence of low-angle grain boundaries (LA-GBs) in the single-crystal-like GaAs plays a critical role in limiting of its performance but an effective passivation of these GBs can boost the photo-conversion efficiency ~3-4 times. In this study, two physical hydrogen-based passivation techniques and a chemical sulfide treatment were employed for the passivation of LA-GBs in the single-crystal-like GaAs experimentally. A considerable reduction in the dark saturation current of single-crystal-like GaAs SCs from $J_0 \sim 2 \times 10^{-3}$ A/cm$^2$ to $\sim 3.5 \times 10^{-4}$ A/cm$^2$ (at $V = -500$ mV) were observed by trioctylphosphine sulfide (TOP:S) chemical treatment. A significant enhancement of photon conversion efficiency of flexible single-crystal-like GaAs SCs was consequently achieved with increases of ~24%, 12.8%, 14.5%, and 64% for $V_{oc}$, $J_{sc}$, $FF$, and overall efficiency, respectively which resulted in final efficiency performance of 13.5% (two times of the previous record, 7.6%) after anti-reflection coating (ARC). Further material and device characterizations were conducted on the TOP:S treated single-crystal-like GaAs to understand the effect and mechanism of the TOP:S passivation on the single-crystal-like GaAs film including photoluminescence (PL), atomic force microscopy (AFM), scanning probe force microscopy (SPFM). A uniform distribution of surface potential and lower potential barrier height at grain boundaries obtained by SPFM along with ~125% enhancement in the PL peak of
single-crystal-like GaAs film after the TOP:S treatment suggest partial passivation of the energy states at GBs resulting in the efficiency improvement of flexible GaAs SCs. Incident photon-to-current efficiency (IPCE) measurements are also being conducted on the passivated SCs and the results will be integrated into the resulting short circuit current to be compared with the $I-V$ characteristics of SC at 1 Sun AM 1.5G.
IMPROVEMENT OF INGAP/GAAS INTERFACE REALIZED BY OPTIMIZED INGAP COVER LAYER FOR HIGH EFFICIENCY REAR-HETERO-JUNCTION SOLAR CELLS

Presenting Author: Meita Asami

Topic: Materials for photovoltaics and other energy technologies

Format: Contributed

Session: 2, 5

Date: 8/3/2021

Time (in MDT): 11:30:00 AM

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InGaP/GaAs rear-hetero-junction (RHJ) solar cells are expected to achieve high power conversion efficiency (PCE). Fig. 1 shows the standard structure of RHJ solar cells. To realize high PCE InGaP/GaAs RHJ solar cells, we need to make an optimization of the growth temperature for InGaP rear emitter to improve carrier lifetime and surface roughness. It is known that the InGaP grown at high temperature has longer carrier lifetime, but it has rougher surface morphology [1]. Rough surface morphology of InGaP induces crystal defects at the interface between InGaP and GaAs. As shown in Fig. 2, we found that growing thin low temperature grown InGaP on high temperature grown InGaP improves the surface morphology of InGaP while keeping the long carrier lifetime in an entire InGaP layer. The crystal quality at the interface between InGaP and GaAs was examined by photoluminescence (PL) measurements of the double hetero-structure samples shown in Fig. 3. PL results indicate that the crystal quality at the interface between low temperature grown InGaP and GaAs is higher compared with that of the interface between high temperature grown InGaP and GaAs. Thus, the thin low temperature grown InGaP can improve the performance of RHJ solar cells. To further improve the quality of the InGaP rear emitter with our new concept, we optimize the thickness and growth temperature of low temperature grown InGaP. In the presentation, we will report the device performance of RHJ solar cells with optimized InGaP layers.

SILICON CRYSTAL GROWTH: THE MOST SIGNIFICANT ENABLER FOR A RELIABLE, COST-EFFECTIVE CLEAN ENERGY

Presenting Author: srinivasamohan (Mohan) Narayanan

Topic: Materials for photovoltaics and other energy technologies

Format: Invited

Session: 3, 1

Date: 8/3/2021

Time (in MDT): 1:00:00 PM

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Abstract<br />Solar Photovoltaics has emerged as the fastest growing source of clean energy enabling the energy transition from fossil fuels to support the efforts combating the climate challenge. Since 2004 the annual installation of solar photovoltaics has increased from 1 GW to about 120 GW in 2020. While various materials have been tried commercially as the PV device material for the past 4 decades, crystalline silicon (Mono crystalline and Multi crystalline) has consistently dominated the commercial PV scene during this period. With the continuous advancement in PV and crystal growth technologies it is very clear that the crystalline silicon will sustain its position for a few more decades. From Fig 1, it can be concluded that PV installation increased substantially since 2005 as the cost decreased while reliability, project viability increased. The share of multi crystalline silicon as substrate was consistently increasing since 2005. However, since 2016, the trend has reversed. Photovoltaic modules based on monocrystalline (Mono) silicon substrates have become the dominant modules for all the geographic regions and applications (utility, commercial and Industrial, residential roof top). From a less than a few hundred megawatts (MW) in 2000 now the production capacity of mono has grown to about 100 gigawatts (GW).<br />Fig 1. During the past decade, the cost of PV modules has substantially decreased while the reliability of the modules has improved resulting in longer extended warranty of the module. (Figure 2) One of the key enablers is the advancement in the crystal growth manufacturing technology.<br />Figure 2. During the past two years, Mono silicon-based modules have almost displaced the multicrystalline silicon-based modules due to the lower Levelized cost of electricity (LCOE).<br />Figure 3: In this presentation, the factors Contributed to this drastic shift will be discussed: 1. The size of wafer has increased from a 4” diameter to 12” diameter, 2. the minority carrier lifetime has increased to take advantage of the advanced cell technologies, 3. the capital and operational costs of the crystal growth pullers have decreased substantially, 4. Gallium dopant has reduced the light induced degradation as boron-oxygen pairs are eliminated. In the paper these factors and the impact on LCOE by silicon crystal growth will be discussed in detail.
PULLING THIN SINGLE CRYSTAL SILICON WAFERS FROM A MELT: THE NEW, LEADING EDGE SOLAR SUBSTRATE

Presenting Author: Nathan Stoddard

Topic: Materials for photovoltaics and other energy technologies

Format: Invited

Session: 3, 3

Date: 8/3/2021

Time (in MDT): 1:30:00 PM

Authors: Parthiv Daggolu, Peter Kellerman, Alex Martinez, Sarah Cole, Ashwin Vutha, Jesse Appel, Mallory Jensen and Nathan Stoddard Leading Edge Equipment Technologies

PULLING THIN SINGLE CRYSTAL SILICON WAFERS FROM A MELT: THE NEW, LEADING EDGE SOLAR SUBSTRATE

Parthiv Daggolu, Peter Kellerman, Alex Martinez, Sarah Cole, Ashwin Vutha, Jesse Appel, Mallory Jensen and Nathan Stoddard

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The Floating Silicon Method (FSM) has been established as a viable, stable method for growing single crystal ribbons directly from a silicon melt. With intense helium jet cooling to drive the linear progress of a [111] facet, pulled in the <110> direction, ribbons in the 0.6 – 3.0 mm thickness range can be grown at linear growth rates from 0.3 mm/s to >6 mm/s as reported in the literature. We report on recent progress towards growing (100) oriented ribbons with a net thickness of less than 200 microns and a ribbon width up to 18 cm using a stable, continuous process in the Leading Edge prototype furnace. Typical crystalline defect types are described as well as values of critical impurities like oxygen, carbon, dopants, and metals that are relevant for use as wafers for solar cells.
IN SITU VISUALIZATION OF TRAVELING SOLVENT GROWTH OF THIN Si<sub>X</sub>Ge<sub>1-X</sub> CRYSTALS

Presenting Author: Ping-Ting Chiang

Topic: Materials for photovoltaics and other energy technologies

Format: Contributed

Session: 3, 5

Date: 8/3/2021

Time (in MDT): 2:00:00 PM

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Abstract

Thin Si<sub>X</sub>Ge<sub>1-X</sub> crystal growth by the traveling solvent method was visualized. A germanium wafer was sandwiched by two (100) silicon wafers between two quartz plates for the growth. It was found that the temperature gradient and the stability of melting interface was crucial for a planar growth. Otherwise, the constitutional supercooling could induce faceted and further dendritic growth. *In situ* visualization of the melting and growth with different temperature profiles was carried out to better understand the growth mechanism. The result showed that the growth interface changed from planar to faceted and then dendritic when the temperature gradient gradually increased. For x~0.8, the temperature gradient at around 1 K/mm was an optimal for planar growth. The initial growth velocity was higher due to the buildup of a local concentration field near the interfaces. However, the average growth velocity was consistent with the theoretical value estimated by the diffusion equation. Moreover, as the interface became unstable, it was observed that solvent trapping occurred at the tips rather than in the grooves of the facets. Figure 1. The growth interface changed as the temperate increased from (a) to (c).
IN SITU SOLIDIFICATION STUDY OF Si$_{1-X}$Ge$_X$ ALLOY FOR THERMOELECTRIC APPLICATIONS

Presenting Author: Gavin Sison

Topic: Materials for photovoltaics and other energy technologies

Format: Contributed

Session: 3, 6

Date: 8/3/2021

Time (in MDT): 2:15:00 PM

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IN SITU SOLIDIFICATION STUDY OF Si$_{1-X}$Ge$_X$ ALLOY FOR THERMOELECTRIC APPLICATIONS<br>Gavin Sison, Chung-Wen Lan*Chemical Engineering Department, National Taiwan University, Taipei, Taiwan ROC*Email: cwlan@ntu.edu.tw<br>The usefulness of a thermoelectric material is determined by its figure of merit which is proportional to electrical conductivity and thermal resistivity. In a polycrystalline system, grain boundaries decrease thermal conductivity but can retain electron transport properties [1]. SiGe is one such material that can be operated at temperatures up to 1300K and has the potential to be manufactured in bulk [2]. We report an in-situ method for observing the bulk growth of polycrystalline Si$_{1-x}$Ge$_x$ alloys by melting silicon and germanium wafers between a desired substrate and a quartz observation window at 1400°C. The effects of substrate material, cooling rates, and alloy composition on crystal growth and subsequent mechanisms are discussed.

Figure 1: Electron backscatter diffraction (EBSD) analysis inverse pole figures for Si$_{0.7}$Ge$_{0.3}$ grown on (a) silicon carbide at 100 K/min, (b) silicon nitride at 100 K/min, (c) silicon carbide at 20 K/min, and (d) silicon nitride at 20 K/min. References:<sup>[1]</sup>Joshi G, Lee H, Lan Y, Wang X, Zhu G, Wang D, Gould RW, Cuff DC, Tang MY, Dresselhaus MS, Chen G, Ren Z. Enhanced thermoelectric figure-of-merit in nanostructured p-type silicon germanium bulk alloys. Nano Lett. 2008 Dec;8(12):4670-4.<sup>[2]</sup>Mukannan Arivanandhan, Genki Takakura, D. Sidharth, Maeda Kensaku, Keiji Shiga, Haruhiko Morito, Kozo Fujiwara, Crystallization and re-melting of Si$_1$-xGex alloy<br/>semiconductor during rapid cooling. Journal of Alloys and Compounds. Volume 798, 2019, Pages 493-499
COLOSSAL GRAINS FOR A NEW STRUCTURAL PARADIGM IN THIN-FILM PHOTOVOLTAICS

Presenting Author: Eric Colegrove

Topic: Materials for photovoltaics and other energy technologies

Format: Invited

Session: 4, 1

Date: 8/3/2021

Time (in MDT): 3:00:00 PM

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II-VI based thin-film photovoltaics (PV) have experienced substantial commercial success on a foundation of fast large-scale deposition and processing. This type of processing, regardless of material type, nearly always results in small grain (nm to several um diameters) polycrystalline material that, if not for effective grain boundary (GB) and defect passivation, would severely limit PV performance. In the case of CdTe based PV technology, the nearly ubiquitous CdCl$_2$ treatment is used, in part, to passivate the polycrystalline p-type absorber even though Cl is known to (and used to) compensate p-type II-VI materials. Given that $V_{OC}$ is still the most limited performance metric and it can only be improved through higher p-type absorber concentrations, CdCl$_2$ treatments may be holding the technology back. In this talk, we will discuss results related to a process by which small grain CdSeTe material is rapidly transformed into very large grain material (100-1000um diameters, Fig. 1a). This explosive recrystallization, which we have termed colossal grain growth (CGG), occurs by a Cl free process with thin films (<10um) deposited using the same fast deposition techniques the industry has relied on for more than a decade. Our modeling suggests that GB recombination becomes significantly less important at these grain sizes and thus may eliminate the need for a CdCl$_2$ treatment. This result is complimented by previous results of epitaxial growth at high rates on single crystal seed layers. Thin CdSeTe CGG seed layers can be used for rapid epitaxy of CdTe to complete a standard device stack (Fig.1b). This is an optimistic view and the current limitations and challenges related to this process and these materials will also be discussed, including alloy and substrate roughness sensitivity, intragrain material quality, and complex defect chemistry. These challenges are not insignificant but overcoming them may enable a new structural paradigm for thin-film PV.
SOLUTION GROWTH OF LARGE SINGLE CRYSTALS OF N-TYPE TIN MONOSULFIDE

Presenting Author: Sakiko Kawanishi

Topic: Materials for photovoltaics and other energy technologies

Format: Contributed

Session: 4, 3

Date: 8/3/2021

Time (in MDT): 3:30:00 PM

Authors: Sakiko Kawanishi, Tohoku University, Sendai, Japan Issei Suzuki, Tohoku University, Sendai, Japan Takahisa Omata, Tohoku University, Sendai, Japan Hiroyuki Shibata, Tohoku University, Sendai, Japan

Tin monosulfide (SnS) is one of potential candidates as a material for photovoltaic devices because of its attractive properties such as suitable band gap (~1.08 eV) and high light absorption coefficient. Its increasing attention also comes from the nontoxic and abundant components of SnS. However, SnS crystals generally exhibit p-type conduction because of unintentional formation of Sn vacancies and the corresponding hole generation. The fabrication of p-n homojunction solar cells was then difficult because of the difficulty in fabricating n-type SnS. Recently, single crystals of Cl-doped SnS of a few mm in width were grown from SnCl$_2$ solvent and they exhibit n-type conduction. In this study, the solution growth of large Cl-doped and Br-doped SnS single crystals was demonstrated using a molten Sn-based solvent. The addition of halogen sources (SnCl$_2$ or SnBr$_2$) in the solvent significantly enhanced both lateral growth along the (100)-plane and vertical growth of SnS crystals. The maximum size of the obtained crystals reached a diameter and thickness of over 16 mm and 0.7 mm, respectively. In addition to the compositional analysis, the crystals were characterized via electrical measurements and photoelectron spectroscopies. Both the Cl-doped and Br-doped SnS single crystals exhibited degenerate n-type conductivity with a high electrical conductivity of 11.1 and 18.9 S cm$^{-1}$ at 300 K for Cl-doped and Br-doped SnS, respectively. Furthermore, the photoelectron spectroscopy results also indicated n-type conductivity. Therefore, we successfully obtained the large n-type SnS crystals, which would be suitable for the fabrication of p-n homojunction SnS solar cells.
OPTICAL AND CRYSTALLINE INHOMOGENEITY OF NA DOPED TYPE-II SILICON CLATHRATE FILMS

Presenting Author: Yinan Liu

Topic: Materials for photovoltaics and other energy technologies

Format: Contributed

Session: 4, 4

Date: 8/3/2021

Time (in MDT): 3:45:00 PM


Silicon clathrates are cage-like, crystalline silicon inclusion compounds showing great promise for photovoltaics and battery applications. Silicon clathrates have been synthesized in the presence of alkali atoms, such as Na, which serve as interstitial guests in the cages. Type-II silicon clathrate powder can be prepared with low Na concentration creating a heavily doped semiconductor with a direct or nearly direct bandgap near 2.0eV and Na guests can be viewed as shallow donors.<br />Silicon clathrates in thin film form are more interesting than powders due to their potential for practical applications. Films synthesized on diamond silicon wafers using a two-step process (formation of the precursor NaSi film followed by thermal decomposition of the precursor into the clathrate phase) have been reported. Using a similar approach, we have synthesized low Na content type-II silicon clathrate films. We find, however, that the optical and electronic properties of the films are strongly influenced by inhomogeneities and defect phases present in the material and we report techniques for minimizing these effects.<br />X-ray diffraction, Raman scattering spectroscopy, and Electron Paramagnetic Resonance (EPR) measurements all provide evidence for a disordered or amorphous silicon-like phase which is dominant near the film surface. SEM imaging provides additional evidence of a defective surface layer and shows the films are made up of grains from 10-100 microns in lateral size. Spatially resolved time-of-flight secondary ion mass spectrometry data also exhibit inhomogeneity with regions of high Na content at the film surface and near grain boundaries surrounding low Na content regions we associate with high-quality clathrate phase. After detecting the inhomogeneities, techniques to remove or reduce these effects are studied. By separating the film from the silicon substrate, high-quality silicon clathrate structure is exposed and detected at the buried interface. Acid etching is also applied to remove the disordered top surface and expose higher quality silicon clathrate structure.<br />With the high-quality clathrate surfaces and films produced, optical measurements are taken and interpreted. Absorption measurements support a room temperature bandgap near 1.7eV and an above gap absorption coefficient nearly two orders of magnitude larger than diamond silicon. Room temperature photoluminescence (PL) is also observed. Temperature dependence of the PL intensity and of the Na hyperfine line observed in EPR spectra are consistent with Na as a shallow donor. This makes type II
clathrate an interesting candidate for silicon based solar cells, LEDs and sensors. This work was supported by NSF grant #1810463.
LUMINESCENCE OF RARE EARTH DOPED CRYSTALS

Presenting Author: Dobroslawa Kasprowicz

Topic: Materials for photovoltaics and other energy technologies

Format: Contributed

Session: 4, 5

Date: 8/3/2021

Time (in MDT): 4:00:00 PM

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LUMINESCENCE OF RARE EARTH DOPED CRYSTALS Dobroslawa Kasprowicz<sup>1</sup>* , Paweł Głuchowski<sup>2</sup>, M. Chrunik<sup>3</sup>, Andrzej Majchrowski<sup>3</sup><sup>1</sup>Faculty of Materials Science and Technical Physics, Poznan University of Technology, Pl. Marii Skłodowskiej-Curie, 60-965 Poznan, Poland<sup>2</sup>Institute of Low Temperature and Structure Research of Polish Academy of Sciences, Okólna 2, 50-422 Wroclaw, Poland<sup>3</sup>Institute of Applied Physics, Military University of Technology<i>,</i>Kaliskiego 2, 00-908 Warszawa, Poland<br />email: dobroslawa.kasprowicz@put.poznan.pl<br />

Abstract

The rare earth ions doped up-conversion materials have been extensively studied in recent years and widely applied in optical devices such as lasers [1], solar cells [2], light emitting diodes (LEDs) [3] or 3D displays [4]. The vibrational properties of Kgd(WO<sub>4</sub>)<sub>2</sub> crystals doped with selected Pr<sup>3+</sup>, Eu<sup>3+</sup>, Tb<sup>3+</sup>, Ho<sup>3+</sup>, Er<sup>3+</sup>, Tm<sup>3+</sup> and/or Yb<sup>3+</sup> ions were studied by the μ-Raman spectroscopy. Moreover, the luminescence of above mentioned materials were measured using optical spectroscopy methods. In the proposed systems Yb<sup>3+</sup> ions were used as energy sensitizers and the up-converted luminescence originated from the transitions between the energy levels of other co-doped rare earth ions [5]. It was shown that all investigated systems exhibited multicolor up-conversion luminescence in VIS spectral range under 980 nm laser irradiation. The investigated materials are very promising as a new generation energy converters with significant potential applications in novel optical devices.

Figure 1. The luminescence spectra of Kgd(WO<sub>4</sub>)<sub>2</sub>:Yb<sup>3+</sup>/Ho<sup>3+</sup> after excitation at 980 nm [5].


Acknowledgements

This work was supported by the Polish Ministry of Sciences and Higher Education: 0511/SBAD/2151.
LUMINESCENCE OF NOVEL Bi$_3$TeBO$_9$ CRystalline MATERIALS DOPED WITH RARE EARTH IONS

Presenting Author: Taras Zhezhera

Topic: Materials for photovoltaics and other energy technologies

Format: Contributed

Session: 4, 6

Date: 8/3/2021

Time (in MDT): 4:15:00 PM

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Luminescence of novel Bi$_3$TeBO$_9$ (BTBO) microcrystalline powders doped with selected rare earth ions (RE$^{3+}$), belonging to the category of bifunctional materials, exhibit nonlinear optical properties (NLO) and effective luminescent properties of active RE$^{3+}$ ions. In the studies of BTBO crystals a high efficiency of second harmonic generation (SHG) - the highest among borate materials was discovered. The intensity of SHG signal is about 20 times higher than that of SHG generated in the well-known NLO KDP crystal [1,2].

In this work, we present the results of investigation of vibrational properties of BTBO:Nd$^{3+}$ powders studied by Raman spectroscopy and optical spectroscopy methods. It should be noted that, the characteristic emission of Nd$^{3+}$ ions at about 890 and 1064 nm ($\lambda_{exc}=327$ nm) were measured and analysed. The intensity of SHG signal is about 20 times higher than that of SHG generated in the well-known NLO KDP crystal [1,2]. The microcrystalline powders were synthesized by means of the modified Pechini method [3]. In this work, we present the results of investigation of vibrational properties of BTBO:Nd$^{3+}$ powders studied by Raman spectroscopy and optical spectroscopy methods. It should be noted that, the characteristic emission of Nd$^{3+}$ ions at about 890 and 1064 nm ($\lambda_{exc}=327$ nm) were measured and analysed. The intensity of SHG signal is about 20 times higher than that of SHG generated in the well-known NLO KDP crystal [1,2]. The microcrystalline powders were synthesized by means of the modified Pechini method [3].
Acknowledgments: This work was supported by the research Project of the Ministry of Sciences and High Education 0511/SBAD/2151.
MODELING AND IN-SITU NEUTRON IMAGING TO UNDERSTAND THE BRIDGMAN GROWTH OF DOPED SCINTILLATOR CRYSTALS

Presenting Author: Jeffrey Derby

Topic: Modeling of Crystal Growth Processes

Format: Invited

Session: 3, 1

Date: 8/2/2021

Time (in MDT): 1:00:00 PM

Authors: Jeffrey J. Derby, University of Minnesota, Minneapolis, Minnesota, United States  Chang Zhang, University of Minnesota, Minneapolis, Minnesota, United States  Swanand Pawar, University of Minnesota, Minneapolis, Minnesota, United States  Didier Perrodin, Lawrence Berkeley National Laboratory, Berkeley, California, United States  Anton Tremsin, University of California-Berkeley, Berkeley, California, United States  Edith D. Bourret, Lawrence Berkeley National Laboratory, Berkeley, California, United States

For nearly a century, Bridgman crystal growth has been carried out in the dark, since there have been no direct methods to observe what transpires within these systems. We present groundbreaking experiments that employ neutron scattering to visualize, \textit{in situ}, the compositional field that develops during the Bridgman growth of a mixed-halide scintillator crystal. These provide, for the very first time, a direct observation of melt crystal growth within a system large enough to display the complex interplay of heat transfer, fluid flow, segregation, and phase change. We describe and apply computational models to predict the macroscopic transport of heat, mass, and momentum along with phase-change phenomena in the crystal growth system employed in these neutron imaging experiments. Not only do the experimental observations serve to validate the modeling results, but, more importantly, the model provides a rigorous framework to understand the mechanisms that are responsible for the complicated evolution of interface shape and dopant distribution observed in the growth experiment. Ultimately, the understanding obtained by model and experiment will close the loop between materials quality, growth conditions, and process development. This approach will provide a rigorous path forward for process optimization and control, accelerating the incremental advancements that have, in the past, typically relied on empiricism, experience, and intuition.
CHALLENGES IN MODELING OF GRAIN STRUCTURES FOR MULTI-CRYSTALLINE SILICON CASTING

Presenting Author: Chung-Wen Lan

Topic: Modeling of Crystal Growth Processes

Format: Invited

Session: 3, 3

Date: 8/2/2021

Time (in MDT): 1:30:00 PM

Authors: Chung-Wen Lan, National Taiwan University, Taipei, Taiwan

CHALLENGES IN MODELING OF GRAIN STRUCTURES FOR MULTI-CRYSTALLINE SILICON CASTING<br />
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The development of grain structures multi-crystalline silicon (mc-Si) casting plays a crucial role in the materials quality for solar cells [1-2]. As more two grains are involved in grain competition, two GBs could interact and the GB leftover is important to the quality of the grown ingot. Literatures have shown theoretically the interactions involving $\Sigma^3$ GBs [3].

Interactions between CSL and non-$\Sigma$ GBs during directional solidification were illustrated experimentally [4]. Beside the grain competition, nucleation of new grains through twinning at the grain groove or tri-junction is also crucial [5]. We have carried out three-dimensional (3D) modelling of the grain boundary (GB) interaction and evolution based on phase fields by considering anisotropic GB energy and mobility for mc-Si [6]. The twin nucleation at the tri-junction groove, as well as the T-matrices for twining [7], have also been considered in the simulation [8]. In this presentation, in addition to the review of previous works, the challenges, such as detailed kinetics and morphologies near the grooves, for a more realistic simulation will be addressed.

INVESTIGATIONS OF GAS FLOW INSTABILITIES IN UP-FLOW AND DOWN-FLOW HVPE REACTORS

Presenting Author: Markus Zenk

Topic: Modeling of Crystal Growth Processes

Format: Contributed

Session: 3, 5

Date: 8/2/2021

Time (in MDT): 2:00:00 PM

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The Hydride Vapor Phase Epitaxy (HVPE) is currently the main growth technique for the fabrication of bulk GaN crystals or the production of single freestanding GaN wafers. Similar to other VPE methods, gas flow and mass transport phenomena strongly influence the uniformity of growth rate, material composition and doping in the HVPE process and thus can influence the remaining built in strain of the crystal. However, the nature of this method lead to a quite complex interplay between physical properties of the gas flow and the reactor geometry and consequently to a number of challenges in the reactor design. The HVPE of GaN usually applies metallic Ga, HCl and NH<sub>4</sub> as precursors and a mixture of N<sub>2</sub> and H<sub>2</sub> as a carrier gas. Initially, in a separate reactor zone, HCl reacts with Ga melt surface building GaCl. The formation of GaN occurs close to the thermodynamic equilibrium and requires high partial pressures of GaCl and NH<sub>3</sub> to achieve a reasonable growth rate. For the prevention of NH<sub>4</sub>Cl formation at low temperatures and parasitic depositions of GaN on the reactor parts at high temperatures, the precursors should be transported into the reactor by separated gas lines and should be mixed only in a short distance of several cm away from the substrate. These and some other aspects determine possible gas flow conditions in the HVPE reactor. Thereby, the resulting gas flow can reveal severe instabilities, which significantly reduce the performance of the HVPE growth process. This contribution investigates numerically the gas flow and the mass transport in vertical HVPE reactors using a conventional axial symmetrical growth geometry. The relative significance of different flow and transport phenomena was evaluated in dependence on the gravity direction. The performed simulations shows that buoyancy effects due to density differences between the gas lines is the main factor causing the deformation of laminar flow pattern and the formation of recirculation cells in the growth zone. Baroclinic instabilities were identified as source for these phenomena. In contrast, typical temperature gradients reveal a minor impact on the stability of the gas flow. Based on these results major differences of the species transport in up-flow and down-flow HVPE reactors are formulated. The performed analyzes of interplay and relative significance of different flow effects in the HVPE environment allows to provide a general framework for reactor design and scaling.
TECHNICAL CHALLENGES OF GROWING SUPER-HEAVY MONO-CRYSTALLINE SILICON AND ITS COUNTERMEASURES

Presenting Author: Lijun Liu

Topic: Modeling of Crystal Growth Processes

Format: Invited

Session: 4, 1

Date: 8/2/2021

Time (in MDT): 3:00:00 PM

Authors: Lijun Liu, Xi’an Jiaotong University, Xi’an, China, Jiancheng Li, Xi’an Jiaotong University, Xi’an, China, Junling Ding, Xi’an Jiaotong University, Xi’an, China

The quality of mono-crystalline silicon grown by the Czochralski (CZ) technique is always better than that of multi-crystalline silicon or mono-like crystalline silicon grown by the directional solidification technique. The energy conversion efficiency of solar cells made of mono-crystalline silicon is indeed higher than that made of multi-crystalline silicon or mono-like crystalline silicon. However, the cost of mono-crystalline silicon is also higher than that of multi-crystalline silicon and mono-like crystalline silicon. The main reason is that much bigger/heavier silicon ingot can be obtained with the directional solidification technique than that obtained with the CZ technique in a run at its current status of technology. In order to decrease the cost of mono-crystalline silicon and make it comparable to the multi-crystalline/mono-like crystalline silicon, we need to grow super-heavy mono-crystalline silicon basing on the CZ technique to improve the productivity. In this talk, we will discuss about the main technical challenges of growing super-heavy mono-crystalline silicon whose weight is over 1300 kg basing on the CZ technique. In this aspect, we will analyze the technical challenges to grow mono-crystalline silicon of super-long, super-large and super-heavy features, respectively. Basing on this analysis, some countermeasures will be advised. Particularly, the continuous-charging CZ method (CCZ) will be discussed in detail and some results will be given. A technology roadmap combined with the CCZ technique for growing mono-crystalline silicon and the fluidized bed reactor (FBR) technique for silicon particle feedstock is recommended.

Keywords: mono-crystalline silicon, CCZ technique, solar cells

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INSULATING BAFFLE IN VB GROWTH

Presenting Author: Natasha Dropka

Topic: Modeling of Crystal Growth Processes

Format: Contributed

Session: 4, 3

Date: 8/2/2021

Time (in MDT): 3:30:00 PM

Authors: Natasha Dropka, Leibniz-Institut für Kristallzüchtung, Berlin, Germany; Aleksandar G. Ostrogorsky, Illinois Institute of Technology, Chicago, Illinois, United States

Interface shape under the insulating baffle in vertical Bridgman systems Natasha Dropka<sup>a</sup> and A.G. Ostrogorsky<sup>b</sup>, <sup>a</sup>Leibniz-Institut für Kristallzüchtung, Max-Born-Str. 2, 12489 Berlin, Germany, natascha.dropka@ikz-berlin.de <sup>b</sup>Illinois Institute of Technology, 10W 32nd street, Chicago, IL60616-3793, USA, AOstrogo@IIT.edu

Abstract

In the vertical Bridgman (VB) configuration, the shape of the solid-liquid (S-L) interface controls the yield and quality of single crystals. The concave interface is known to be unfavorable, promoting formation of defects and cracks, and reducing the yield of single crystals. The shape of the interface depends on: i) the thermal conductivities of the nearby materials, ii) the furnace temperature profile; iii) the growth rate and (iv) the direction and intensity of the melt flow. To reduce the concavity of the S-L interface, the crystal grower typically selects a crucible material having low thermal conductivity, reduces the growth rate and fine-tunes the temperature profile of the furnace. In this work, 3D numerical simulations were conducted using the commercial software Ansys CFX - to determine the impact of the thermal conductivity of the disk-shaped baffle positioned horizontally above the S-L interface [1,2]. The simulations were conducted for CdTe because CdTe and CZT are notoriously difficult to grow, in part due to their low thermal conductivity (λ<sub>CZT</sub> ~1 W/m-K). Thus, in the conventional VB configuration (without a baffle), the S-L interface of CZT is concave, even at a diminishing growth rate. We will present the results of the present numerical simulations conducted for a fused silica (SiO<sub>2</sub>) crucible, while three baffle materials were considered: i) POCO graphite (k<sub>POCO</sub>=60 W/m-K), 2) a solid fused silica disk, having thermal conductivity k<sub>SiO2</sub>=1.5 W/m-K, transparent to thermal radiation below 4.5 μm, and 3) an impermeable SiO<sub>2</sub> jacket packed with SiO<sub>2</sub> frit or microspheres, to minimize both heat conduction and thermal radiation (k<sub>effective</sub>=0.3 W/m-K). The numerical simulations demonstrate that the lower is the effective thermal conductivity of the baffle, the more convex the interface is. The role of the “insulating” baffle is to minimize the axial heat flow, allowing the external tubular heater to supply heat radially in, thus generating the desired convex interface.<br />

WEAK STEFAN FORMULATION FOR BULK CRYSTAL GROWTH WITH NON-SMOOTH INTERFACES

Presenting Author: Eyan Noronha

Topic: Modeling of Crystal Growth Processes

Format: Contributed

Session: 4, 4

Date: 8/2/2021

Time (in MDT): 3:45:00 PM

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Most heat transfer models for bulk crystal growth rely on the classical Stefan formulation to evaluate interface motion during phase change. However, when the interface is non-smooth the use of the classical Stefan formulation may lead to singularities. To address this problem, we propose a simulation model based on the weak formulation of the Stefan problem. Numerical solutions of the weak Stefan formulation are obtained using the finite volume method. This approach provides an energy-conserving discretization scheme that accurately evaluates heat transfer around non-smooth interfaces. We apply the weak formulation to numerically simulate the solidification of silicon in the horizontal ribbon growth process. Results exhibit a limitation on the ribbon's pull speed, which previous classical Stefan models have failed to demonstrate. A comparison of heat transfer between radiation and gas cooling shows that gas cooling increases the pull speed limit for the same amount of heat removed.
ADVANCED APPROACH FOR OXYGEN TRANSPORT SIMULATION IN CZ SILICON CRYSTAL GROWTH

Presenting Author: Dmitry Borisov

Topic: Modeling of Crystal Growth Processes

Format: Contributed

Session: 4, 5

Date: 8/2/2021

Time (in MDT): 4:00:00 PM

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AdvanceD Approach for oxygen transport simulation in cz silicon crystal growth<br />
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Modeling of oxygen transfer during Czochralski (Cz) silicon crystal growth still is a big challenge due to oxygen evacuation from the melt free surface [1], affected by strong anisotropy of turbulent mass transport. To predict the crystal oxygen concentration with good accuracy, usually a 3D LES/DNS simulation approach is required [2], which demands significant computation resources and time. We present the new advanced 2D axisymmetric Anisotropic Reynolds Averaged Navier-Stokes (ARANS) turbulence model, which is characterized by quite elaborated accuracy of predicting oxygen distribution for the different process conditions and crystal diameters and is significantly less power and time consuming in comparison to 3D unsteady modeling. After the growth of 215 mm diameter Si monocrystals, several 8-inch wafers cut from the crystals have been analyzed using the Fourier-transform infrared spectroscopy (FTIR) for oxygen concentration in facility of Fraunhofer CSP and iTechSolar. The crystal oxygen concentration has been decreased by about 10% by optimization of the growth process conditions using the new 2D ARANS approach. The comparison between experimental and calculated results is discussed in detail. This work was supported by the Foundation for Assistance to Small Innovative Enterprises (FASIE, Russia) within ERA.Net RUS Plus Project, grant number ERA-RUS-41114 0042017.<br />

INFLUENCE OF CRUCIBLE ROTATION ON THE TEMPERATURE AND OXYGEN DISTRIBUTIONS IN CZOCHRALSKI GROWN SILICON FOR PHOTOVOLTAIC APPLICATIONS

Presenting Author: Daniel Vizman

Topic: Modeling of Crystal Growth Processes

Format: Contributed

Session: 4, 6

Date: 8/2/2021

Time (in MDT): 4:15:00 PM

Authors: Daniel Vizman, West University of Timisoara, Timisoara, Romania Alexandra Popescu, West University of Timisoara, Timisoara, Romania Martin Bellmann, SINTEF Materials and Chemistry, Trondheim, Norway

The performance of single-crystalline silicon for photovoltaic applications is limited through the presence of oxygen. In Czochralski (Cz) single-crystal growth the dissolution of the quartz crucible at high temperatures contaminates the melt with oxygen, which is then reflected in the growing ingot. Most solar cells today are made from boron doped silicon (p-type). The ultimate efficiency potential of each material is limited by the presence of defects and impurities, which reduce the minority carrier lifetime. In Cz-silicon, the carrier lifetime is dominated by the well-known boron-oxygen defect. In order to study the influence of crucible rotation on the temperature and oxygen concentration distribution, four crucible rotation rates were considered, 2, 4, 6 and 8 rpm. Temperature boundary conditions for the local three-dimensional numerical simulations were taken from a two-dimensional global simulation. Information about the flow state were obtained from evaluating the amplitude of temperature fluctuations and from the corresponding Power Spectral Density. First, it can be observed that the temperature fluctuations are more intense near the crystal edge than at the center of the melt. The increase of crucible rotation generates, at first, an increase in temperature fluctuations and, after reaching a critical value, it generates a decrease in temperature fluctuations. The melt flow behavior at the crystal axis under the S-L interface is dominated by buoyancy and is less influenced by the increase of crucible rotation. Contrary to the central part, the melt flow near the crystal edge is strongly affected by the crucible rotation such that, at first, the increase of the crucible rotation rate (2 - 6 rpm) leads to an increase in the turbulence level of the melt convection. For a higher crucible rotation rate (8 rpm), the melt becomes once again less turbulent due to a higher centrifugal force that damps the flow convection. Regarding the O-concentration distribution, it was found that the concentration has a homogeneously radial distribution under the solid-liquid interface. Also, it was concluded that by increasing the crucible rotation rate, first the level of oxygen concentration under the S-L interface decreases and, from a critical crucible rotation rate, the O-concentration increases. For higher crucible rotation rates, the amplitude of oxygen concentration fluctuations is slightly increasing with the crucible rotation rate in opposite to the amplitude of temperature fluctuations, which is decreasing.
TOP-DOWN AND BOTTOM-UP MODELING OF AGGREGATION AND ASSEMBLY IN COMPLEX MATERIAL SYSTEMS

Presenting Author: Christopher Mundy

Topic: Modeling of Crystal Growth Processes

Format: Invited

Session: 3, 1

Date: 8/3/2021

Time (in MDT): 1:00:00 PM

Authors: Christopher Mundy, Pacific Northwest National Laboratory, Richland, Washington, United States

Herein, I will discuss progress in defining a theoretical framework to describe the assembly and aggregation processes in complex systems. It is well established that reduced models provide a useful path forward in describing nucleation and assembly. The experimental systems that we will consider will have different assembly outcomes that depend on the underlying solution conditions (pH, ionic strength, electrolyte). We will discuss our approach to modeling the effects of the solution conditions using the tools of colloidal theory in conjunction with molecular simulation. We will establish the important role of the short-range molecular detail in conjunction with long-range mean field phenomena to establish quantitative reduced models of assembly. Both bulk and interfacial systems will be considered. This work is supported by the U.S. Department of Energy (DOE), Office of Science, Office of Basic Energy Sciences (BES), Division of Material Sciences and Engineering and supported by the DOE, Office of Science, BES, Division of Chemical Sciences, Geosciences, and Biosciences. PNNL is a multiprogram national laboratory operated for the DOE by Battelle under contract no. DE-AC05-76RL01830.
CRISTAL STRUCTURES VIA SELF-ASSEMBLY SIMULATIONS

Presenting Author: Julia Dshemuchadse

Topic: Modeling of Crystal Growth Processes

Format: Invited

Session: 3, 3

Date: 8/3/2021

Time (in MDT): 1:30:00 PM

Authors: Julia Dshemuchadse, Cornell University, Ithaca, New York, United States

Crystallization occurs spontaneously in nature, seemingly with only minimal local information to guide it. While it might be intuitive that some high-symmetry building blocks can assemble a simple crystal, the growth of more complex structure types from a minimalistic set of rules is far more mysterious. We believe that a deeper understanding of how complex order emerges on any length scale can be gained by studying abstract particle models that mimic the behavior of both soft and hard condensed matter. We simulate the growth of a variety of crystal structures with mutually attractive point particles through classical molecular dynamics. We characterize the process of assembly, as well as the structural properties of the final assemblies under varying conditions. By quantifying the mechanisms occurring during the formation of a crystal, we begin to elucidate how complex, long-range ordered structures emerge from short-range interactions of remarkable simplicity. Our work contributes to a fundamental understanding of self-assembly processes into crystalline materials, thereby enhancing our ability to predict emergent crystal structures from local interactions, in turn enabling principled structural materials design.
MODELLING OF THE LOW-TEMPERATURE GROWTH OF ZINC OXIDE NANORODS IN BATCH REACTORS

Presenting Author: Ondřej Černohorský

Topic: Modeling of Crystal Growth Processes

Format: Contributed

Session: 3, 5

Date: 8/3/2021

Time (in MDT): 2:00:00 PM

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Low-temperature solution growth is an attractive method for the preparation of semiconductor nanostructures. This method is cost-effective, largely scalable, and can be operated at low temperatures below the boiling point of water, which allows for the deposition on a large variety of substrates including fabrics or polymers. Despite the widespread applications of low-temperature solution growth, basic phenomena taking place during the growth are still not well understood. Usually, the growth is carried out in batch reactors, where the precursor solutions are mixed and heated to desired growth temperature, which produces the supersaturation necessary for the growth. As the growth continues, the concentration of chemical precursors, and thus also the supersaturation at the interface between the nanostructures and the solution, decreases with time, which can affect the growth mechanism of the nanostructures and also their shape and physical properties. To understand the basic phenomena during the growth, it is necessary to estimate the interface supersaturation. The interface supersaturation is, however, a complex function of many parameters such as the growth temperature, concentration of reactants, or pH of the growth solution. These parameters vary with time as the growth proceeds. Another important factor affecting the interface supersaturation is the transport of the growth units towards the interface, which depends on the diffusion coefficient of the growth units in the solution, the growth velocity of the nanostructures, and their density and arrangement on the substrate.

We analyzed the time evolution of the growth of ZnO nanorod arrays by chemical bath deposition together with the time evolution of the chemical composition of the growth solution. The growth was conducted on two types of substrates: (a) sol−gel seed layers with high nanorod density, (b) and on GaN substrates patterned by focused ion beam lithography with precise control of the geometric arrangement of the nanorods in the arrays. We identified the diffusion-limited growth for the arrays with a high density of nanorods, where the reactants are consumed at a high rate, and thus the supply of the reactants from the bulk solution via diffusion is the rate-limiting process. Consequently, the height of the nanorods is sensitive to the position within the array. On the other hand, in the reaction-limited growth regime, the nanorods grow with the same growth rate, independent of the position.
within the pattern. The interface supersaturation was calculated using the numerical solution of diffusion-reaction equation using experimentally determined growth velocities and reaction constants.
POPULATION-BALANCE STUDY OF PROTEIN CRYSTAL GROWTH FROM SOLUTION USING A HYPERBOLIC RATE LAW

Presenting Author: Douglas Barlow

Topic: Modeling of Crystal Growth Processes

Format: Contributed

Session: 3, 6

Date: 8/3/2021

Time (in MDT): 2:15:00 PM

Authors: Douglas Barlow, Jacksonville University, Jacksonville, Florida, United States Emilie Lavoie-Ingram, Jacksonville University, Jacksonville, Florida, United States Jahan Bayat, Purdue University Fort Wayne, Fort Wayne, Indiana, United States

Kinetic data for crystal size, recently reported for bulk protein crystal growth from solution, is shown to obey a hyperbolic rate law. Given this rate law, the linear growth rate is established and mass-balance methods are then used to derive analytic time dependent expressions for the nucleation rate, the supersaturation and the distribution function for crystal sizes. Our population-balance approach involves a truncated Fokker-Planck equation along with an integro-differential equation for mass conservation. This model is used to describe two cases of protein crystal growth from solution for which kinetic size data has been reported--one lysozyme, the other beta-lactoglobulin. Additionally, we show that this empirical rate law for crystal size is approximately related to the Burton-Cabrera-Frank growth rate. Further, insight into the two-step, or rather multi-step, process is obtained. In both growth cases studied here, the process was multi-step. We hypothesize that the hyperbolic tangent rate law most accurately describes growth beginning at the time when the crystal phase becomes the more dominate form in the solution and can thus be used to predict a cross-over time when the final intermediate stage is about to be depleted.
CRYSTAL GROWTH BY DIMERS - THE CASE OF OLANZAPINE

Presenting Author: Jeremy Palmer

Topic: Modeling of Crystal Growth Processes

Format: Invited

Session: 4, 1

Date: 8/3/2021

Time (in MDT): 3:00:00 PM

Authors: Jeremy C. Palmer, University of Houston, Houston, Texas, United States

Olanzapine is an antipsychotic drug used to treat schizophrenia and bipolar disorder. Of the more than 60 known crystalline forms of olanzapine, all but one contain molecules arranged in centrosymmetric dimer motifs. The prevalence of this motif has led to speculation that the dimers preform in solution. Here, I will discuss results from our recent study [Warzecha et al., Nat. Chem., 12, 914-920, (2020)] providing the first unambiguous evidence to support this hypothesis. Using a combination of time-resolved in situ scanning probe microscopy and molecular simulation, we show that the crystals grow through a non-classical mechanism involving the incorporation of preformed dimers. The growth rate of crystal layers exhibits a quadratic dependence on the solute concentration, characteristic of the second-order kinetics of the incorporation of dimers. Our analysis reveals that growth by dimers is preferred due to accumulation of adsorbed dimers on the crystal surface, where it is complemented by dimerization and expedites dimer incorporation into growth sites.
DIABAT METHOD FOR POLYMORPH FREE ENERGIES: EXTENSION TO MOLECULAR CRYSTALS

Presenting Author: Baron Peters

Topic: Modeling of Crystal Growth Processes

Format: Invited

Session: 4, 3

Date: 8/3/2021

Time (in MDT): 3:30:00 PM

Authors: Baron Peters, University of Illinois, Champaign, Illinois, United States Kartik Kamat, University of Illinois, Champaign, Illinois, United States Rui Guo, University College, London, United Kingdom Sally Price, University College, London, United Kingdom Susan Reutzel-Edens, Eli Lilly, Indianapolis, Indiana, United States

Lattice-switch Monte Carlo and the related diabat methods have emerged as efficient and accurate ways to compute free energy differences between polymorphs. In this work, we introduce a one-to-one mapping from the reference positions and displacements in one molecular crystal to the positions and displacements in another. Two features of the mapping facilitate lattice-switch Monte Carlo and related diabat methods for computing polymorph free energy differences. First, the mapping is unitary, so that its Jacobian does not complicate the free energy calculations. Second, the mapping is easily implemented for molecular crystals of arbitrary complexity. We demonstrate the mapping by computing free energy differences between polymorphs of benzene and carbamazepine. Free energy calculations for thermodynamic cycles, each involving three independently computed polymorph free energy differences, all return to the starting free energy with an extremely high degree of precision. The calculations provide a force field independent validation of the method, and demonstrate the precision of the individual free energy differences.
MESOPHASES CAN ASSIST ZEOLITE NUCLEATION

Presenting Author: Andressa Antonini Bertolazzo

Topic: Modeling of Crystal Growth Processes

Format: Contributed

Session: 4, 5

Date: 8/3/2021

Time (in MDT): 4:00:00 PM

Authors: Andressa Antonini Bertolazzo, University of Utah, Salt Lake City, Utah, United States Laura J. S. Lopes, Los Alamos National Lab, Los Alamos, New Mexico, United States Debdas Dhabal, University of Utah, Salt Lake City, Utah, United States Valeria Molinero, University of Utah, Salt Lake City, Utah, United States

The zeolite synthesis is a well known example of non-classical nucleation. Structure directing agents (SDA) are used to facilitate zeolite formation. After mixing the silica source, SDA and solvent, nanoparticles with a rich silica core and SDA shell forms and, with time, they aggregate and evolve to a more ordered structure that is the birth place of zeolite crystals. Spectroscopy techniques are not able to characterize this order evolution in molecular scale. Considering that mesophases are known to be part of mesoporous silica formation in similar synthesis condition to zeolite and also that they have intermediate order between liquid and crystal, we hypothesize that the intermediate phase can be a mesophase. We investigate how the stability of a mesophase impacts zeolite formation. Using a simple model for zeolites, we show that a mesophase appears in the pathway of zeolite formation even when it is unstable. We propose that mesophases could be the intermediate phase for zeolites with large channels. We suggest that the order of the SDA should also be followed during synthesis, which would clarify the existence of a mesophase in the zeolite nucleation pathway.
HOW DO ANTFREEZE PROTEINS RECOGNIZE AND BIND ICE IN A VAST EXCESS OF WATER?

Presenting Author: Amish Patel

Topic: Modeling of Crystal Growth Processes

Format: Invited

Session: 3, 1

Date: 8/4/2021

Time (in MDT): 1:00:00 PM

Authors: Amish Patel, University of Pennsylvania, Philadelphia, Pennsylvania, United States  Sean Marks, University of Pennsylvania, Philadelphia, Pennsylvania, United States  Aniket Thosar, University of Pennsylvania, Philadelphia, Pennsylvania, United States

The preference that certain surfaces display for ice over liquid water enables them to facilitate the formation of ice through heterogeneous nucleation. Interestingly, such a preference is also responsible for life and death in the frigid polar environments. Fish, insects and other organisms are able to survive such forbidding environments with the help of remarkable molecules known as antifreeze proteins (AFPs), which suppress freezing by binding nascent ice nuclei and passivating them. Thus, being able to preferentially bind ice in a vast excess of water is the key to AFP function. However, how AFPs are able to perform one of the most challenging molecular recognition tasks in all of biology - distinguishing between two different phases of water - has long been a source of amazement and intrigue; not only are there no chemical differences to leverage, the structural differences between water and ice are also subtle. Early suggestions that crystalline materials with a lattice spacing similar to that of ice ought to interact preferentially with ice, have now been replaced with a much more nuanced understanding that while lattice matching may help a surface interact better with ice, numerous other factors such as surface curvature, roughness, and flexibility, also play an important role. Indeed, none of the available AFP structures appear to rely on lattice matching; instead, they display both hydrophobic and hydrophilic residues at the putative ice-binding sites. Moreover, the chemical pattern of the ice-binding site varies from protein to protein, and the ability of AFPs to suppress freezing depends sensitively on this pattern, so that even point mutations can render them non-functional. Clearly, the chemical template presented by the AFP surfaces confers them with superior ice-binding ability. It stands to reason that this template, and thereby the ability of AFPs to bind ice, must be manifest in certain characteristics of the water in the vicinity of the AFPs ice-binding site. However, what these signatures are, and how they are related to the ability of AFPs to bind ice, as well as the precise mechanism by which these diverse AFPs bind to ice nuclei and inhibit their growth remains unclear. Here we address these questions using a combination of molecular simulations and specialized enhanced sampling techniques. By uncovering the molecular basis for the binding of AFPs to ice, we hope that our work will pave the way for the development of synthetic inhibitors of ice nucleation.
MOLECULAR DYNAMICS INVESTIGATION OF CRYSTAL-MELT INTERFACE KINETICS DURING THE HORIZONTAL RIBBON GROWTH OF SILICON

Presenting Author: Victor Fabiyi

Topic: Modeling of Crystal Growth Processes

Format: Contributed

Session: 3, 3

Date: 8/4/2021

Time (in MDT): 1:30:00 PM

Authors: Victor Abolarin Fabiyi, Clarkson University, Potsdam, New York, United States  Brian Helenbrook, Clarkson University, Potsdam, New York, United States  Eunsu Paek, Clarkson University, Potsdam, New York, United States

Horizontal ribbon growth (HRG) of single-crystal silicon wafers is an approach for fabricating high-quality silicon wafers for solar cells faster and at lower costs than the conventional Czochralski growth process (CZ). However, the horizontal ribbon growth commercialization has been stalled by the lack of fundamental understanding of the crystal-melt interface's physical processes. In this work, we provide atomistic insights into the growth processes of HRG by modeling a continuous silicon crystal growth from molecular dynamics (MD) using the forced velocity simulations (FVS) approach. We studied nucleation events and various growth modes of silicon crystal from its melt at high pulling speeds (<i>~0.005 – 0.05 Å/ps</i>) and determined kinetics based on the identified growth-undercooling relationships. We also explain the instabilities that develop at higher pulling speeds, especially on step structures of silicon vicinal to the low index Si(111) crystal orientation from MD simulations. The determination of interface temperature without thermostat effects facilitated by the FVS method leads to increased kinetic coefficients for rough and stepped growth modes. We report an increase in kinetic coefficient as step-size increased and a breakdown of linear velocity-undercooling relationship at a large step-size of <i>23.10 Å</i> due to the onset of interface roughening. The analysis of temperature gradients across the melt and crystal parts of the interface showed that interface roughening develops at higher pull speeds when heat removal from the liquid is reduced significantly. Crystal-melt interface instabilities appear in the form of grooves that served as nucleation sites for the formation of grain boundaries and dislocations at undercooling as low as ~<i>4 K</i> a value lower than previously observed from molecular dynamics.
THERMODYNAMIC INTEGRATION PATHWAYS FOR CALCULATING IMPURITY AND DEFECT FREE ENERGIES IN SILICON

Presenting Author: Jinping Luo

Topic: Modeling of Crystal Growth Processes

Format: Contributed

Session: 3, 4

Date: 8/4/2021

Time (in MDT): 1:45:00 PM

Authors: Jinping Luo, Xi’an Jiaotong University, Xi’an, China Chenyang Zhou, Xi’an Jiaotong University, Xi’an, China Yunjie Cheng, Xi’an Jiaotong University, Xi’an, China Lijun Liu, Xi’an Jiaotong University, Xi’an, China Talid Sinno, University of Pennsylvania, PHILADELPHIA, Pennsylvania, United States

The segregation of impurities and formation of intrinsic point defects are fundamentally important in silicon crystal growth and strongly impact the quality of the resulting crystal for both microelectronic and photovoltaic applications. In this presentation, we describe a framework for computing impurity segregation coefficients and total formation free energies of intrinsic point defects based on alchemical thermodynamic integration pathways. We show that this approach is an efficient way to calculate free energies in both solid and liquid phases with full consideration of both configurational and vibrational entropic contributions.<br />We first consider the equilibrium segregation of interstitial oxygen and substitutional carbon in silicon using Tersoff-based potential models. The estimated carbon segregation coefficient is found to be in good agreement with experimental values, while that of oxygen is significantly underestimated. We discuss possible reasons for the latter discrepancy from the perspective of limitations of the empirical potential model and highlight the need for incorporating new metrics in future empirical potential fitting. In particular, we show that errors in the predicted density of the bulk liquid and solid phases can strongly impact the predicted segregation coefficient, particularly for interstitial impurities, such as oxygen.<br />Next, the formation free energies of vacancies and self-interstitials in silicon are evaluated comparatively based on several empirical interatomic potential models. It is shown that both the configurational entropy and anharmonicity constitute very important contributions to the total entropy at elevated temperatures, which together result in a large decrease of the point defect formation energies. We analyze the anharmonic feature of the vacancy ground state basin as well as the density of states (DOS) in the crystal and show that the sources of high entropy are qualitatively very different among the different potential models.
FORMATION OF STRUCTURAL IMPERFECTIONS IN DISLOCATION-FREE SINGLE CRYSTALS WITH COVALENT AND METALLIC BONDS

Presenting Author: Vitalyi Talanin

Topic: Modeling of Crystal Growth Processes

Format: Contributed

Session: 3, 5

Date: 8/4/2021

Time (in MDT): 2:00:00 PM

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Igor Evgenievich Talanin, Zaporozhye Professional Pedagogical College, Zaporozhye, Ukraine

We examined the effect of impurity on defect formation during crystal growth and introduced into the classical theory the crystal growth parameters (growth rate, temperature gradients, cooling rate, and crystal diameter). This allowed us to link together the complex processes of interaction of intrinsic point defects and impurities, to consider the transformation of the defect structure during crystal cooling. The results were presented in monograph [1]. A model of high-temperature precipitation of impurities was developed, which can be used to describe the formation of precipitates near the crystallization front and their transformation during crystal cooling. The diffusion model made it possible to conclude that it has common character and can be applied to perfect crystals of other materials. As example, we considered dislocation-free single crystal of germanium [2]. Since the diffusion model of defect formation is based on the model of high-temperature precipitation of impurities, precipitates formed near crystallization front are responsible for creation of a defect structure. The theoretical consideration of the diffusion model was based on two theories of the formation of a solid. These two theories (classical and probabilistic) were based on completely different physical principles. Despite this, they led to completely identical results and confirmed the fact that high-temperature precipitation is primary when creating a defect structure in silicon and germanium crystals [3]. We made the assumption that high-temperature precipitation is main in the process of defect formation in crystals of various types. This assumption, first of all, concerns high-temperature precipitation in metal crystals. The aim of this work is to show the possibility of high-temperature precipitation in metals (dislocation-free copper single crystals) using the classical and probabilistic approaches. To achieve this, it is necessary to show the possibility of creating stable impurity complexes at high temperatures. The results suggest that high-temperature precipitation of impurities is a main of the defect formation processes in crystals with covalent and metallic bonds.

NEW MODELS FOR PARTICLE MIGRATION UNDER THERMAL GRADIENTS

Presenting Author: Swanand Pawar

Topic: Modeling of Crystal Growth Processes

Format: Contributed

Session: 3, 6

Date: 8/4/2021

Time (in MDT): 2:15:00 PM

Authors: Swanand C. Pawar , University of Minnesota, Minneapolis, Minnesota, United States  Kerry Wang , University of Minnesota, Minneapolis, Minnesota, United States  Nathan T. Morgan , University of Minnesota, Minneapolis, Minnesota, United States  Jeffrey J. Derby , University of Minnesota, Minneapolis, Minnesota, United States

Large, second-phase particles, typically tens of microns in size, are formed during crystal growth when solute-rich liquid droplets are shed by deep solidification cells that form under constitutionally unstable conditions. This presents a special challenge for the growth of large, high-quality crystals of cadmium telluride (CdTe) and cadmium zinc telluride (CZT) needed for gamma spectrometers, in which tellurium-rich particles are deleterious to the performance of such devices. Brine inclusions found in natural sea ice represent another example of second-phase particles embedded in crystalline ice. Temperature gradient zone melting (TGZM) is a technique that may be used to remove these inclusions trapped within a crystal during growth. It was first discovered when Arctic explorers found that aged sea ice was potable due to the thermal migration of brine packets under diurnal heating of floating ice by the sun. The migration of these particles occurs at temperatures high enough to melt the solutally-enriched particles embedded within the surrounding solid matrix. Under a temperature gradient, the warmer end of the particle melts and the cooler end solidifies, moving it uphill along the gradient. The different solute solubility at the temperatures at each end of the particle gives rise to a concentration gradient, with diffusion of the solute across the particle controlling the migration velocity. In addition, solute is conserved within the particle while climbing the gradient, which leads to a lengthening of the particle to reduce its average solute level consistent with the thermodynamics of the liquidus curve. In this presentation, we describe a new, one-dimensional, pseudo-steady state model derived to describe particle migration in TGZM. This gives an analytical, closed-form solution for particle speed and length as a function of time. The pseudo-steady state assumption is assessed by comparing it with a detailed, one-dimensional finite difference model. Predictions from this model are shown to be in excellent agreement with experimental measurements of a brine-ice system. We finally discuss finite element calculations proposed to address particle shape evolution in which long particles are postulated to pinch-off to form smaller particles during migration. This work has been supported in part by U.S. Department of Homeland Security, 2012-DN-077-ARI066-06, and no official endorsement should be inferred.
SMART DEVELOPMENT OF VERTICAL GRADIENT FREEZE CRYSTAL GROWTH RECIPES

Presenting Author: Natasha Dropka

Topic: Modeling of Crystal Growth Processes

Format: Invited

Session: 4, 1

Date: 8/4/2021

Time (in MDT): 3:00:00 PM

Authors: Natasha Dropka, Leibniz Institute for Crystal Growth, Berlin, Germany Klaus Böttcher, Leibniz Institute for Crystal Growth, Berlin, Germany Martin Holena, Leibniz Institute for Catalysis, Rostock, Germany

The crystal growth process development is a difficult task due to a multi-disciplinary nature of the phenomena, phase change, scaling problems, optimization of numerous interdependent parameters and especially the dynamic character of the process with a pronounced time lag. Common experimental and CFD approaches to the derivation of the crystal growth process recipes are laborious, costly and time consuming. The common optimization approach for process development that is typically implemented in a commercial crystal growth software (e.g. <sup>1,2</sup>) is based on “inverse modelling” strategy described in <sup>1</sup>. Still, this approach is limited to a small number of independent parameters. Recent tremendous success of artificial neural networks (ANN) in detecting the complex patterns and relationships in non-linear static and dynamic data sets in other fields trigger the first feasibility studies on the application of ANN for the prediction of transport phenomena in the crystal growth furnaces of semiconductors and optimization of the growth parameters i.a. <sup>3-6</sup>. In this study, two supervised machine learning techniques: Feed Forward ANN and Regression Trees (Decision Trees where the target variables are real numbers) were applied. As a process example, Vertical Gradient Freeze growth of 4 inch GaAs crystals was used. Training data were generated by 2D CFD simulations. ANN technique was applied to solve both, well-posed “normal” and ill-posed “inverse” problems by correlating heating power of 5 heaters and growth rate on the one hand and axial temperature gradients in the melt and crystal, interface deflection and interface position on the other hand. We also used Regression Trees to analyze and rank influences of process parameters (the power of heaters) on the growth of low-cost high-quality crystals. The latter is characterized i.a. by the high growth velocity (guaranteed by predefined typical values of axial temperature gradients in the GaAs) and by the flat solid/liquid interface. Pros and cons of this approach will be discussed and results compared with “inverse modelling” strategy given in <sup>1</sup>.<sup>1</sup>.<sup>1</sup> M. Kurz, G. Müller, Journal of Crystal Growth 208 (2000) 341-349. <sup>2</sup> https://www.str-soft.com/crystal-growth/vgf-iii-v/ <sup>3</sup> Y. Dang, L. Liu, Z. Li, Journal of Crystal Growth 522 (2019) 195-203. <sup>4</sup> Y. Tsunooka et al., CrystEngComm 20 (2018) 6546-6550. <sup>5</sup> A. Boucetta et al., Applied Physics Express 12 (2019) 125503. <sup>6</sup> S. Schimmel et al., Crystals 11(2021) 254-281.
THERMAL ANALYSIS OF AL DROPLET CRYSTALLIZATION AND MODELING OF THE NUCLEATION PROCESS: HOW TO INTERPRET EXPERIMENTAL DATA?

Presenting Author: Zdeněk Kožíšek

Topic: Modeling of Crystal Growth Processes

Format: Contributed

Session: 4, 3

Date: 8/4/2021

Time (in MDT): 3:30:00 PM

Authors: Zdeněk Kožíšek, Institute of Physics of the Czech Academy of Sciences, Prague, Czech Republic
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The crystallization of Aluminum (Al) droplet of the mass m = 9.9 mg was detected by the Differential Scanning Calorimetry (DSC) at the temperature $T_c \approx 642 \text{°C}$ (undercooling $\Delta T \approx 18 \text{ K}$) using a broad range of cooling rates 2-20 K/min. In the next step, the repeated DSC measurements at the isothermal conditions with undercooling of ca. $\Delta T \approx 6 \text{ K}$ discovered that the crystallization event occurred after a relatively long time delay $\tau \approx 10 - 50 \text{ min}$. Experimental data confirmed the stochastic nature of crystal nucleation similarly to other systems [1].

At the crystallization temperature $T_c$, we analyzed the DSC data using the Johnson-Mehl-Avrami (JMA) model under the assumption that nucleation and growth occur at $T_c$ and determined the kinetic Avrami coefficient $n = d + 1 < 2$. However, the JMA model fails as the dimensionality of the growth $d < 1$ is unrealistic.

The Al droplet crystallization at the undercooling $\Delta T \approx 6 \text{ K}$ was modeled via numerical solution of the standard kinetic model of nucleation [2] to determine the size distribution of nuclei. As the Al growth rate is extremely high (tens of meters per second), we supposed the formation of only several nuclei and determined the interfacial energy limit, when the first nuclei were formed within the system. The experimental value of the time delay of crystallization event is high in respect to high growth rate and, thus, the crystallization probably occurs by a two-step mechanism [2], i.e. when the structure of small subcritical clusters differs from the larger ones and thus the nucleation kinetics is slow.

SIMULATION-AIDED DESIGN AND INTERPRETATION OF RESULTS OF MICROGRAVITY-BASED SOLIDIFICATION EXPERIMENTS

Presenting Author: Vladimir Riabov

Topic: Modeling of Crystal Growth Processes

Format: Contributed

Session: 4, 4

Date: 8/4/2021

Time (in MDT): 3:45:00 PM


The preparation and interpretation of microgravity experiments conducted on the International Space Station (ISS) can be challenging because of the remote location of the equipment. Although a “ground unit” is typically available on Earth, it is not located in the laboratory of the principal investigator. Furthermore, test experiments in the ground unit cannot fully duplicate heat transfer conditions of the weightless environment, and thus be a reliable reference for experiment design. Under such conditions, numerical simulations are a valuable tool both for preparing the experiments and interpreting the results obtained under terrestrial and micro-gravity conditions. In this work, we developed a detailed 3D model of the “SUBSA” furnace located at the ISS, and demonstrate its use in our present investigation which includes melt growth and vapor growth of InI crystals on the ISS. In 2002, the SUBSA furnace was designed and built for the growth of InSb crystals in the Microgravity Science Glovebox (MSG) at the ISS. The SUBSA furnace features a transparent section without heating elements, where the axial temperature gradient is high. In our present investigation, we have used the same furnace to grow four InI crystals from the melt, and two InI crystals from the vapor phase (2018-2021). InI crystals have ~20 times lower thermal conductivity than InSb crystals. As a result, during melt growth, the InI crystals were exposed to extremely high temperature gradients. To reduce the axial temperature gradient, we added external jackets made from high thermal conductivity material to the growth ampoules. The SUBSA furnace could not be modeled as asymmetric because of its rectangular shape and right-angled transparent section, which contains a convoluted geometry. The rectangular shape of the transparent section further complicates modelling of radiative heat transfer, which dominates in the zone. At present, numerical simulations are being conducted to resolve an apparent discrepancy between the readings of the 5 thermocouples located in the SUBSA furnace, and the observed position of the solid and molten material. The 3D simulation will be presented, along with the calibration and growth experiment results conducted in microgravity and in the SUBSA ground unit. The developed model should be useful for upcoming microgravity investigations planned to be conducted in the SUBSA facility.
NUMERICAL OPTIMIZATION OF GAS MANAGEMENT FOR THE GROWTH OF HIGH-PURITY, HIGH-QUALITY GERMANIUM SINGLE CRYSTALS

Presenting Author: Natasha Dropka

Topic: Modeling of Crystal Growth Processes

Format: Contributed

Session: 4, 5

Date: 8/4/2021

Time (in MDT): 4:00:00 PM

Authors: Natasha Dropka, Jörg Fischer, Alexander Gybin, Nikolay Abrosimov, Radhakrishnan Sumathi

High Purity Germanium (HPGe) crystals are essential for radiation detection in astrophysics in the endeavor to understand the nature of universe. As a member of the international GERDA (The GERmanium Detector Array [1]) / LEGEND (Large Enriched Germanium Experiment for Neutrinoless double beta Decay [2]) collaboration, Leibniz-Institut für Kristallzüchtung (IKZ) has been engaged in the development of HPGe Czochralski (Cz) crystal growth technology, i.e. the growth process and the equipment [3]. The Cz growth of HPGe crystals with a targeted net concentration of electrically active impurities in the range of 10<sup>9</sup> - 10<sup>10</sup> cm<sup>-3</sup> is a challenging task that puts extraordinary hard constrains on i.a. a crystal growth furnace design, process parameters and a choice/assignment of hot zone materials. The goal of this study was to investigate the influence of gas management, particularly the geometry of the hot zone (open vs. closed purging system), choice of gas atmosphere (H<sub>2</sub> vs. Ar) and gas flow rates (0-5 l<sub>N</sub>/min) on the transport phenomena in the Cz-HPGe growth of 2-inch crystals. The final goal was to optimize the gas management for the growth of high quality Ge crystals with even larger diameters. For this purpose, a series of 3D CFD and electro-magnetic simulations was performed using commercial software Ansys. The obtained results were verified with crystal growth experiments performed in in-house Cz furnace adopted for this purpose. The numerical findings will be discussed and the most influential features identified with respect to the crystal quality and the scale up.<br/>

Extended Nucleation and Superfocusing in Colloidal Nanocrystal Synthesis

Presenting Author: Celso de Mello Donega

Topic: Nanocrystals, quantum dots, and nanowires

Format: Invited

Session: 2, 1

Date: 8/3/2021

Time (in MDT): 10:30:00 AM

Authors: P. Tim Prins,† Federico Montanarella,† Kim Dümbgen,‡ Yolanda Justo,‡ Johanna C. van der Bok,† Stijn O.M. Hinterding,† Jaco J. Geuchies,† Jorick Maes,‡ Kim De Nolf,‡ Sander Deelen,§ Hans Meijer,§ Thomas Zinn,# Andrei V. Petukhov,† Freddy T. Rabouw,† Daniel Vanmaekelbergh,† Zeger Hens,‡ and Celso de Mello Donega†,*

The hot injection synthesis of colloidal semiconductor nanocrystals is renowned for producing nanocolloids with superb size dispersions.1-4 This results in ensembles with optical properties closely resembling those of each individual nanocrystal,1,2 which has proven essential for the application of semiconductor nanocrystals in a variety of technologies (displays, lighting, photodetection, photovoltaics, luminescent solar concentrators). Burst nucleation and diffusion-controlled size focusing during growth have been invoked to rationalize this characteristic,5,6 yet experimental evidence supporting the pertinence of these concepts is scant. Using a well-established CdSe nanocrystal synthesis7 followed with in situ X-ray scattering, we show that nucleation is an extended event that overlaps with growth and can last for 15-20% of the reaction time.8 Moreover, we find that size focusing outpaces predictions of diffusion-limited growth. This observation supports the conclusion that nanocrystal growth is dictated by the surface reactivity, which drops sharply for larger nanocrystals. Kinetic reaction simulations demonstrate this so-called superfocusing can lengthen the nucleation period and promote size-focusing. The finding that narrow size dispersions can emerge from the counteracting effects of extended nucleation and reaction-limited size focusing ushers in an evidence-based perspective that turns hot injection into a rational scheme to produce monodisperse semiconductor nanocolloids.
Small Angle X-ray Scattering insights into the fundamental processes governing nucleation and growth of colloidal nanocrystals

**Presenting Author:** Benjamin Abecassis

**Topic:** Nanocrystals, quantum dots, and nanowires

**Format:** Invited

**Session:** 2, 3

**Date:** 8/3/2021

**Time (in MDT):** 11:00:00 AM

**Authors:** None

Probing the physicochemical processes at play during the formation of colloidal nanocrystals is hard because one needs to look at small time and length scales in solution at harsh temperature and chemical conditions. We will show how it is possible to make progresses in this direction by using small angle X-scattering (SAXS) at synchrotrons. We will first recall some basic principles on SAXS and show how this technique can yield quantitative information on nucleation and growth of nanocrystals in solution providing that adapted sample environments are used. Afterwards, we will detail how the formation mechanism of semi-conducting quantum dots and nanoplatelets can be assessed using this method and provide unprecedented insight which complements other techniques.
Abstract Book - ACCGE-22//OMVPE-20

Monitoring Time Evolution of the Local Structure of Semiconductor Nanocrystals with X-rays during Synthesis

Presenting Author: Sanjit K. Ghose

Topic: Nanocrystals, quantum dots, and nanowires

Format: Invited

Session: 2, 5

Date: 8/3/2021

Time (in MDT): 11:30:00 AM

Authors: Names of co-authors: Matthew Greenberg, Jonathan Owen, Ai Kagawa

Modern advanced functional materials are complex in nature or by design, and serve a wide array of applications from energy production and storage to advanced manufacturing. Most of the modern synthesis processes in the solid state, from the melt, or in solution, remain an Edisonian process of trial and error. Designing and synthesizing the next-generation of materials requires a means to monitor the changes occurring along the reaction pathway during synthesis. These studies can offer a fundamental understanding of the physical and chemical changes during synthesis that is required to rationally steer the reaction or transformation process towards targeted product structures and properties. Advanced synchrotron X-ray facilities have been very successful in providing the necessary tools for time-resolved analyses of the synthesis processes. The major advantage of Synchrotron X-ray techniques over other techniques is the non-invasive probing with an atomic resolution of the structure and/or state of stable or transient species during synthesis stages (mixing of the reactants, pre-nucleation, nucleation and growth). In this presentation, I shall provide examples of monitoring time resolved structure of colloidal semiconductor nanocrystals — PbS/PbSe and CsPbX3 (X=Cl,Br,I) — during their synthesis stages using synchrotron X-ray scattering and diffraction techniques from NSLS II. I shall conclude my presentation with an outlook on a few on-going efforts in high throughput & intelligent measurements at NSLS II using Artificial Intelligence & Machine Learning techniques.
Discrete Growth in Semiconductor Nanocrystals: Nanoplatelets and Magic-Sized Clusters

Presenting Author: David J. Norris

Topic: Nanocrystals, quantum dots, and nanowires

Format: Invited

Session: 3, 1

Date: 8/3/2021

Time (in MDT): 1:00:00 PM

Authors: David J. Norris, ETH Zurich

Semiconductor nanocrystals (NCs) typically grow through continuous, incremental addition of material. Slight differences in the growth process between individual crystallites cause statistical distributions in their size and shape, which are detrimental for their optical properties. Consequently, much work has focused on improving synthetic protocols to control these distributions. Interestingly, during these efforts, syntheses were discovered that exhibit a different type of growth process. The NCs jump from one discrete size to the next in a series. Through purification, a specific size can then be isolated, providing an alternative approach to uniform NCs. Unfortunately, the fundamental mechanism behind such discrete growth and how it differs from the continuous process have remained poorly understood.

In this talk, we will discuss two major classes of NCs that have exhibited discrete growth: semiconductor nanoplatelets (NPLs) and magic-sized clusters (MSCs). NPLs are quasi-two-dimensional crystallites that exhibit a precise thickness of only a few atomic layers but much larger lateral dimensions. MSCs are isotropic particles for which only specific “magic” sizes appear during synthesis, presumably due to their enhanced stability over particles that are slightly smaller or larger. We have recently worked to develop a general understanding of the growth mechanism behind discrete growth in these semiconductor NCs.1–4 We begin by describing a simple model that can explain the highly anisotropic shape of NPLs. We then adapt this model to see if it can also rationalize the growth of MSCs. While differences do exist between NPLs and MSCs, we find that the growth of these materials are closely connected. We believe that by understanding the underlying process of NPLs and MSCs, this process can be exploited more broadly, potentially moving us toward more uniform nanomaterials.
Halides ligands in II-VI semiconductor nanoplatelets: a new tool for stress release and design of thick nanoplatelets.

**Presenting Author:** Sandrine Ithurria

**Topic:** Nanocrystals, quantum dots, and nanowires

**Format:** Invited

**Session:** 3, 3

**Date:** 8/3/2021

**Time (in MDT):** 1:30:00 PM

**Authors:** Nicolas Moghaddam, Corentin Dabard, Hong Po, Xiang Zhen Xu, Thomas Pons, Emmanuel Lhuillier, Sandrine Ithurria

Two-dimensional II-VI semiconductor nanoplatelets (NPLs) present exceptionally narrow optical features due to their thickness defined at the atomic scale. Since thickness drives the band-edge energy, its control is of paramount importance. The native carboxylate ligands can be replaced by halides ligands co-stabilized by amines. This exchange induced a red shift of the optical features. And, the improved surface passivation leads to an increase in the fluorescence quantum efficiency. At high temperature, these halides ligands can also partially dissolve cadmium chalcogenide NPLs through the edges. The released monomers then recrystallize on the wide top and bottom facets, leading to an increase in NPL thickness. This dissolution/recrystallization process is used to increase NPL thickness from 3 MLs to 9 MLs in steps of 2 monolayers. When the metal halide precursor is co-introduced with a chalcogenide precursor, core/shell homo- and heterostructures are achieved. Finally, when an incomplete layer is grown, NPLs with steps are synthesized. These stress-free homostructures are comparable to type I heterostructures, leading to recombination of the exciton in the thicker area of the NPLs. Following the growth of core/crown and core/shell NPLs, it affords a new degree of freedom for the growth of structured NPLs with designed band engineering, which has so far been only achievable for heteromaterial nanostructures.
ADVENT OF PLASMONIC BEHAVIOR - NUCLEATION AND GROWTH OF GOLD NANOPARTICLES PROBED BY NONLINEAR OPTICAL SPECTROSCOPY

Presenting Author: Yovan De Coene

Topic: Nanocrystals, quantum dots, and nanowires

Format: Contributed

Session: 3, 5

Date: 8/3/2021

Time (in MDT): 2:00:00 PM


In 1951 Turkevich pioneered a simple method to prepare monodisperse gold nanoparticles through reduction of chloroauric acid by trisodium citrate. While its simplicity makes it one of the most widely used methods until this day, the underlying mechanism of the Turkevich synthesis is complex, consisting of multiple nucleation and growth stages. Particularly the early growth stages are, despite decades of research, still poorly understood.

We recently developed in-situ techniques based on second- and third harmonic light scattering, to study the self-assembly and crystallization of polymers and metal-organic frameworks, opening a window into structural changes occurring during these processes. By combining harmonic light scattering, multiphoton fluorescence and traditional spectroscopic and microscopic techniques, we were able to shed new light on the mechanisms and structural transformations underlying the different stages of the Turkevich synthesis. We found indications of nonclassical two-step nucleation (often found in proteins), where liquid-liquid demixing proceeds the nucleation of gold particles. A transition from molecular gold nanoclusters to plasmonic gold nanoparticles is accompanied by sharp transitions in nonlinear optical signals. In later growth stages evidence for surface smoothening and size and shape focusing are unraveled by the unique combination of the different nonlinear optical probes, each sensitive to different structural characteristics.

Our findings highlight the potential of nonlinear optical spectroscopy to probe morphological and structural changes in real time during crystal growth.

ENGINEERING BRIGHTNESS-MATCHED INDIUM PHOSPHIDE QUANTUM DOTS

Presenting Author: Reyhaneh Toufanian

Topic: Nanocrystals, quantum dots, and nanowires

Format: Contributed

Session: 3, 6

Date: 8/3/2021

Time (in MDT): 2:15:00 PM

Authors: Reyhaneh Toufanian, Boston University, Boston, Massachusetts, United States  Allison M. Dennis, Boston University, Boston, Massachusetts, United States

The inherent size-tunable optoelectronic properties of semiconductor nanocrystal quantum dots (QDs) has made them suitable candidates for applications in biosensing and imaging. However, differences in brightness, defined as the product of molar extinction coefficient ($\varepsilon$) and quantum yield (QY), across emitters of different colors, remain a challenge for their use in multiplexing applications as larger emitters absorb more photons than their smaller blue/green emitting counterparts. Indium phosphide (InP) QDs with a large Bohr radius of $\sim 10$ nm and a bulk band gap of 1.35 eV, have tunable emission in a wide spectral range, providing superior color tuning compared to that of CdSe QDs. In this study, the effect of core composition, shell composition, and shell thickness on optical properties including high energy absorption, quantum yield (QY), and the relative brightness of InP/ZnS and InP/ZnSe core/shell and InP/ZnSe/ZnS core/shell/shell QDs at different excitation wavelengths are examined. By taking advantage of the unique optical properties of InP, the 33-fold brightness-mismatch between green and red commercial CdSe/ZnS QDs was reduced to 5-fold in InP/ZnS QDs. Our analysis revealed that the incorporation of an intermediate ZnSe shell alters the absorption onset of the QDs and results in excitation energy dependent QYs. The deposition of a 4-monolayer thick optically absorbing ZnSe shell into the InP heterostructure followed by the post-synthetic treatment of the QDs in a solution of trioctylphosphine and zinc oleate, generated InP/ZnSe/ZnS core/shell/shell QDs that are approximately 10-fold brighter than InP/ZnS core/shell heterostructures. By increasing the InP core size and simultaneously tailoring the thickness of the ZnSe intermediate shell, we have produced heavy metal-free, brightness-matched green and red emitters. This study highlights the ability to overcome the inherent brightness mismatch seen in QDs through concerted materials design of heterostructured core/shell InP-based QDs.  

![Image](http://files.abstractsonline.com/CTRL/0D/3/016/234/FD7/4BB/DA5/5C1/723/5F0/765/E1/g1179_1.gif)
BENDING OF CORE-SHELL NANOWIRES BY ASYMMETRIC SHELL DEPOSITION

Presenting Author: Spencer McDermott

Topic: Nanocrystals, quantum dots, and nanowires

Format: Contributed

Session: 4, 1

Date: 8/3/2021

Time (in MDT): 3:00:00 PM

Authors: Spencer McDermott, McMaster University, Hamilton, Ontario, Canada Ryan B. Lewis, McMaster University, Hamilton, Ontario, Canada

The incorporation of freestanding semiconductor nanowires into devices has allowed for material combinations, strain states and geometries unachievable in bulk devices. Very recently, spontaneous bending of asymmetric core-shell nanowires has been presented as a novel means to control nanowire geometry, opening up exciting possibilities for strain-gradient engineering in bent nanowires. The process of depositing an asymmetric shell on a bending nanowire by a directional flux is non-trivial and leads to both a geometry and strain variation along the wire. In this presentation, we will present a model for the bending evolution of nanowires under a directional flux, together with GaAs-InP and GaAs-(Al,In)As core-shell nanowire growth experiments. Large local variations (shell thickness, curvature, and strain) are shown to be a direct result of the directional shell growth process. Furthermore, we will show how bending is dependent on core-shell material, deposition angle of the incident flux, and relative shell thickness to the core. Lastly, wire shadowing—the process of the incident flux being blocked on a nanowire by a neighboring nanowire—is revealed as a novel approach for creating wire-to-wire contacts, potentially enabling new nanowire device structures. This work shows that bending from asymmetric core-shell nanowires, although complex, can be predicted and used to further expand the integration of nanowires into devices.
CARRIER COLLECTION KINETICS IN CORE-SHELL GAAS NANOWIRE P-N JUNCTIONS GROWN BY OMVPE

Presenting Author: Mingze Yang

Topic: Nanocrystals, quantum dots, and nanowires

Format: Contributed

Session: 4, 2

Date: 8/3/2021

Time (in MDT): 3:15:00 PM

Authors: Mingze Yang, Simon Fraser University, Burnaby, British Columbia, Canada
Karen L. Kavanagh, Simon Fraser University, Burnaby, British Columbia, Canada
Simon P. Watkins, Simon Fraser University, Burnaby, British Columbia, Canada

III-V core-shell nanowire (NW) junction diodes are under active investigation for various device applications, including tunnel field effect transistors, photovoltaic devices, and optical detectors. The core-shell radial junction structure enables electron- or photo-induced electron-hole pairs (EHPs) to be collected with shorter diffusion lengths due to the small NW dimensions. Furthermore, the collection of the EHPs inside the core is free from surface recombination, potentially improving the energy harvesting efficiency. To date however, the promise of this approach has not been realized in devices such as NW solar cells. We report on the growth of core-shell n-p+ GaAs NWs and show how the electron beam induced current technique (EBIC) can provide detailed spatially resolved information about the carrier collection kinetics in these structures on the nanometre scale. NW devices were grown by a hybrid growth method using organometallic vapor phase epitaxy (OMVPE) and atomic layer deposition. The NW cores were grown via the Au-catalyst vapor-liquid-solid method using trimethylgallium, which results in rather low tapering at 400°C and yields a triangular cross-section with {112}A surfaces. The p+ shell growth is obtained by vapor-solid growth using triethylgallium as a precursor, which results in shell growth with a truncated triangular geometry with three wide facets having {112}B surfaces and three narrow facets having {112}A surfaces (see figure). As a result, the shell thickness varies considerably between the {112}A and {112}B facets. The hybrid growth method permits electrical characterization of individual core-shell NWs in an SEM without removing them from the original substrate, and without lithographic processing. EBIC linescans were performed both parallel and perpendicular to the NW axis, with the beam oriented perpendicular to the {112}A or {112}B surface planes. The highly facetted nature of the NW cross sections resulted in a strong dependence of the EBIC current on the orientation of the beam with respect to the facets, as well as on the beam energy. The EBIC linescans were modelled using Monte Carlo simulations using detailed definition of the beam dependent EHP generation rate. The simulations fit the transverse EBIC linescans well and were sensitive to small details in the geometric structure of the device, as well as beam orientation, and yielded estimates of the minority carrier diffusion lengths in the core and shell, as well as the depletion widths as a function of radial direction.
MOVPE GROWTH OF GAAS NANOWIRES DIRECTLY ON FLEXIBLE PLASTIC SUBSTRATES

Presenting Author: Vladislav Khayrudinov

Topic: Nanocrystals, quantum dots, and nanowires

Format: Contributed

Session: 4, 3

Date: 8/3/2021

Time (in MDT): 3:30:00 PM

Authors: Vladislav Khayrudinov, Aalto University, Espoo, Finland Anastasiia Sorokina, Aalto University, Espoo, Finland Hua Jiang, Aalto University, Espoo, Finland Tuomas Haggren, The Australian National University, Canberra, Australia Harri Lipsanen, Aalto University, Espoo, Finland

III-V semiconductor nanowires (NWs) have been extensively studied over the last two decades, propelling the research of numerous intriguing nanowire-based functional devices such as lasers, light-emitting diodes (LEDs), all-optical logic components, solar cells and photodetectors. At the same time, the development of flexible and wearable electronics has been progressing at an unprecedented pace resulting in vast range of applications, from flexible photodetectors and photonic circuits to bendable batteries, soft solar cells and many more. III-V semiconductor are particularly promising for flexible optoelectronic devices due to their extraordinary properties such as direct tunable band gap, efficient light scattering and trapping, excellent strain relaxation and high carrier mobility. In particular, GaAs nanowires have been used in a myriad of applications including solar cells and lasers, photodetectors and light-emitting diodes (LEDs). We have previously reported for the first time on the direct growth of light-emitting InAs and InP NWs on flexible plastics substrates. Although growth on plastics has always been very challenging (especially using MOVPE and MBE) due to temperature limitations, we showed that the direct growth on polyimide flexible substrates is possible and it is, in fact, straightforward and very efficient. Using a new isolated low-temperature growth regime, we achieved good-quality crystal structure NWs that have strong light emission, electrically active, possess interesting nonlinear optical properties and can be used for flexible nanowire-based devices and all-solid-state passively Q-switched and mode-locked lasers. In this work we further develop our growth approach and show light-emitting GaAs NWs grown directly on flexible plastic substrates. The GaAs NWs were grown using metal-organic vapor phase epitaxy system on polyimide substrates directly inside the growth reactor. We show that the GaAs NWs are optically active and emit light even at room temperature. To the best of our knowledge, this is the first demonstration of GaAs NWs on plastic substrates. We believe that our results will further advance the development of the nanowire-based flexible electronic devices.
CUINSE2 NANOSTRUCTURES GROWN BY MBE

Presenting Author: Alessandro Cavalli

Topic: Nanocrystals, quantum dots, and nanowires

Format: Contributed

Session: 4, 4

Date: 8/3/2021

Time (in MDT): 3:45:00 PM

Authors: Alessandro Cavalli, INL, Braga, Portugal  Sascha Sadewasser, INL, Braga, Portugal

Photovoltaic systems are the ideal method to harvest solar energy, but market-leading Silicon solar cells have limited potential for improvement in efficiency. The most promising class of materials is Cu(In,Ga)Se$_2$ (CIGS): they are lighter, flexible, and significantly cheaper to produce, with a tunable direct bandgap and a high absorption coefficient in the visible spectrum. A record cell efficiency of 23.35% was demonstrated, but it is still more than 10% lower than the Shockley-Queisser theoretical performance limit (33.7%). Additionally, CIGS semiconductors contain indium, a relatively rare element. The use of nanowires (NW) as the PV absorber material can help in both these areas. In fact, they allow ~10x lower material consumption, thanks to high absorption-to-volume ratio through light-trapping, as well as an enhanced performance compared to planar layers. It is well-known that the use of co-evaporation under vacuum is essential to obtain high-quality materials for CIGS solar cells, thus we have focused on Molecular Beam Epitaxy deposition. By using an Al$_2$O$_3$ mask, we achieved position controlled growth of isolated CuInSe$_2$ nanostructures. We are currently working on elongating the structures to obtain true 1D morphology, determining their crystalline structure by Transmission Electron Microscopy, and developing solar cell devices based on the nanostructures.

Fig. 1 SEM top-view (left) and 10° cross-section (right) of CuInSe$_2$ grown by MBE.

QUANTUM DOTS BASED WAVELENGTH SHIFTING PHOTON DETECTION SYSTEM FOR LAR/LXE DETECTORS

Presenting Author: Reyhaneh Toufanian

Topic: Nanocrystals, quantum dots, and nanowires

Format: Contributed

Session: 4, 5

Date: 8/3/2021

Time (in MDT): 4:00:00 PM

Authors: Reyhaneh Toufanian, Capesym Inc., Natick, Massachusetts, United States  Amlan Datta, Capesym Inc., Natick, Massachusetts, United States  Shariar Motakef, Capesym Inc., Natick, Massachusetts, United States

Wavelength shifting photon detection systems (PDS) are an essential component of noble liquid detectors used in a myriad of applications including spectroscopy in high energy physics, γ-ray astronomy, neutrinoless ββ-decay and medical imaging. However, the vacuum ultraviolet (VUV) scintillation light produced by these detectors must be shifted to higher wavelengths suitable for detection by standard photodetectors. 1,1,4,4 Tetraphenyl Butadiene (TPB) is the most commonly used wavelength shifter (WLS) material currently used in noble liquid detectors. However, its limited Stokes shift, photo-degradation, and instability in noble environments have hindered its widespread application. These deficiencies pose accuracy, reliability, and longevity challenges for detectors which are expected to operate for a long time in experimental facilities that are costly to set up and maintain. Here, a new quantum dot (QD) based WLS material composed of CsPbBr₃ with a photoluminescence quantum yield (PLQY) as high as 70% is reported. By taking advantage of the size-dependent optoelectronic properties of QDs, their emission wavelength was optimized to match the highest quantum efficiency region of the SiPMs. Using widely scalable solution-based synthetic techniques, we have demonstrated the deposition of the QD-based WLS material on a large area PDS substrate, providing a pathway to the fabrication of meter-sized PDS and their extensive use in other WLS applications.
STRUCTURAL, OPTICAL AND ROOM TEMPERATURE MAGNETIC PROPERTIES OF SOL-GEL SYNTHESIZED (CO, FE) CO-DOPED SnO$_2$ NANOPARTICLES

Presenting Author: Ezhil Vizhi

Topic: Nanocrystals, quantum dots, and nanowires

Format: Contributed

Session: 4, 6

Date: 8/3/2021

Time (in MDT): 4:15:00 PM

Authors: Ezhil Vizhi R, VIT University, Vellore, India Renu Rajan, VIT University, Vellore, India

Co-Fe co-doped SnO$_2$ nanocrystals with different dopant concentrations (Co=15wt% and Fe= 1, 3, 5wt%) were synthesized by sol-gel technique. XRD spectra revealed the formation of pure SnO$_2$ phase, indicating that the synthesis was effective in diluting the Co and Fe ions into the SnO$_2$ lattice. The structures of the samples were confirmed to be tetragonal and reductions in lattice parameters confirmed the incorporation of dopant ions in SnO$_2$ lattice. The diffuse reflectance spectroscopy data reveals an increase in the range of absorption and a decrease in energy band gap with an increase in Fe concentration. TEM/SAED confirms the nanoparticle size and crystalline nature of the samples. The room temperature ferromagnetism was noticed for all the samples, where the magnetization increases with an increase in Fe concentration, whereas the coercivity is more for the sample with less iron concentration. It has been concluded that the ferromagnetic properties depend not only on the distribution of defects but also on the surface diffusion of the dopant ions and nanometric size of the materials. Keywords SnO$_2$, Room temperature ferromagnetism, Diluted Magnetic Semiconductor, nanoparticles
SYNTHESIS AND STRUCTURAL CHARACTERIZATION OF VLS GROWN Sn3O4 NANOWIRES

Presenting Author: Olivia Berengue

Topic: Nanocrystals, quantum dots, and nanowires

Format: Poster

Session:

Date:

Time (in MDT):

Authors: Olivia Maria Berengue, São Paulo State University, Guaratinguetá, Brazil Rosana Alves Gonçalves, São Paulo State University, Guaratinguetá, Brazil Mauricio Ribeiro Baldan, São Paulo State University, Guaratinguetá, Brazil

Since the discovery of carbon nanotubes by Iijima [1], there is a growing search for synthesizing high quality nanostructures with new physical and chemical properties. The need to obtain these important new features has been justified by the countless original optoelectronic devices arising from them. Among all the inorganic nanostructures ever synthesized, the oxide ones are deserves great attention because of their unique combination of interesting properties such as optical transparency and high electrical conductivity with high bandgaps has been originating the most promising technologies for the future. In this work, we report on the synthesis and the investigation of nucleation mechanism of self-catalyzed tapered Sn<sub>3</sub>O<sub>4</sub> nanostructures grown by a chemical vapor deposition (CVD) approach associated with the carbothermal reduction process. A group of techniques, which also provided data on crystalline structure and compositional aspects, characterized belts and wires. The structural characterization, specifically, of morphology showed the presence of nanobelts, grown by the well-known vapor-solid (VS) process, and nanowires synthesized by a self-catalytic process. In addition, Field Emission Gun Scanning Electron Microscopy (FEG - SEM) measurements revealed that self-catalyzed samples have inverted tapered structure. In order to understand nucleation and initial stages of the nanowires growth, XRD, HRTEM and Raman Spectroscopy techniques were performed. All the as-synthesized samples were found to be high crystalline quality Sn<sub>3</sub>O<sub>4</sub> nanostructures with no phase mixing with other tin oxides. This result revealed that our experimental approach was effective to select only the non-stoichiometric phase of tin oxide. To the best to our knowledgement, this is the first time this phase selectivity is achieved in a CVD approach. In addition, some insights on nucleation and growth of inverted tapered nanowires could be explained by considering the hole of catalyst in the control of nanowire diameter: at initial stages of growth, by decreasing the contact angle β, it can be seen an increase of both the contact area and the radius R of the droplet. After this stage, the nanowire’s radius R, consequently, should be greater than the initial radius of the contact area of the nuclei on the Sn droplet.<br />

Acknowledgements: Authors thank Brazilian Research funding agencies Coordenação de Aperfeiçoamento de Pessoal de Nível Superior - Brasil (CAPES) - Finance Code 001 and Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP) Grant number 21816-4.<br />

LOW TEMPERATURE SYNTHESIS AND STRUCTURAL REFINEMENT OF β-Sb<sub>2</sub>O<sub>3</sub> NANOSTRUCTURES

Presenting Author: Rosana Gonçalves

Topic: Nanocrystals, quantum dots, and nanowires

Format: Poster

Session: ,

Date:

Time (in MDT):

Authors: Rosana Alves Gonçalves, Universidade Estadual Paulista "Júlio de Mesquita Filho", GUARATINGUETA, Brazil Luiz Felipe Vinhas, Universidade Estadual Paulista "Júlio de Mesquita Filho", GUARATINGUETA, Brazil Lincoln Avila Cagnoni, Universidade Estadual Paulista "Júlio de Mesquita Filho", GUARATINGUETA, Brazil Maurício Ribeiro Baldan, Instituto Nacional de Pesquisas Espaciais (INPE), São José dos Campos, Brazil Olivia Maria Berengue, Universidade Estadual Paulista "Júlio de Mesquita Filho", GUARATINGUETA, Brazil

Antimony trioxide (Sb<sub>2</sub>O<sub>3</sub>) is a wide gap semiconductor with two allotropes phases: cubic (α-phase) and orthorhombic (β-phase). Both phases have important optical properties and have been used for applications as flame retardants, sensors and as catalytic agents [1]. Recently, Sb<sub>2</sub>O<sub>3</sub> has also been identified as a promising candidate for Li-ion battery applications [2] and as an ethanol electrocatalyst [3]. In this work, we synthesized β-Sb<sub>2</sub>O<sub>3</sub> belts by the vapor-solid (VS) growth mechanism driven by a low-cost carbothermal reduction process. Synthesis parameters such as inert gas flow and evaporation/solidification temperature were changed in order to promote the transition from micro- to nanostructures. Experiments of Field Emission Gun-Scanning Electron Microscopy (FEG-SEM), X-Ray Diffraction (XRD) and Raman Spectroscopy were carried out and data on crystalline quality, phase and morphology for samples were obtained. The results of FEG-SEM show that as the growth temperature is reduced, the β-Sb<sub>2</sub>O<sub>3</sub> structures undergo a change in the morphology of branched microbelts for submicron rods and belts; moreover, XRD and Raman data indicate a suppression of renucleation effects on structures with decreasing temperature. The changes in gas flow and evaporation/solidification temperature, point to a transition from micro to nanostructures in width and thickness and also selectivity in morphology with structures ranging from long and flexible nanobelts rigid square-section nanobelts. In addition, from the experiments, the critical temperature for the growth of β-Sb<sub>2</sub>O<sub>3</sub> nanobelts was found to be 650 °C. To the extent of our knowledge this is the lowest vapor-phase growth temperature reported for synthesis of β-Sb<sub>2</sub>O<sub>3</sub> nanobelts. Kinetic and thermodynamic theory approaches have been used to explain changes in the growth of structures and to determine a growth model.<br/>

Acknowledgements: This study was financed in part by the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior - Brasil (CAPES) - Finance Code 001 and Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP) Grant number 21816-4.7

Abstract Book - ACCGE-22//OMVPE-20

SPATIALLY HIGH-RESOLUTION I-V CHARACTERIZATION OF FREESTANDING CORE-SHELL NANOWIRES

Presenting Author: Juliane Koch

Topic: Nanocrystals, quantum dots, and nanowires

Format: Poster

Session: ,

Date: 

Time (in MDT):

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III-V semiconductor nanowire (NW) heterostructures hold the promise to provide nano-scaled electronic and optoelectronic devices at ultra-low costs. This goal requires advanced epitaxial growth modes along with cost-competitive lithography procedures, and is of crucial importance for large area applications such as nano-scaled devices for solar energy conversion. While nanoimprint lithography along with selective area epitaxy reduces costs substantially, there are methods and growth modes such as vapour-liquid-solid (VLS) epitaxy along with annealing of thin Au layers or colloidal nanoparticle deposition that enable Au-seeded, epitaxially complex core-shell NW heterostructures at any wafer size. However, a precise NW characterization and, moreover, its heterojunctions with high spatial resolution is difficult to obtain, especially, details of the NW foot that serves as the bottom (hetero)contact.

In order to study microscopic details of the NW structure and its composition, we investigated p-GaAs/i-GaInP/n-GaInP core-shell-shell NWs for optoelectronic applications standing upright on the growth substrates. Cores of the NWs were grown via VLS epitaxy followed by epitaxial shell growth in a reactor for low-pressure horizontal metalorganic vapor-phase epitaxy. SEM in combination with EDX measurements on the freestanding NWs and XRD measurements for planar layers reveal the contrast of NW shell and planar layer growth. Furthermore, high-resolution I-V measurements demonstrate unexpected conduction channels at the NW base. We employ a combination of material-selective wet chemical etching of as-grown coaxial NWs and a multi-tip scanning tunnelling microscope (MT-STM) operated as a four-point nano-prober to obtain spatially resolved I-V analysis. The co-axial NWs were embedded in height-controlled photoresist to selectively etch the GaInP-based shells wet-chemically using hydrochloric acid. Thus, the p-doped NW core is exposed at the top of the NW and the n- and p-doped NW regions are accessible for electrical four-point probe measurements with our MT-STM. These measurements revealed a conduction channel causing substantially degraded core-shell pn-junction performance. The leakage in the as-grown vertical NWs is localized at the base of the NWs, where a buried contact of the n-GaInP shell to the p-GaAs substrate is formed. This charge-separating buried junction is also visualized in an electron beam-induced current mode of the MT-STM. Based on the localization of the leakage mechanism, a well-defined route for preparation procedures and optimization of future NW core-shell pn-junction emerges.

In summary, our high-end characterization methods enable a direct relation between the NW structures und the electronic properties of as-grown co-axial NWs, which is crucial for potential applications such as NW-based solar energy conversion.
GROWTH PECULIARITIES OF RARE-EARTH DOPED NAYF<sub>4</sub>NANOPARTICLES WITH THE "CORE-SHELL" STRUCTURE BY THE SOLVOTHERMAL METHOD FOR PHOTONIC APPLICATIONS

Presenting Author: Alexandr Koshelev

Topic: Nanocrystals, quantum dots, and nanowires

Format: Poster

Session: ,

Date: 

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At this time the development of approaches to improve the luminescent characteristics of nanomaterials is a key factor in the development of nanophotonics. The low luminescence efficiency of nanocrystals associated with a high concentration of surface defects requires optimization of its photophysical parameters in order to increase quantum yield. One of the powerful tools for improving of the nanoparticles luminescence properties is the design «core-shell» structures [1, 2]. This technique includes an epitaxial growth of the surface layer on the «core» particle. The inert shells act as a spatial barrier between the luminescent centers and the surface defects, reducing the non-radiative loss of the excitation energy. Active shells doped with sensitizer ions make it possible to further increase the exciting radiation quantity by migrating energy through the core-shell interface. One of the most promising classes of luminescent materials is fluoride based nanoparticles doped with rare-earth elements. In this work, we studied the features of the production of NaYF<sub>4</sub> nanoparticles doped with Yb<sup>3+</sup> and Er<sup>3+</sup> ions, which are the most currently used in nanophotonics and biotechnology. The initial «core» nanoparticles and «core-shell» structures were grown by the solvothermal method in a high-boiling organic solvents medium (a mixture of oleic acid and 1-octadecene) at a process temperatures of 280-320°C. Trifluoroacetates of the corresponding elements were used as precursors. Nanoparticles with a diameter of 15 to 150 nm were grown. The NaYF<sub>4</sub>: Yb<sup>3+</sup>, Er<sup>3+</sup> nanoparticles were comprehensively characterized by XRD-analysis and fluorescent spectroscopy, scanning and transmission electron microscopy. Varying the synthesis conditions (the duration and temperature of the process, the components ratio) makes it possible to obtain NaYF<sub>4</sub> particles with both cubic and hexagonal crystal structures with a characteristic morphology (fig. 1). The kinetic dependences of the shell thickness on precursor composition and the duration of synthesis have been studied. Nanoparticles with the «core-shell» structure demonstrate significantly higher efficiency of upconversion luminescence compared to the original «core» ones. The prospects of application the obtained nanoparticles for photonic technologies are discussed.

![Image](http://files.abstractsonline.com/CTRL/F4/1/9CF/1AF/AC3/463/6A5/D8D/8C8/2A1/3CE/A4/g1128_1.jpg)
Fig. 1 EDX elemental mapping of a) Y L-line (red), Yb M-line (green) of «core-shell» β-NaYF₄(Yb,Er) and b) Ca L-line (green), Y L-line (blue) of «core-shell» α-NaYF₄(Yb,Er)@CaF₂.


SYNTHESIS AND CHARACTERIZATION OF CERIUM OXIDE NANOPARTICLES BY COMBUSTION METHOD

Presenting Author: Jayabharathi P

Topic: Nanocrystals, quantum dots, and nanowires

Format: Poster

Session: 

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Cerium oxide (CeO$_2$) nanoparticles were synthesized by using a simple and rapid combustion route using cerium nitrate hexahydrate as the oxide and glycine as fuel. The fuel to oxidizer ratio was maintained at 1. The glycine nitrate solution was ignited in air at 500°C as the precursor underwent a combustion process yielding yellow colour powder. The powder XRD pattern confirms the cubic phase of the synthesized sample. The high-resolution scanning electron microscope images reveal the morphology of the sample to be spherical in shape with an average particle size of about 25 nm with good uniformity and homogeneity. From the FTIR spectrum, the peak at 568 cm$^{-1}$ is attributed to Ce-O bond. The UV absorbance measurement was done at room temperature and their band gap energy has been estimated. CeO$_2$ nanoparticles synthesized using combustion method are found to enhance the performance when used as an anodic material in dye sensitized solar cells.
SYNTHESIS AND CHARACTERIZATION OF TRANSITION METAL DOPED PVP COATED Fe3O4 ZnS CORE SHELL MAGNETIC OPTICAL NANOPARTICLES BY CO PRECIPITATION METHOD.

Presenting Author: DIMPLE SHAH

Topic: Nanocrystals, quantum dots, and nanowires

Format: Poster

Session:

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The current paper reports the polyvinylpyrrolidone (PVP) coated transition metal doped Fe3O4-ZnS core shell nanoparticles synthesized in aqueous medium at ambient condition by co-precipitation method. The X-ray diffraction was used for the structural characterisation while scanning electron microscope for morphology and particle size distribution and energy dispersion spectrum for the elemental confirmation. The synthesised nanoparticles have the crystallite size in the range of 10-12 nm as confirmed by the X-ray diffraction and electron microscopy. The optical properties were studied by UV–vis absorption and photoluminescence spectra. The room temperature magnetic hysteresis loop of transition metal doped PVP-Fe3O4-ZnS shows the superparamagnetic behaviour of the cores. A significant improvement in the photoluminescent (PL) intensity was observed as a result of ZnS shell and transition metal doping of the shell. In addition to the PL improvement, saturation magnetisation enhancement was also observed. The synthesised multifunctional nanoparticles can be promising candidates for applications in simultaneous bio-labelling, imaging, cell sorting and separation.
INFLUENCE OF PH ON SYNTHESIS OF BISMUTH MOLYBATE (Bi<sub>2</sub>MoO<sub>6</sub>) NANOPLATES VIA SOLVOTHERMAL ROUTE

Presenting Author: Priscilla D Trixy

Topic: Nanocrystals, quantum dots, and nanowires

Format: Poster

Session: ,

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In our present work, bismuth molybdate (Bi<sub>2</sub>MoO<sub>6</sub>) nanoplates have been synthesized by solvothermal process without using any surfactant. The results show that it is feasible to obtain the desired phase Bi<sub>2</sub>MoO<sub>6</sub> by varying the pH of the initial precursor solution. The orthorhombic phase of the material was confirmed by employing powder X-ray diffraction technique. The morphology of the samples was studied using high resolution scanning electron microscope which revealed the growth of the nanoplates on increasing pH. The functional groups were identified using FTIR technique which ensured the presence of Bi-O and Mo-O modes of vibrations. The UV-DRS analysis was used to investigate the absorption properties of the prepared samples. A decrease in the absorption band edge was observed with the increase in pH denoting the occurrence of blue shift in the absorption spectra. As the synthesized Bi<sub>2</sub>MoO<sub>6</sub> nanoplates are smaller in dimensions, they tend to have a large surface area which in turn will enhance the sensitivity and response rate when used in semiconducting metal oxide gas sensors.
STRUCTURAL, MORPHOLOGICAL AND MAGNETIC PROPERTIES OF HARD AND SOFT NANOCOMPOSITE FERRITES FOR PERMANENT MAGNET APPLICATIONS

Presenting Author: Ezhil Vizhi

Topic: Nanocrystals, quantum dots, and nanowires

Format: Poster

Session: 

Date:

Time (in MDT):

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Permanent magnets have gained an utmost importance in lots of fields, due to large saturation, magnetism ($M_s$), high coercivity ($H_c$) and the high curie temperature ($T_c$). The hard and the soft ferrite nano composites has been synthesized by the sol gel auto combustion technique. The citric acid was taken as the fuel and the metal to fuel ratio was maintained as 1:1. The thermal decomposition analysis of the as synthesised material was performed from 500°C to 1250°C by the TGA/DSC. The structural analysis was done by X-ray diffraction (XRD) and the sample was confirmed to be M-type hexaferrite through the lattice parameters. The structural morphology of the sample was examined by the scanning electron microscope (FE-SEM) and the transition electron microscopy (TEM) to confirm the presence of the hard and the soft ferrite materials. The magnetic parameters of the sample such as saturation magnetism ($M_s$), Remanent magnetism ($M_R$), squareness ratio ($S$) and coercivity ($H_c$), and further the synthesised material is used for permanent magnet applications.

Keywords: Permanant magnets, sol gel method, TGA/DSC, XRD, TEM, VSM, M-type hexaferrite

References
DEVELOPMENT OF HARD AND SOFT NANOCOMPOSITE FERRITES FOR BIOMEDICAL APPLICATIONS

Presenting Author: Ezhil Vizhi

Topic: Nanocrystals, quantum dots, and nanowires

Format: Poster

Session: ,

Date:

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Magnetic nanocomposites find a large number of applications in the field of science and technology like permanent magnets, telecommunication, biomedicine, environmental remediation, etc. The synthesis and characterization studies of magnetic nanocomposites which can find prominence in biomedical applications are explored. The material can be prepared by sol-gel method followed by self-propagating combustion technique for which suitable fuel material has to be chosen. The phase formation temperature has to be optimized. The as-synthesized samples are characterized by TGA, XRD, Raman Spectroscopy, SEM and VSM for its thermal, structural, morphological and magnetic properties. The average size, magnetization ($M_{s}$) and coercivity ($H_{c}$) of the composites are studied according to varying annealing temperatures. Based on the characterization results we can optimize the novel material for biomedical applications.

Keywords: Magnetic nanocomposites, biomedical applications, Sol gel method, TGA, XRD, Raman Spectroscopy, SEM, VSM
STRUCTURAL AND MAGNETIC PROPERTIES OF SPARK PLASMA SINTERED BA\textsubscript{0.5}Sr\textsubscript{0.5}Fe\textsubscript{12}O\textsubscript{19}/Y\textsubscript{3}Fe\textsubscript{5}O\textsubscript{12} NANOComposite FERRITES FOR PERMANENT MAGNET APPLICATIONS

Presenting Author: Ezhil Vizhi

Topic: Nanocrystals, quantum dots, and nanowires

Format: Poster

Session:

Date:

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Structural and magnetic properties of spark plasma sintered Ba\textsubscript{0.5}Sr\textsubscript{0.5}Fe\textsubscript{12}O\textsubscript{19}/Y\textsubscript{3}Fe\textsubscript{5}O\textsubscript{12} nanocomposite for permanent magnet applications. Irfan <sup>1</sup>, R Ezhil Vizhi<sup>1</sup>*, P Saravanan <sup>2</sup>, Defence Metallurgical Research Laboratory, Centre for functional materials, Vellore Institute of Technology, Vellore-632014, India<br />
<br />
Permanent magnets are used in a number of technological instruments and play an important part in our everyday lives, including engines, generators, and even cellphones. Permanent magnets made of rare-earth metal alloys, such as SmCo and NdFeB, has very high energy product ((BH)<sub>max</sub>). However, high cost, low Curie temperature (Tc), deprived oxidation states and poor corrosion resistance limit its application aspects in technical devices. In comparison to the rare earth based permanent magnets, hard/soft ferrites are promising candidate for advanced permanent magnetic materials due to their low cost, excellent corrosion resistance and high electrical resistivity<sup>[1]</sup>-<sup>[3]</sup>. In order to obtain pure hard/soft ferrites phase several techniques are available in literature such as one-pot synthesis, sol-gel combustion, co-precipitation, conventional solid-state reaction, techniques have been employed. Among this, one-pot synthesis technique is a low-cost and energy-efficient bottom-up approach in synthesizing hard/soft nanocomposite ferrites<sup>[4]</sup>, <sup>[5]</sup>. Herein, we made an attempt to fabricate high dense hard/soft ceramic composite with different weight ratios (x=90/10 and 80/20) using spark plasma sintering (SPS) with controlled grain growth. X-ray diffraction studies indicated the formation of single phase crystalline phases of Ba\textsubscript{0.5}Sr\textsubscript{0.5}Fe\textsubscript{12}O\textsubscript{19}/Y\textsubscript{3}Fe\textsubscript{5}O\textsubscript{12}. Room temperature magnetic properties revealed the effective exchange coupling between hard and soft magnetic moment with improved saturation magnetization (M<sub>sat</sub>) and coercivity (H<sub>c</sub>) for x=90/10 sample.<br />

Keywords: Hard/soft nanocomposite, Magnetic properties, Ba\textsubscript{0.5}Sr\textsubscript{0.5}Fe\textsubscript{12}O\textsubscript{19}/Y\textsubscript{3}Fe\textsubscript{5}O\textsubscript{12},Permanent Magnet
METAMORPHIC INASb SUPERLATTICES FOR LONG WAVE OPTOELECTRONICS AND QUANTUM INFORMATION DEVICES

Presenting Author: Sergey Suchalkin

Topic: Narrow Bandgap Semiconductors and Devices

Format: Invited

Session: 3, 1

Date: 8/2/2021

Time (in MDT): 1:00:00 PM

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Metamorphic short-period InAsSb superlattices (SLs) [1,2] represent a new class of semiconductor materials with potential applications in very long-wavelength and terahertz optoelectronics as well as quantum information processing. One of the major advantages of the SLs is its exceptional flexibility in controlling the bandgap and carrier dispersion simply by variation of the layer composition and width. The large (~5.9%) lattice constant mismatch between InAs and InSb makes it impossible to grow thick layers of bulk InAsSb alloys or InAs\textsubscript{1-x}\textsubscript{x}Sb\textsubscript{x}/InAs\textsubscript{1-y}\textsubscript{y}Sb\textsubscript{y} SLs using standard InAs or InSb substrates. Therefore, a virtual substrate (VS) approach must be used, which allows continuous variation of the material lattice constant and thus growth of bulk materials and SLs in the entire composition range. We present designs and results from metamorphic InAsSb-based SLs grown on (100) GaSb substrates. A GaSb buffer layer was followed by a 2800 nm graded buffer with the composition varied from GaSb to an Al\textsubscript{0.58}In\textsubscript{0.42}Sb or Al\textsubscript{0.4}In\textsubscript{0.6}Sb unstrained VS. Then InAs\textsubscript{0.7}Sb\textsubscript{0.3}/InAs\textsubscript{0.25}Sb\textsubscript{0.75} SLs or InAs\textsubscript{0.48}Sb\textsubscript{0.52}/InSb SLs with lattice constants of 6.25\AA{} and 6.33\AA{} respectively were grown. The bandgap of metamorphic SLs with periods below 10 nm can be varied from 400 meV down to zero and further to negative values (band inversion). In addition to the potential application as a new very long-wave optoelectronics materials, the metamorphic SLs demonstrates intriguing physical properties such as Dirac-type carrier dispersion and high g-factor. The prospects for realization of topologically nontrivial states in metamorphic short-period InAsSb superlattices as well as their application in proximity-coupled semiconductor-superconductor devices will be discussed.

LOW-THRESHOLD INAS-BASED INTERBAND CASCADE LASERS WITH ROOM-TEMPERATURE EMISSION AT 6.3UM

Presenting Author: James Gupta

Topic: Narrow Bandgap Semiconductors and Devices

Format: Invited

Session: 3, 3

Date: 8/2/2021

Time (in MDT): 1:30:00 PM

Authors:
STRUCTURE AND LUMINESCENT PROPERTIES OF EPITAXIAL PbSe FILMS ON III-V SUBSTRATES

Presenting Author: Kunal Mukherjee

Topic: Narrow Bandgap Semiconductors and Devices

Format: Contributed

Session: 3, 5

Date: 8/2/2021

Time (in MDT): 2:00:00 PM

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PbSe is a rocksalt-structured narrow bandgap IV-VI semiconductor. It has a direct bandgap of 0.28 eV at room temperature, close to that of InAs, but exhibits properties that are distinct from its III-V counterpart due to differences arising from the mixed-ionic/metalllic/covalent nature of bonding in PbSe. Among these properties, PbSe has a lower Auger coefficient compared to III-V materials of comparable bandgaps that is beneficial for mid-infrared light emission. Indeed, PbSe has been used commercially in mid-infrared lasers and detectors for decades, but at the same time our fundamental understanding of this material lags III-Vs and many basic properties remain underexplored. A modern understanding of the relationship between the structure of PbSe and resultant properties, particularly how it deviates from trends in III-V, may present new opportunities in mid-IR optoelectronics. Towards this goal, heterogeneous integration of PbSe with cost effective III-V or Si/Ge substrates offers both a means probe the growth and properties of PbSe as well as combine functionality in a hybrid platform. The low growth temperature for epitaxy of PbSe, being below 350 °C, makes it a good candidate for integration with compatible substrates if the mismatch in crystal structure and lattice constants may be mediated. In this work, we demonstrate a route to epitaxial films of PbSe directly on III-V substrates of GaAs and InAs using molecular beam epitaxy and study the structure and luminescent properties of the resultant thin films. We develop a synthesis method for single crystal cube-on-cube epitaxy of PbSe using a high-temperature pre-growth surface treatment on 1% lattice-mismatched InAs (001) and 8% mismatched GaAs (001). The crystal structure mismatch causes PbSe to nucleate as islands, but the film coalesces within tens of nanometers ultimately leading to threading dislocation densities in the film exceeding 10^9/cm^2. Despite this, we measure strong mid-infrared luminescence at room-temperature (3-5 µm) from such thin uncapped PbSe films with reasonably long minority carrier lifetimes in the range of 20-200 ns which is unusual considering the proximity to the III-V/IV-VI heterointerface along with the extended defects. We also harness the thermal expansion mismatch between PbSe and GaAs (Δα=14ppm/K) to additionally probe the impact of lattice strain on light emission as a function of temperature. We will discuss possible recombination mechanisms occurring in PbSe and consider its unique suitability for high-mismatch integration.
Large ZnGeP\(_2\) single crystals for high power middle infrared laser output

Presenting Author: Chunhui Yang

Topic: Nonlinear Optical and Laser Host Materials

Format: Invited

Session: 2, 1

Date: 8/3/2021

Time (in MDT): 10:30:00 AM

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Large ZnGeP\(_2\) single crystals for high power middle infrared laser output were grown through the Vertical Bridgman technique, and then large aperture OPO devices with a typical dimension of 25×25×(30~40) mm were obtained from ZGP crystal ingots. Specifically, the cracking issue was solved by precise control of crystal defects, and the absorption coefficient at ~2.0 μm was significantly reduced to ~0.05 cm\(^{-1}\) with the treatment of thermal annealing and electron irradiation. Finally, the key parameters, such as the average dislocation density, FWHM of X-ray rocking curve, the damage threshold, and the optical heterogeneity were measured with values of ~2.5×10\(^2\) cm\(^{-1}\), 11-22″, 3.5 J/cm\(^{-2}\), and ≤2.57×10\(^{-5}\) respectively, which confirmed the high quality of these crystals. Furthermore, a ZGP master-oscillator power-amplifier (MOPA) system was demonstrated using a Ho:YAG MOPA as the pumping source. It was shown that with the increase of ZGP OPO length, the threshold became much lower and the optical-to-optical conversion efficiency saw a significant increase. The threshold of 40 mm ZGP OPO device was as low as 14.06 W (0.469 mJ, 0.318 mJ/mm\(^2\)) and the output power is 51.7 W with the highest slope efficiency of 61.4% and optical-to-optical conversion efficiency of 53.6% under the pump power of 96.45 W. Thus, high-energy of joule-level or mid-wave laser of hundred-watt-level output could be achieved by using the 25 mm×25 mm×(30~40) mm ZGP devices based MOPA system.

Fig 1. (a) \(\phi 60\) mm×100 mm ZGP single crystal ingot and the typical ZGP OPO devices; (b) ZGP OPO devices with different length for high-power mid-infrared laser output.
CDSiP<sub>2</sub> AND ZnGeP<sub>2</sub>: COMPARISON OF NLO MATERIALS FOR HIGH AVERAGE POWER MID IR GENERATION

**Presenting Author:** Kevin Zawilski

**Topic:** Nonlinear Optical and Laser Host Materials

**Format:** Contributed

**Session:** 2, 3

**Date:** 8/3/2021

**Time (in MDT):** 11:00:00 AM

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ZnGeP<sub>2</sub> (ZGP) has been the state of the art non-linear crystal for mid wave IR generation for many years. CdSiP<sub>2</sub> (CSP) is a nonlinear optical chalcopyrite semiconductor developed as a wider-band-gap analog of ZnGeP<sub>2</sub> to enable mid-infrared generation with widely-available 1- and 1.55-micron pump laser sources. CSP has a higher nonlinear coefficient ($d_{36}=84.5$ pm/V) than ZGP ($d_{36}=79$ pm/V), and its lower thermal conductivity (13.6 W/mK vs 35 W/mK for ZGP) is more than offset by nearly 10-fold lower absorption losses in the 1.06- to 2.1-micron wavelength range, making CSP an attractive alternative to ZGP even for 2-micron-pumped OPO power-scaling. ZGP and CSP crystals are grown through similar horizontal gradient freeze processes. CSP growth involves many challenges when compared to the growth of ZGP including: a higher melting temperature that tests the limits of fused silica ampoules, a more reactive melt, and a higher propensity for twinning. Even with these growth challenges, recent advances in crystal growth from stoichiometric melts using the horizontal gradient freeze (HGF) technique have resulted in scaling boule diameters from 19 to 28 millimeters. CSP parts with apertures up to 10 x 10 mm<sup>2</sup> have been fabricated. Two laser architectures were explored to pump CSP crystals at 2 microns. Both setups used a Ho:YAG laser pump source with >80W of average power available. Pulse widths of ~20ns and rep rates of ~10kHz were used. The first architecture was a ring OPO with two CSP crystals that produced 27 W of average power, demonstrating the viability of CSP as a material capable of producing high average power output in the mid wave IR. The second architecture was an OPO seeded OPA train of multiple crystals that was used to directly compare the thermal lenses generated by pumping either CSP or ZGP with high average power 2 micron light. The CSP crystals demonstrated significantly less thermal lensing than the ZGP crystals. Thermal lensing at high average power output has been a limiting factor in ZGP crystals, causing damage as the thermal lens increases with increasing power. The lower thermal lensing in CSP will allow for higher average power output from CSP crystals compared with ZGP.
NONLINEAR CRYSTALS FOR PHASE MATCHED TERAHERTZ GENERATION

Presenting Author: Benoit Boulanger

Topic: Nonlinear Optical and Laser Host Materials

Format: Invited

Session: 2, 4

Date: 8/3/2021

Time (in MDT): 11:15:00 AM

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The 0.1-10 Terahertz (THz) frequency range is very important for both academic research and industrial applications such as control, sensing, imaging and spectroscopy. When monochromaticity, wavelength tunability and energy are targeted, which is the new frontier in THz generation, the best alternative is nonlinear Difference-Frequency-Generation (DFG) or optical rectification. We studied eight isotropic, uniaxial or biaxial crystals that we identified as enabling THz emission from phase-matched DFG: YCOB, BNA, LBO, CSP, AGS, CdSe, ZnO and GaP [1]. We focused on the 0.3 – 2.0 THz range over which we measured transmission spectra under polarized light by using the Time-Domain Spectroscopy (TDS) method. Thanks to the transmission spectra recorded in polarized light, it has been possible to determine the principal values of the absorption coefficient and of the refractive index in the 0.3 – 2 THz range. The principal values of the refractive indices as a function of wavelength in the visible-infrared transparency range were also calculated from Sellmeier equations ever published. From the previous data, we calculated the coherence length $l_c$ of DFG corresponding to the eight possible phase-matching types considering the situation where the effective coefficient is non-zero and the spatial walk-off angle is nil. We were able to calculate such conditions for all the eight selected crystals. Then, we were able to determine the PM conditions using the coherence length curves. We found interesting and complementary phase-matching conditions in the eight studied nonlinear crystals that can be grouped into three families with respect to the pumping wavelengths: BNA, AGS and GaP in the visible range; BNA, CSP and ZnO in the near infrared around 1 µm; YCOB, LBO and CdSe in the mid-infrared around 2 – 3 µm. According to the absorption of the generated THz wave, the total ranking is the following: GaP > CSP > ZnO > AGS > YCOB ≈ BNA = LBO [1]. Since the eight crystals were studied in the same conditions, the reliability and relevance of their mutual comparison is ensured. These data provide a fantastic roadmap for future THz generation experiments.[1] C. Bernerd, <sup>P</sup>
KLTN SUPERCRYSTALS WITH GIANT BROADBAND REFRACTION

Presenting Author: Eugenio DelRe

Topic: Nonlinear Optical and Laser Host Materials

Format: Invited

Session: 3, 1

Date: 8/3/2021

Time (in MDT): 1:00:00 PM

Authors: Eugenio DelRe, University of Rome La Sapienza, Rome, Italy

We discuss the spontaneous formation of ferroelectric supercrystals in bulk potassium-lithium-tantalate-niobate. The phenomenon is observed as the crystal is cooled below its room-temperature Curie point and causes visible laser light to be scattered in a manner wholly analogous to X-ray diffraction from an atomic lattice. The lattice emerges in 3D with a lattice constant that is determined by spatial scale associated to growth striations. These are approximately periodic oscillations in the composition of the disordered solid-solution along the growth axis that occur as the crystal is pulled. The scale can range from fractions to tens of micrometers, depending on the specific growth protocol. Mesoscopically, the supercrystals emerge as a three-dimensional periodic network of high-dimensional topological defects, a volume mosaic of interwoven ferroelectric domains that minimizes volume charge and strain. Each defect appears as a combination of 6 independent spontaneous polarization vortices forming a cube-like element, a hyper-vortex. The pattern forms a birefringent 3D photonic crystal with surprising properties. Principal among these is the appearance of giant broadband optical refraction. The phenomenon is observed when visible light is focused onto the cores of the polarization vortices or onto the cores of the anti-vortices, i.e., the polarization saddle-points that form as the vortices coalesce to form a superlattice. The focused light enters and exits the sample propagating along the normal to the crystal facets irrespective of input launch angle and wavelength, exiting parallel to the original beam. Inside the sample, the beam fails to spread on consequence of diffraction and does not suffer any form of chromatic walk-off. No wavelength-sensitive modal structure is observed, the result being an overall behavior that can only be described by assuming a giant broadband refraction across the entire visible spectrum. From a practical perspective, we discuss how giant refraction can be used to enhance nonlinear effects and in innovative imaging schemes. From a fundamental perspective, we review recent spectroscopic, X-ray, structural, and optical results that help shed light on the origin of giant refraction. The figure shows a microscope image of the sample surface. <p><a href="http://files.abstractsonline.com/CTRL/82/C/499/CE5/D15/490/1B8/912/01F/60C/249/12/g1157_1.jpg" target='_blank' address=no >img src="http://files.abstractsonline.com/CTRL/82/C/499/CE5/D15/490/1B8/912/01F/60C/249/12/g1157_1.jpg" alt="" border="0" /></a></p>
TUNABLE 4-12 MICRON OP-GAP OPO CRYSTALS GROWN BY HVPE ON OP-GAAS TEMPLATES

Presenting Author: Peter Schunemann

Topic: Nonlinear Optical and Laser Host Materials

Format: Invited

Session: 3, 3

Date: 8/3/2021

Time (in MDT): 1:30:00 PM

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Orientation-patterned gallium phosphide (OP-GaP) is an exciting new quasi-phase matched (QPM) nonlinear optical crystal which can be pumped at 1- and 1.55-microns for efficient frequency comb spectroscopy in the 4-12 μm molecular fingerprint region. Despite numerous device demonstrations to date, epitaxial growth and processing of OP-GaP is severely limited by the quality and availability of GaP substrates. For nearly a decade researchers have been developing heteroepitaxial growth of GaP on orientation-patterned gallium arsenide (OP-GaAs) templates, successfully demonstrating OP-GaP layers up to 350 μm in thickness with excellent domain fidelity. Despite these successes, no nonlinear frequency conversion has yet been demonstrated using these GaP-on-GaAs QPM layers, suggesting that issues such as stress-birefringence (induced by the lattice and thermal-expansion mismatch between GaP and GaAs), bowing, or unwanted absorption may impede device performance. Here we report for the first time efficient and broadly-tunable frequency conversion in OP-GaP layers up to 1.2-mm thick grown by hydride vapor-phase epitaxy (HVPE) on 3-inch MBE-grown OP-GaAs templates. The multi-grating wafer design enabled discrete wavelength tuning via stepped adjacent gratings with fixed periods, continuous tuning via fan gratings, and bandwidth engineering via chirped gratings. The gratings had short periods ranging from 14 to 35.2 microns that propagated up to 300 microns in height before dropping out due to overgrowth. Polished, AR-coated, 3-mm-long OPO crystals were fabricated and pumped at 1040 nm (5.5W, 100 MHz, 2.5 ps) with a Chromacity Yb-fiber laser, yielding output powers of 140, 90, and 60 mW at idler wavelengths of 5.6, 7.8, and 10.7 μm respectively.
INVESTIGATION ON NUCLEATION KINETICS, GROWTH AND CHARACTERIZATION OF UREA PHTHALIC ACID THIRD ORDER NLO SINGLE CRYSTALS

Presenting Author: Ezhil Vizhi

Topic: Nonlinear Optical and Laser Host Materials

Format: Contributed

Session: 3, 4

Date: 8/3/2021

Time (in MDT): 1:45:00 PM

Authors: Ezhil Vizhi R, VIT University, Vellore, India  Dhivya R, VIT University, Vellore, India

Nucleation and growth kinetics give information about the crystal growth process, which can be utilized in the growth of large size crystals. Urea phthalic acid (UPA) was synthesized by slow evaporation method. Solubility was analyzed gravimetrically and it is observed that it exhibits positive temperature coefficient of solubility which is suitable for bulk growth. Metastable zonewidth and induction period was observed by adopting polythermal method and isothermal method. Based on the classical nucleation theory, the other nucleation parameters such as interfacial energy, Gibbs critical free energy and radius of critical nuclei were calculated. UPA was synthesized and subsequently grown by slow cooling technique [2]. The crystal system and lattice parameters were confirmed by single X-ray diffraction analysis [1]. Fourier transform infrared (FT-IR) analysis was performed to identify the functional groups and their corresponding assignment. The cut off wavelength of the grown crystal was 238 nm and band gap energy was found to be 3.5eV from UV-vis-NIR spectrum. The fluorescence of the grown crystal was identified from the photoluminescence spectrum. The mechanical stability of the grown crystal was estimated by Vickers microhardness studies and it is evident that the grown crystal belongs to soft material category. The dielectric constant and dielectric loss were studied as a function of various frequencies at different temperatures. The third order nonlinear optical susceptibility was estimated by the Z- scan technique and UPA crystal is a promising candidate for nonlinear optical application.

Keywords: phthalic acid, slow cooling, Nucleation kinetics, single crystal XRD.

References
SYNTHESIS, GROWTH AND CHARACTERIZATION OF SEMIORGANIC BARIUM HYDROGEN MALATE SINGLE CRYSTAL

Presenting Author: Ezhil Vizhi

Topic: Nonlinear Optical and Laser Host Materials

Format: Contributed

Session: 3, 5

Date: 8/3/2021

Time (in MDT): 2:00:00 PM

Authors: Ezhil Vizhi R, VIT University, Vellore, India  Kavitha S, VIT University, Vellore, India

A single crystal of barium hydrogen malate was grown by adopting the slow evaporation technique. The structure and space group of the grown crystal was identified by using single crystal X-ray diffraction method. Fourier Transform Infrared studies were performed to identify the various functional groups present in the grown crystal. Optical transparency of the crystal was analyzed by UV-visible spectral analysis and the optical band gap values of the grown material was determined by drawing the Tau's plot. The frequency dependent dielectric constant and dielectric loss of the grown crystals were studied for different temperature. Mechanical behavior of the grown material was studied with help of Vicker’s microhardness measurement. The nonlinear optical properties of the grown crystals were confirmed by second harmonic generation test which shows the suitability of NLO application.

Keywords: Single crystal XRD, Vicker’s Microhardness, Dielectric constant, Slow evaporation technique.

References:
SIC POWER DEVICE MASS COMMERCIALIZATION: PRESENT STATUS AND BARRIERS TO OVERCOME

**Presenting Author:** Victor Veliadis

**Topic:** Silicon Carbide and Gallium Oxide Materials and Devices

**Format:** Invited

**Session:** 2, 1

**Date:** 8/2/2021

**Time (in MDT):** 10:30:00 AM

**Authors:** Victor Veliadis, PowerAmerica/NCSU, Raleigh, North Carolina, United States

In an increasingly electrified technology driven world, power electronics is central to the entire manufacturing economy. Silicon (Si) power devices have dominated power electronics due to their low cost volume production, excellent starting material quality, ease of processing, and proven reliability. Although Si power devices continue to make significant progress, they are approaching their operational limits primarily due to their relatively low bandgap and critical electric field that result in high conduction and switching losses, and poor high temperature performance. In this presentation, the favorable material properties of Silicon Carbide (SiC), which allow for highly efficient power devices with reduced form factor and cooling requirements, will be highlighted. Comparison with the material properties of GaN, as well as those of emerging ultra wide-bandgap materials like Ga2O3, Diamond, and AlN will provide perspective as well as insight into future trends. Specifics of SiC substrate and epitaxial growth will be summarized as a segue to SiC device fabrication that will be outlined with an emphasis on the processes that do not carry over from the mature Si manufacturing world and are thus specific to SiC. In particular, the talk will stress the design and fabrication of SiC MOSFETs that are currently being inserted in the majority of SiC based power electronic systems. SiC fab models will be analyzed and the vibrant U.S. SiC manufacturing infrastructure will be presented, Fig. 1. Fig. 1. The U.S. SiC fab infrastructure mirrors that of Si. Fab considerations and cost reduction strategies will be stressed elucidating the path to the projected $1B SiC device market by 2022. Barriers to SiC mass commercialization will be identified and detailed. These include the higher than silicon device cost that is primarily driven by the elevated cost of substrates, reliability and ruggedness concerns and tradeoffs, and the impact of material and processing issues. The latter comprise the presence of basal plane dislocations, the need for improved wafer planarity, minimizing defect generation during processing, and reducing threshold-voltage-instability by forming a high quality SiC/gate-oxide interface. The impact of a trained workforce, capable of skillfully inserting SiC into power electronics systems, will be discussed in terms of accelerating SiC mass commercialization. Finally, the recent global push for transportation electrification and for tackling the climate crisis will provide the framework for discussing SiC power technology high-volume applications and growth prospects.
Silicon carbide (SiC), as a semiconductor material, enables the design and fabrication of high-power density solid state power devices that enable smaller, lighter and more efficient power conversion systems. With the unique properties of SiC, such as relatively wide bandgap combined with high thermal conductivity, SiC MOSFETs have opened a new generation of power management systems in renewable energy, industrial power supply, and battery electric automotive applications. Likewise, GaN HEMT devices fabricated on semi-insulating SiC substrates deliver much higher bandwidths and power levels with very high efficiencies.

While SiC exhibits superior material properties, crystal growth techniques required to grow SiC are very different and significantly more challenging than conventional growth processes for other crystalline materials. Other widely used semiconductor materials, such as silicon, have significantly lower melting temperatures, allowing for direct crystal growth techniques from melted source materials. In contrast, single crystal SiC substrates can be obtained by sublimation and recrystallization on a seed crystal, a technique called seeded sublimation growth or physical vapor transport (PVT). During this session, we will analyze the details of the SiC crystal growth via PVT in comparison to conventional techniques, discuss the associated challenges and possible solutions. We will also review the processing of grown SiC crystals into substrates.

As SiC device technologies expand into commercial markets, large diameter substrates become more desirable. In addition to diameter, the usable area on such substrates impact the cost of the device. The usable area of SiC substrates can be limited by the defects in the material. As a part of this session, we will examine various aspects of how defects form and behave in SiC crystals, and their transference into subsequent epitaxial layers prior to device fabrication.
EFFECT OF SURFACE RELAXATION & X-RAY ABSORPTION ON DISLOCATION CONTRAST IN SYNCHROTRON GRAZING-INCIDANCE X-RAY TOPOGRAPHS IN OFF-AXIS 4H-SIC CRYSTALS

Presenting Author: Tuerxun Ailihumaer

Topic: Silicon Carbide and Gallium Oxide Materials and Devices

Format: Contributed

Session: 2, 5

Date: 8/2/2021

Time (in MDT): 11:30:00 AM

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The contrast of dislocations lying on the basal plane in off-axis 4H-SiC crystals, such as basal plane dislocations, deflected threading screw and mixed dislocations are simulated using a more sophisticated ray-tracing simulation method, which is based on the orientation contrast mechanism. The effects of surface relaxation combined with X-ray absorption are both considered in this simulation method in order to further evaluate the factors contributing to the dislocation contrast formation. Comparison of the simulated results with the actual grazing-incidence topographic images of the dislocations reveals that the dislocation contrast is dominated by surface relaxation effect, which mainly occurs for diffractions near the crystal surface. Depth analysis shows that the diffracted X-ray beam from regions below the dislocation contribute additional contrast to the image formation. With consideration of X-ray absorption, the simulated contrast of the dislocation gradually weakens as the diffraction position gets deeper into the crystal. Detailed discussion on each type of dislocation on the basal plane including inclined dislocation contrast is presented in this paper. The full BPD loop contrast is also simulated and thus the Burgers vectors of all types of BPDs can be determined by comparing with the simulated results.
COMPLETE CHARGE COLLECTION CRITERIA IN PARTIALLY DEPLETED 250 µM THICK 4H-SIC EPITAXIAL SCHOTTKY BARRIER RADIATION DETECTOR

Presenting Author: Joshua Kleppinger

Topic: Silicon Carbide and Gallium Oxide Materials and Devices

Format: Contributed

Session: 2, 6

Date: 8/2/2021

Time (in MDT): 11:45:00 AM

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Being a wide bandgap (WBG) semiconductor and having very high average threshold displacement energy, highly crystalline 4H-SiC epilayers fits best for high-resolution radiation detection applications in harsh environment. Development on the growth of thicker epilayers is gaining high impetus for detection and measurements of penetrating radiations like x- and γ-rays. While thicker epilayers are expected to absorb x-/γ-rays efficiently, challenges arise at high operating bias voltages needed for full depletion of the epilayers. High leakage currents due to thermionic trap assisted tunneling (TTAT) is of primary concern which necessitates to identify and characterize the intrinsic defects responsible for such phenomenon. Effects of extrinsic factors such as spatial variation of barrier height responsible for affecting the carrier flow mechanism through the Schottky junctions also needs to be addressed for assessing reliable and durable operation of these devices. We present fabrication and characterization of high-resolution vertical Schottky barrier radiation detectors on 250 µm thick 4H-SiC epitaxial layers using our proprietary device design. The effective carrier concentrations and built-in voltages were calculated from the capacitance-voltage (C-V) measurements to be $9.8 \times 10^{13}$ cm$^{-3}$ and 1.9 V, respectively. From the current-voltage (I-V) characteristics it was observed that the current remained less than 100 pA up to a reverse bias of 700 V. Radiation detection measurements with 241Am alpha particles show that for a depletion width (active region) up to the range of the incident alpha particles (18 µm) is not enough for full charge collection due to the longer transit time in the neutral region (from the edge of the depletion region to the detector cathode). In fact, full charge collection does not occur until the depletion width is greater than 40 µm. At this width, the energy resolution of the detector for 5486 keV alpha particle signal was observed to be 0.48% (FWHM). We will also present the results obtained from deep level transient spectroscopy (DLTS) to correlate the charge carrier trap centers that affect the device performance, especially at high operating bias.
MODELING OF GA\textsubscript{2}O\textsubscript{3} CRYSTAL GROWTH AND EPITAXY

Presenting Author: Alex Galyukov

Topic: Silicon Carbide and Gallium Oxide Materials and Devices

Format: Invited

Session: 2, 1

Date: 8/3/2021

Time (in MDT): 10:30:00 AM


Gallium oxide is a wide-bandgap material with unique properties, which has a potential to reduce the manufacturing cost of high-power electronics. However, the acute spike in the interest to this material is quite recent and its widespread adoption by industries requires further improvement of production technologies in terms of material quality, yield, and production costs. Since modeling is known to be an effective tool for enhancing the general understanding of the process and addressing specific technological issues, we would like to demonstrate how it can be used with different techniques of Ga\textsubscript{2}O\textsubscript{3} growth from the melt, different commonly used methods have the same limiting factor, namely, active evaporation of oxygen from the melt surface. It causes the loss of gallium and oxygen stoichiometry in the melt, subsequent formation of crystal defects, and even loss of monocrystalline structure. To address this issue, we present an advanced chemical model including the following aspects of the process: Ga\textsubscript{2}O\textsubscript{3} melt is considered as solution of Ga\textsuperscript{3+} and O\textsuperscript{2-} ions, a nonstoichiometric evaporation of gallium and oxygen containing gas species is allowed at the free melt surface, kinetics of thermal decomposition of molecular oxygen and additional compounds in the gas phase is accounted for. The chemical model is coupled with the global heat and mass transport in both gas phase and melt. To illustrate, the model is applied to 2-inch Ga\textsubscript{2}O\textsubscript{3} crystal growth by Czochralski method with different partial pressures of CO\textsubscript{2} gas. Effect of the furnace design and gas composition on the melt stoichiometry is discussed. In case of HVPE, for both O\textsubscript{2} and H\textsubscript{2}O as an oxygen-containing precursor, simulation requires accurate account of temperature and flow pattern, species mass transport, and surface chemical reactions. Furthermore, in case of MOCVD, numerical modeling inevitably involves simulation of gas-phase chemical reactions. TMGa decomposition in the gas-phase, its reaction with oxygen to form DMGa-O-CH\textsubscript{3} complex, following formation of (DMGa-O-CH\textsubscript{3})\textsubscript{2} dimers are all an integral part of the chemical model necessary to evaluate the the effect of various process parameters on deposition rate and uniformity.
Gallium oxide is a wide bandgap semiconductor that presents different stable and metastable polymorphs. The only thermodynamically stable at high temperatures is the monoclinic beta phase. However, the hexagonal alpha and the orthorhombic epsilon phases have very promising characteristics and lately attracted much attention for electronic and optoelectronic applications (e.g., power diodes and transistors, solar blind UV photodetectors). Note that also these metastable phases are indeed very stable up to at least 600 °C. The increasing attention towards these alternative polymorphs derives from: (i) higher lattice symmetry with respect to beta-Ga$_2$O$_3$ which can favour heterostructure fabrication, (ii) simpler deposition conditions at lower temperature on cost-effective sapphire substrates, (iii) in addition, the epsilon polymorph exhibits ferroelectric properties. So far, little is known about appropriate technologies for synthesis of the metastable Ga$_2$O$_3$ phases. In this talk, a literature survey will be presented along with own data on epitaxial growth of Ga$_2$O$_3$. The major aim is to provide useful guidelines for the synthesis of various phases by the usual epitaxial growth technique (MOVPE, HVPE, mist-CVD, MBE, and PLD). A picture of nucleation and growth mechanisms of different Ga$_2$O$_3$ polymorphs as a function of ambient and precursors will be provided.
INVESTIGATION OF OMVPE GROWTH FOR BETA GALLIUM OXIDE BY THERMODYNAMIC AND EXPERIMENTAL STUDIES

Presenting Author: Ken Goto

Topic: Silicon Carbide and Gallium Oxide Materials and Devices

Format: Contributed

Session: 2, 5

Date: 8/3/2021

Time (in MDT): 11:30:00 AM

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Beta-gallium oxide (β-Ga<sub>2</sub>O<sub>3</sub>) is one of the ultra-wide bandgap semiconductor materials, which is expected to have a high energy saving on power device applications. To realize β-Ga<sub>2</sub>O<sub>3</sub> devices, precise control of layer thickness and carrier density is required for the drift layer with high crystallinity, and much effort has been put into research on various epitaxial growth techniques to achieve those requirements. Among them, organometallic vapor phase epitaxy (OMVPE) is a promising growth technique because it can grow with atomic layer precision and realize sharp doping profiles. Actually, device demonstrations using β-Ga<sub>2</sub>O<sub>3</sub> layers grown by the OMVPE method have been actively reported in recent years. However, the details of the β-Ga<sub>2</sub>O<sub>3</sub> formation mechanism by the chemical reaction between OM and oxygen (O<sub>2</sub>) are not well understood. In this paper, thermodynamic analysis and experimental demonstration of β-Ga<sub>2</sub>O<sub>3</sub> growth by OMVPE using triethylgallium (TEG) and O<sub>2</sub> as precursors were performed. The β-Ga<sub>2</sub>O<sub>3</sub> formation mechanism was investigated by calculating the equilibrium partial pressures of gaseous species coexisting in the growth system. The calculation results revealed that the O<sub>2</sub> supplied to the growth system is first consumed by the combustion of hydrocarbons and H<sub>2</sub> derived from TEG, and then used for the growth of β-Ga<sub>2</sub>O<sub>3</sub>. Therefore, a high input partial pressure of O<sub>2</sub> and a high growth temperature are preferable for the OMVPE growth of β-Ga<sub>2</sub>O<sub>3</sub> to achieve complete combustion of hydrocarbons and H<sub>2</sub>. The OMVPE growth of β-Ga<sub>2</sub>O<sub>3</sub> was demonstrated on the c-plane sapphire substrates under the optimum conditions suggested by the thermodynamic analysis. The growth was carried out at a growth temperature of 800 to 1000 °C for 1 hour under a total reactor pressure of 20 Torr, a TEG input partial pressure (P<sub>TEG</sub>) of 2×10<sup>-2</sup> Torr, and an input VI/III ratio (= 2P<sub>O2</sub>) of 100. A growth rate of approximately 1.4 µm/h was achieved at 800 and 900 °C without a formation of Ga droplets. The β-Ga<sub>2</sub>O<sub>3</sub> layers were highly (-201) oriented crystals with a smooth surface and a uniform layer thickness as can be seen
from the figure. In addition, the incorporation of carbon and hydrogen impurities into the grown layer was less than the background of the measurement system, suggesting the CO$_2$ and H$_2$O formed by the complete combustion of hydrocarbons and H$_2$ do not become doping gases.
KINETIC MONTE CARLO SIMULATIONS FOR HOMOEPITAXY ON Ga<sub>2</sub>O<sub>3</sub>(100)

Presenting Author: Wolfram Miller

Topic: Silicon Carbide and Gallium Oxide Materials and Devices

Format: Contributed

Session: 2, 6

Date: 8/3/2021

Time (in MDT): 11:45:00 AM

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We developed a kinetic Monte Carlo (KMC) model which comprises adsorption, diffusion, and desorption and reflects the structure of β-Ga<sub>2</sub>O<sub>3</sub> with its two kinds of atoms: Ga and O. The knowledge gained from metal organic vapour phase epitaxy (MOVPE) experiments combined with AFM and TEM characterisation was used for the setup of rules and activation energies for the various surface processes. Both growth on flat and vicinal surfaces have been studied as a function of growth parameters. On a vicinal surface ((100) oriented with an offcut of 6° towards [00-1]) different growth modes have been observed when using different desorption energies. While low desorption energy (high desorption rate) leads to step bunching, intermediate to step flow growth mode, the high desorption energy (low desorption rate) leads to nucleation on terraces with a final configuration similar to step bunching.
CZOCHRALSKI GROWTH AND PHYSICAL PROPERTIES OF BULK β-GA₂O₃ SINGLE CRYSTALS

Presenting Author: Zbigniew Galazka

Topic: Silicon Carbide and Gallium Oxide Materials and Devices

Format: Invited

Session: 3, 1

Date: 8/3/2021

Time (in MDT): 1:00:00 PM

Authors: Zbigniew Galazka, Leibniz Institute for Crystal Growth, Berlin, Germany

As the worldwide energy consumption increases significantly, energy saving becomes an important goal for power electronic devices to improve voltage conversion efficiency. For that purpose, power devices based on wide bandgap semiconductors SiC and GaN (E₉ = 3.3 eV and 3.4 eV, respectively) have successfully been developed. To further increase the conversion efficiency and switching high voltages the research focuses nowadays on ultra-wide bandgap oxide semiconductors, in particular on monoclinic β-GA₂O₃. It is an n-type semiconductor with a bandgap of 4.85 eV, large breakdown filed of 8 MV/cm, a wide doping range with free electrons (about four orders of magnitude, mid 10⁻¹⁵ cm⁻³ to mid 10⁻¹⁹ cm⁻³), a good carrier mobility (around 150 cm²/V·s), and a low on-resistance. The availability of bulk single crystals grown from the melt (Czochralski, EFG, and Bridgman methods) [2] enables wafer preparation for homoepitaxial growth of epi-layers, and subsequent device fabrication. However, β-GA₂O₃ is thermally unstable at high temperatures, that in a combination with high melting point of about 1800°C makes the growth of large single crystals of high structural quality really challenging. In particular, utilization of iridium crucibles and high decomposition rate of Ga₂O₃ require specific solutions for crystal growth. Here, I will discuss particularities of the growth of bulk β-GA₂O₃ single crystals by the Czochralski method [2-4]. This includes thermodynamic aspects of the growth, impact of doping and free carriers on the growth stability, basic structural quality, as well as electrical and optical properties of obtained crystals. The electrical properties will be discussed in view of the growth conditions, doping, and post-growth heat treatment.


Growth and wafering of Gallium Oxide

Presenting Author: Allen Brady

Topic: Silicon Carbide and Gallium Oxide Materials and Devices

Format: Invited

Session: 3, 3

Date: 8/3/2021

Time (in MDT): 1:30:00 PM

Authors:

β-Ga2O3 Growth and Wafer Fabrication SYNOPTICS began growing β-Ga2O3 under an AFRL contract FA8650-15C-1796 in 2015. Currently, 50mm diameter boules are consistently grown to lengths up to 35mm from seeds oriented along the [010] direction. SYNOPTICS has grown boules as both unintentionally doped (UID) and doped with Mg and Fe using high purity (99.99+) oxides to obtain semi- and highly insulating substrates. Doping levels for Mg were 0.10mol% and for Fe ranged from 0.0025mol% to 0.0100mol%. Crystal growth is performed at the melting point of 1820°C via the Czochralski method using iridium crucibles in an induction-heated furnace using high purity Ga2O3 powder (99.999%). Ga2O3 is known to dissociate at high temperatures into sub-oxides including GaO and Ga2O with O2 evolution in oxygen-deficient atmospheres [1]. Growth in an iridium crucible, however, requires a low-oxygen environment to avoid excess oxidation of Ir to IrO2. SYNOPTICS growth chambers use free-flowing gas at ambient pressure to control the atmosphere. In order to suppress the dissociation of Ga2O3 and minimize excess oxidation of Ir, the growth atmosphere is a mixture of CO2 and O2 supplied to the melt surface. The crystals are rotated between 2 and 10 RPM and pulled at rates ranging between 0.5mm/hr and 2mm/hr during growth. Boules grown are largely free of twins and will occasionally have cleavage cracking on the (100) and (001) planes, the former being predominant. The as-grown boules are oriented to within ~1° of the [010] growth axis and prepared for coring or shaping. 25mm diameter cores are drilled. 50mm diameter cores are obtained by turning down the entire boule on a lathe with a diamond tool. These cores are then encased in epoxy and sliced to ~750μm wafers with a multi-wire saw with a 150μm wire using a B4C loose abrasive. The easily-cleaved (100) plane is used as the reference flat for wafers. The wafers are chemical mechanical polished to average surface roughness of <2Å via AFM scans of 20μm x 20μm. High resolution x-ray rocking curve measurements of the (020) show good crystal quality with FWHM of 84 and 58 arc-sec parallel and perpendicular to the (001) reference flat respectively. Total thickness variation of less than 20 microns have been achieved on 50 mm epi-ready wafers.
ELECTRONIC AND OPTICAL PROPERTIES OF ZN-DOPED B-GA<sub>2</sub>O<sub>3</sub> CZOCHRALSKI SINGLE CRYSTALS

Presenting Author: Jani Jesenovec

Topic: Silicon Carbide and Gallium Oxide Materials and Devices

Format: Contributed

Session: 3, 5

Date: 8/3/2021

Time (in MDT): 2:00:00 PM

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Abstract <br/>β-Ga<sub>2</sub>O<sub>3</sub> has several well-known soluble deep acceptors which impart highly insulating behavior, typically Fe and Mg. Here we investigate Zn doping in bulk β-Ga<sub>2</sub>O<sub>3</sub>. Large cylindrical crystals were synthesized at 0.25 at.% Zn concentration via Czochralski (CZ) and vertical gradient freeze (VGF) techniques in an Ar + O<sub>2</sub> environment. Representative crystals were assessed for orientation (electron backscatter diffraction, Raman spectroscopy), purity (glow discharge mass spectrometry and secondary ion mass spectrometry), optical properties (ultraviolet to near infrared absorption), and electrical properties (resistivity, current-voltage). Purity measurements indicate that expected Zn evaporation is insufficient to inhibit doping of Zn into β-Ga<sub>2</sub>O<sub>3</sub>. Hybrid functional calculations show Zn substitutes nearly equally on tetrahedral and octahedral sites, with a <~0.1 eV preference for the octahedral (Ga<sub>II</sub> site), due to a similar size to Ga in both coordinations. Further, calculations show Zn<sub>Ga</sub> acts as a deep acceptor with trapping levels ~1.3 eV and ~0.9 eV above the valence band for one and two holes, respectively. The solubility and electronic behavior of Zn dopants are consistent with measured concentrations in excess of 1×10<sup>18</sup> atoms/cm<sup>3</sup> and electrical measurements that show resistivity 10<sup>11</sup>-10<sup>13</sup> Ω∙cm, with no <i>p</i>-type conduction.
ULTRA-WIDE BANDGAP ALGAN ALLOYS FOR POWER DIODES AND TRANSISTORS

Presenting Author: Andrew Allerman

Topic: Silicon Carbide and Gallium Oxide Materials and Devices

Format: Invited

Session: 4, 1

Date: 8/3/2021

Time (in MDT): 3:00:00 PM

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AlGaN alloys have superior material properties that are appealing for the next generation of high-voltage power devices. Thus, power diodes employing AlGaN alloys are expected to operate at higher breakdown voltages with thinner and more heavily-doped drift regions, leading to lower resistive losses compared to Si-, SiC- and even GaN-based devices. However, ultra-wide bandgap (UWBG) semiconductors including Al-rich AlGaN, diamond, c-BN and β-Ga$_2$O$_3$ all face challenges in having both p- and n-type conductivity, and a process (regrowth or implantation) to achieve selective area doping. We will present how the formation of AlGaN-based heterojunctions and the utilization of polarization fields for doping offer design options not possible for devices based on SiC or other UWBG semiconductors. To address the challenge of bipolar doping in Al-rich AlGaN layers, we employ compositionally graded AlGaN layers and polarization induced electric fields to achieve n-type or p-type conductivity at compositions where conventional impurity doping yields only resistive material. Using polarization induced doping, we will describe a pn diode fabricated in Al-rich AlGaN with breakdown voltage of 1 kV. However, full exploitation of the efficiency gains expected from AlGaN alloys for power management systems also requires power diodes and current switching transistors which employ spatially defined n- and p-type regions. We have demonstrated pn junction diodes formed by anode regrowth on blanket inductively coupled plasma (ICP) etched (0001) n-Al$_{0.3}$Ga$_{0.7}$N drift layers with performance which matches that of continuously grown diodes, and have achieved a breakdown voltage of 1.5 kV. Unlike the case for GaN, we find that pn junction formation by epitaxial regrowth in AlGaN is insensitive to etch damage and impurities at the regrowth interface. Furthermore, we show for the first time a selective p-type area pn junction diode with current-voltage characteristics equal to diodes grown without interruption, and have achieved a breakdown voltage in excess of 1.8 kV. This demonstration supports the promise of UWBG AlGaN alloys for realizing practical, kilovolt-class power diodes and transistors for next generation power systems.

This work was supported by the Laboratory Directed Research and Development program at Sandia National Laboratories. Sandia National Laboratories is a multimission laboratory managed and operated...
Abstract Book - ACCGE-22//OMVPE-20

SYNCHROTRON X-RAY TOPOGRAPHIC IMAGE OF DISLOCATIONS IN 6H-SIC AXIAL SAMPLES

Presenting Author: Hongyu Peng

Topic: Silicon Carbide and Gallium Oxide Materials and Devices

Format: Contributed

Session: 4, 3

Date: 8/3/2021

Time (in MDT): 3:30:00 PM

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Wide bandgap semiconductor, 6H-SiC, is being applied in photoconductive semiconductor switches (PCSS) due to its semi-insulating properties. This material is normally insulating but when illuminated, charge carriers are pumped to the conduction band and the material becomes conductive in proportion to the light intensity. Under the application of voltage and laser, the density as well as the movement of the defects will have an impact on the performance of the device. Characterization and understanding the mechanism of this potentially destructive defect process is of great scientific interest as well to the development of the device. X-ray topography is a powerful, non-destructive technique for the characterization of extended defects in large, single crystals. In this study, threading edge dislocations (TED), threading screw dislocations (TSD) as well as basal plane dislocations (BPD) in 6H-SiC axial samples are revealed using synchrotron rocking curve topography, where the atomic structure information (Burgers vector) of these dislocations are investigated using ray tracing simulation. The understanding of the nature of these dislocations is of great importance as to predict their propagation and movement under the application of voltage and laser, and eventually helps to improve the performance of the device.
STRUCTURAL DEFECTS CHARACTERIZATION OF PVT-GROWN 6H-SIC CRYSTALS USING SYNCHROTRON X-RAY TOPOGRAPHY AND RAY-TRACING SIMULATIONS

Presenting Author: Qianyu Cheng

Topic: Silicon Carbide and Gallium Oxide Materials and Devices

Format: Contributed

Session: 4, 4

Date: 8/3/2021

Time (in MDT): 3:45:00 PM

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Silicon carbide (SiC) based power devices enable energy efficiency enhancement in power handling and conditioning owing to the unique combination of its superior electronic and physical properties, such as excellent chemical resistance, high thermal conductivity, and high breakdown voltage. However, the device performance is found limited by various defects including threading screw/mixed dislocations (TSDs/TMDs), threading edge dislocations (TEDs), and basal plane dislocations (BPDs) within the SiC crystal. To continuously pursue the crystal quality and device performance improvement, this study focused on the investigation of defect configurations in physical vapor transport (PVT) grown 6H-SiC crystal. The major characterization technique employed is synchrotron monochromatic beam X-ray topography (SMBXT) for recording its grazing-incidence images of all six different 1 1-2 12 reflections. Defects including TSDs, TMDs, TEDs, and BPDs were studied in detail in conjunction with ray-tracing simulation technique. The ray-tracing simulation approach based on the orientation contrast mechanism to interpret the topographic contrasts of dislocations resulting from local orientation and d-spacing variation induced by lattice displacements. The dislocation types and corresponding Burgers vectors were identified and analyzed by comparing the simulated images with grazing-incidence topographic contrasts. Dislocation density analysis was also conducted on the 2 inch 6H-SiC wafer, and a distribution trend with higher TSD and TMD densities in regions near the center of the wafer compared to the periphery region was observed. High resolution X-ray diffraction (HRXRD) was also conducted on regions with grain boundaries and micropipes. The broadening of the rocking curve widths confirmed the lattice bending and distortion near defect regions. This study has successfully demonstrated a direct Burgers vectors determination approach for each type of dislocation. This knowledge of dislocation types and their distributions in 6H-SiC wafers can provide crucial feedback for pursuing crystal quality enhancement during growth process.
CHARACTERIZATION OF LATTICE DAMAGE IN HIGH ENERGY ION IMPLANTED 4H-SIC WAFERS AT ROOM TEMPERATURE

Presenting Author: Zeyu Chen

Topic: Silicon Carbide and Gallium Oxide Materials and Devices

Format: Contributed

Session: 4, 5

Date: 8/3/2021

Time (in MDT): 4:00:00 PM

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Silicon Carbide (SiC) is a promising wide bandgap semiconductor for power devices. Due to excellent properties of SiC, such as wide band gap, high break down voltage and thermal stability, SiC devices are able to be operated under harsh environment, such as high temperature, high voltage and high frequency environment. Ion implantation is an inevitable critical process in SiC device fabrication. Conventionally, the implantation energy is of the order of few hundred KeVs and the less than typically about a 1 um implantation box profile can be achieved. To fabricate future generation of SiC power devices such as SiC superjunction FETS, thick epilayers and deep implantation profiles are required. More than 10 um implantation box profile can be achieved by using MeV implantation energy at a ion beam facility. During ion implantation process, original Si or C atoms will be displaced from their regular lattice sites by the incoming ions and the original SiC unit cell will swell up. therefore, there will be inducing lattice strains introduced by ion implantation. After ion implantation, post annealing process is necessary to restore the crystal structure and activate the implanted ions. However, there are residual strains can exist due to incomplete recovery of the lattice structure. The and differencet in atomic size between the dopant atoms and the original SiC atoms also introduces additional strains. In this paper, as-implanted and post-annealed 4H SiC wafers, implanted with 59.8 MeV Al ions and annealed at different temperature areas characterized by Synchrotron Rocking Curve X-ray Topography and Reciprocal Space Mapping. Local lattice strain obtained by Reciprocal Space Mapping and overall lattice strain obtained by Synchrotraon Rocking Curve X-ray Topography are compared between the as implanted wafer and post annealed wafers.
MODELING AS THE POWERFUL TOOL FOR EVALUATION AND IMPROVEMENT OF CRYSTAL QUALITY IN
SIC PVT GROWTH

Presenting Author: Alexey Kulik

Topic: Silicon Carbide and Gallium Oxide Materials and Devices

Format: Contributed

Session: 4, 6

Date: 8/3/2021

Time (in MDT): 4:15:00 PM

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Improvement of the crystal quality remains one of the most challenging and practically important
problems in bulk growth of SiC crystals especially in view of high demand for 8-inch SiC boules.
Numerical modeling, which has been a helpful tool in development of the PVT technology, should
provide approaches to evaluation of different aspects of the crystal quality. In this work, we discuss
several advanced models allowing estimation of quality of bulk SiC crystals grown by PVT technology and
control of crystal quality via the hot zone design and growth conditions. One of the topical killing defects
in bulk SiC is crystal cracking. Cracks in the bulk SiC crystals are caused by high residual tensile stress
present in the crystal at room temperature or stress generated in the crystal during cooling-down of the
growth setup. If the tensile stress is high enough, randomly emerged flaws exceeding a critical size will
lead to cracking of the crystal. In this work, a quantitative fracture mechanics model is applied to predict
Crack formation in bulk SiC crystals grown by PVT method. Another severe defect attracting significant
attention is inclusion of carbon particles into the growing crystal. One of the reasons of the particle
appearing in the crystal is their transport to the growth surface. The origins of the particles are the
source which graphitizes during its sublimation producing free carbon and the wall of the graphite
 Crucible. The particle transport is governed by forces acting on the small pieces of carbon. We study
dynamics of the particle transport in the growth chamber considering the net force acting on the
particle to include the drag, thermophoretic, and gravity forces. One more reason for emergence of
inclusions in SiC crystals is formation of extra phases on the growth surface. Due to this effect, both
carbon and silicon inclusions can appear during growth of SiC by PVT. An advanced approach is used in
this work to predict formation of solid carbon and liquid silicon inclusions on the growth interface. For
the models of crystal characterization to be of practical value, it is important to introduce them into a
complex modeling tool capable of detailed simulation of the PVT process. In the current work, the
models are implemented within the simulation software Virtual Reactor. Therefore, they are coupled
with thorough models of heat- and mass transport governing growth of bulk SiC crystals by PVT.
REGIOSELECTIVITY AND CHEMOSELECTIVITY IN NANOCRYSTAL CHEMISTRY

Presenting Author: Sara Skrabalak

Topic: Symposium on Metal Nanoparticle Nucleation and Growth

Format: Invited

Session: 3, 1

Date: 8/4/2021

Time (in MDT): 1:00:00 PM

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The structural characteristics of a nanocrystal strongly relate to its properties, where increasingly precise chemistry is required that includes regioselective and chemoselective modifications of nanocrystal seeds or templates. This seminar will present recent demonstrations of both. Regioselective deposition of metal on shape-controlled seeds will be discussed, being achieved through judicious control of supersaturation and capping agent concentration during seeded overgrowth. Chemoselective transformation of nanocrystal templates will also be highlighted by use of galvanic replacement. In most demonstrations of galvanic replacement with nanocrystal templates, the oxidation of monometallic templates by ions of a more noble metal is studied. However multimetallic templates offer more than one type of reaction site. This presentation will outline the processes involved during galvanic replacement with Janus-style AgPd dimers and intermetallic nanoparticles. Interestingly, the galvanic replacement is found to be selective within multimetallic nanocrystals while solid-state diffusion processes influence the final multimetallic distribution. These results illustrate how anisotropic and spatially controlled reactivity on nanocrystals is possible, with design criteria toward atomically precise nanocrystals emerging.
RESHAPING OF TRUNCATED PD NANOCUBES AND OCTAHEDRA: ATOMISTIC MODELING AND TEM ANALYSIS

Presenting Author: Jim Evans

Topic: Symposium on Metal Nanoparticle Nucleation and Growth

Format: Contributed

Session: 3, 3

Date: 8/4/2021

Time (in MDT): 1:30:00 PM

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Stability against reshaping of metallic nanocrystals synthesized with tailored far-from-equilibrium shapes is key to maintaining optimal properties for applications such as catalysis and plasmonics. We develop a stochastic atomistic model and perform KMC simulations for reshaping of fcc metal nanocrystals mediated by surface diffusion. The model incorporates realistic diffusion kinetics across and between different facets, along step edges and around corners, etc. We also provide an analytic determination of the energy variation along the optimal pathway for reshaping which involves transfer of atoms across the surface from edges or corners to form new layers on \{100\} side facets for nanocubes, or on \{111\} side facets for octahedra. The effective barrier from this analysis is shown to increase strongly with the degree of truncation of edges and corners in the synthesized nanocrystal. Theory matches and elucidates experimental TEM results for the reshaping kinetics for Pd nanocubes yielding a high effective barrier of $E_{\text{eff}} = 4.6$ eV for the appropriate degree of truncation. Reference: ACS Nano 14 (2020) 8551. *US Department of Energy, Basic Energy Sciences Division of Chemical, Biological and Geosciences under Contract No DE-AC02-07CH11338 to Ames Laboratory.
BULK GRAIN-BOUNDARY MATERIALS FROM METAL NANOCRystals

Presenting Author: Ou Chen

Topic: Symposium on Metal Nanoparticle Nucleation and Growth

Format: Invited

Session: 3, 4

Date: 8/4/2021

Time (in MDT): 1:45:00 PM

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Grain-boundary engineering is essential to unleash the potential of bulk materials in their mechanical, electrical, and thermal-transport properties. Especially, nanoscale grain-boundary conditions most critically determine materials’ properties, which has been investigated both theoretically and in experiments. However, it is difficult to achieve precise nanoscale grain boundary engineering with currently available methods in metallurgy because these methods rely almost exclusively on top-down approaches. Herein, we show a new bottom-up method, the nanocrystal coining method, that can produce tailored grain-boundary conditions with nano-scale precision. The nanocrystal coining method uses chemically-synthesized colloidal metal nanocrystals as the starting materials, and employs surface treatment and a pressure-sintering process. The resulting bulk materials (which we call "nanocrystal coins") possess a centimeter-scale in size, freestanding nature, and a metal-like appearance and conductivity while inheriting the crystal domains of the original nanocrystal building blocks. Nanoindentation measurements confirmed the superior mechanical hardness of the nanocrystal coins due to the Hall-Petch effect. Furthermore, the first example of a single-component bulk metallic glass was produced using the nanocrystal coining method from amorphous palladium nanoparticles. Our nanocrystal coining method can produce materials with as-tailored grain-boundary conditions with at least one-nanometer precision and crystal domain shape, from a wide range of metal components. We believe that our methods can produce ultimately optimized materials whose functionality crucially depends on the domain configuration at nanoscales, such as superhard materials, thermoelectric generators, and functional electrodes.
IMPROVED SCALABILITY OF PALLADIUM NANOCRYSTAL SYNTHESIS

Presenting Author: David Robinson

Topic: Symposium on Metal Nanoparticle Nucleation and Growth

Format: Contributed

Session: 3, 6

Date: 8/4/2021

Time (in MDT): 2:15:00 PM

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Single-crystal, faceted palladium nanoparticles with narrow size distributions can be synthesized by chemical reduction in aqueous solution, and have enabled informative studies of the mechanism of palladium hydride formation using electron microscopy techniques [Sytwu et al., Nano Letters 2018, 10.1021/acs.nanolett.8b00736]. Unfortunately, the most flexible and well characterized synthetic approach [Niu et al., ACS Nano 2010, 10.1021/nn100093y] requires centrifugation of 40 liters of reaction solution per gram of product, which is difficult at typical laboratory scales and inhibits study of macroscopic properties of the material. Similar nanoparticles have been produced from aqueous suspensions that require only about 1 liter per gram [Klinkova et al., Chem. Mater. 2015, 10.1021/acs.chemmater.6b00936]. Also unfortunate is a lack of demonstrated ability to controllably adjust crystal size, especially above 300 nm where hydride formation can introduce lattice defects [Ulvestad et al., Nature Mater. 2017, 10.1038/NMAT4842]. We have refined the aqueous suspension approach to further decrease the reaction volume per gram of product to a few hundred mL per gram, and to produce crystals in the hundreds of nm. We expect this approach to enable macroscopic studies of the hydride formation properties of palladium that complement prior single-particle studies.

Sandia National Laboratories is a multimission laboratory managed and operated by National Technology & Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International Inc., for the U.S. Department of Energy’s National Nuclear Security Administration under contract DE-NA0003525. SAND2021-3779 A
TOTAL SYNTHESIS OF METALLIC MOLECULES

Presenting Author: Xie Jianping

Topic: Symposium on Metal Nanoparticle Nucleation and Growth

Format: Invited

Session: 4, 3

Date: 8/4/2021

Time (in MDT): 3:30:00 PM

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Total synthesis, where desired organic- and/or bio-molecules can be produced from simple precursors at atomic precision and with known step-by-step reactions, has prompted centuries-lasting bloom of organic chemistry since its conceptualization in 1828 (Wöhler synthesis of urea). Such expressive science is also highly desirable in nanoscience, since it represents a decisive step towards atom-by-atom customization of nanomaterials for basic and applied research. Although total synthesis chemistry is less established in nanoscience, recent years have witnessed seminal advances and increasing research efforts devoted into this field. In this talk, I will discuss our recent work on introducing and developing total synthesis routes and mechanisms for atomically precise metal nanoclusters. Due to their molecular like formula and properties (e.g., HOMO-LUMO transition, strong luminescence and stereochemical activity), atomically precise metal NCs could be regarded as “metallic molecules”, holding potential applications in various practical sectors such as biomedicine, energy, catalysis and many others. More importantly, the molecular-like properties of metal nanoclusters are sensitively dictated by their size and composition, suggesting total synthesis of them as an indispensable basis for reliably realizing their practical applications.
POLYMER MEDIATED SYNTHESIS OF METAL OXIDE GRAPHENE COMPOSITE NANOFIBERS FOR GAS SENSING

Presenting Author: Luz Cruz

Topic: Symposium on Metal Nanoparticle Nucleation and Growth

Format: Contributed

Session: 4, 5

Date: 8/4/2021

Time (in MDT): 4:00:00 PM

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Highly porous nanofiber-based structures are of great importance to applications where high surface area is critical to performance. In addition, size, morphology, and high conductivity of these fiber-based nanomaterials are essential for development of highly efficient batteries and gas sensors. Here, we have developed a method to synthesize metal/metal oxide graphitic nanofibers from an electrospun polymer-metal precursor. Upon annealing, metal species diffuse through the polymer/carbon matrix, nucleating as metal nanoparticles and subsequently catalyzing the formation of graphitic structures. In this study, we investigate the role of the polymer matrix and annealing conditions on metal diffusion, clustering, and growth as well as the subsequent evolution of graphene. We utilize these parameters to control the size, number density, surface area of metal and metal oxide nanostructures that ultimately allow us to tune our material for use in Li-ion batteries and sensing elements. Investigation of the particle growth of these nanostructures within a polymer matrix will provide insight to the controlled synthesis and assembly of the nanoparticle constituents and their effect on performance. [1] H. Tang, W. Chen, J. Wang, T. Dugger, L. Cruz, D. Kisailus, Small, 2018, 14, 1703459.
PHASE ENGINEERING OF NANOMATERIALS

Presenting Author: Zhang Hua

Topic: Symposium on Metal Nanoparticle Nucleation and Growth

Format: Invited

Session: 4, 6

Date: 8/4/2021

Time (in MDT): 4:15:00 PM

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In this talk, I will summarize the recent research on phase engineering of nanomaterials (PEN) in my group, particularly focusing on the rational design and synthesis of novel nanomaterials with unconventional phases for various promising applications. For example, by using wet-chemical methods, for the first time, we have successfully prepared novel Au nanostructures (e.g., the hexagonal-close packed (hcp) 2H-Au nanosheets, 4H-Au nanoribbons, and crystal-phase heterostructured 4H/fcc and fcc/2H/fcc heterophase Au nanorods), epitaxially grown metal nanostructures on the aforementioned unconventional Au nanostructures and 2H-Pd nanoparticles, and amorphous/crystalline heterophase Pd and PdCu nanosheets. Currently, my group focuses on the investigation of phase-dependent physicochemical properties and applications in catalysis, (opto-)electronic devices, clean energy, chemical and biosensing, surface enhanced Raman scattering, waveguide, photothermal therapy, etc., which we believe is quite unique and very important not only in fundamental studies, but also in future practical applications. Importantly, the concepts of phase engineering of nanomaterials (PEN), crystal-phase heterostructures, and heterophase nanomaterials are proposed.
CONTINUOUS MICROFLUIDIC CRYSTALLIZATION BY DECOUPLING NUCLEATION AND GROWTH

Presenting Author: Simon Kuhn

Topic: Symposium on Nucleation in Microfluidics

Format: Invited

Session: 1, 1

Date: 8/4/2021

Time (in MDT): 8:30:00 AM


Microfluidic crystallization has the potential to replace traditional batch crystallization as one of the most important separation and purification processes especially in the pharmaceutical industry. Here, we report the design of a modular and decoupled microfluidic system consisting of separate nucleation and growth sections. The developed system makes use of two-phase flow to control the flow of the particles throughout the different crystallizer stages. In the nucleation section, micro-bubbles are introduced to act as heterogeneous nucleation sites, and also to prevent wall attachment of the nuclei. The total bubble surface area per unit volume of the reactor is controlled via the flow rates, which effects the bubble of the diameter and the bubble formation frequency. The continuous crystallization experiments provided proof that the micro-bubbles act as a heterogeneous nucleation site. An enhanced nucleation rate compared to the operation without bubbles was observed, and the presence of micro-bubbles results in the formation of more crystals, which indicates that nucleation is faster than without bubbles, i.e. the metastable zone width is reduced. The growth section, which is kept at a constant temperature, provides the necessary residence time to achieve a certain crystal size. Different configurations of the setup were investigated concerning the presence of the gas phase in the nucleation and/or growth sections. When eliminating the gas phase in the nucleation and/or growth stages the crystallization process proceeded in an uncontrolled manner. Reproducible results were only obtained when gas is present both in the nucleation section (as micro-bubbles) and in the growth section (as gas slugs). For this configuration different growth times and temperatures were investigated, ultimately achieving a crystallization yield of 71%. Furthermore, comparison with batch growth revealed that the developed system results in a narrower span in the size distribution. In conclusion, the microfluidic system with separate nucleation and growth sections can be tuned and manipulated varying the growth temperature and time to achieve a desired crystal mean size with narrow span.
QUANTIFYING NUCLEATION KINETICS VIA SESSILE MICRODROPLET APPROACH

Presenting Author: Ruel Cedeno

Topic: Symposium on Nucleation in Microfluidics

Format: Contributed

Session: 1, 3

Date: 8/4/2021

Time (in MDT): 9:00:00 AM

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Nucleation is a key step in industrial crystallization processes due to its profound effects on the physical properties of the resulting product. Due to the stochastic nature of nucleation, a statistical analysis of numerous independent experiments is needed in quantifying nucleation kinetics. In our previous work, we have addressed this by developing a microfluidic setup allowing facile generation of monodisperse arrays of sessile microdroplets, immersed in an oil film, which can serve as evaporative microcrystallizers. We have also shown that the standard deviation of the grey-level pixels, σ, is a useful image analysis tool in probing the microdroplet dynamics, particularly the onset of nucleation. Although this experimental protocol is a promising approach for nucleation studies, there remains an issue preventing its practical use in kinetic parameter estimation. We have observed that droplets can interact with other droplets. This is because when one droplet crystallizes, water diffuses to the neighboring droplet due to differences in chemical potentials. This leads to nucleation events which are not completely independent one from each other. In this work, we show that our image analysis protocol enables characterization of these diffusive interactions which would be otherwise unobservable in traditional microscopy techniques. Moreover, we demonstrate that if these interactions were not accounted for, large discrepancies in the nucleation kinetic parameters could be obtained. Our new experimental method and data-treatment is a promising approach that can be adapted to study the nucleation kinetics of other salts or pharmaceutical crystals of interest.
MICROFLUIDICS AS A PLATFORM TO ELUCIDATE THE MODES OF CRYSTAL GROWTH MODIFIERS

Presenting Author: Jeffrey Rimer

Topic: Symposium on Nucleation in Microfluidics

Format: Contributed

Session: 1, 4

Date: 8/4/2021

Time (in MDT): 9:15:00 AM

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This presentation will highlight a microfluidics platform developed in our group that we have used to elucidate the effect(s) of growth modifiers operating as either inhibitors or demineralizing agents with the purpose of suppressing or dissolving crystals in deleterious applications, such as human diseases or scale formation. This device is designed with a concentration gradient that distributes the feed streams into six parallel microchannels for side-by-side comparisons of crystal growth/dissolution in the presence of different (macro)molecular modifiers at varying conditions (e.g. supersaturation, pH, etc.). A distinct advantage of this system over bulk crystallization at quiescent conditions is the ability to capture in real time the modification of crystal size and habit, and thus quantify the anisotropic kinetics of growth or dissolution along all principle crystallographic directions. This microfluidics platform has been instrumental in our characterization of modifiers in diverse systems, including calcium oxalate monohydrate crystals (kidney stones), struvite (scale in water treatment), and barite (scale in oil/gas pipelines). In this talk, we will highlight examples from each of these studies to show how microfluidics has provided valuable insight into the macroscopic effects of modifiers. These measurements have also been combined with in situ scanning probe microscopy and molecular dynamic (MD) simulations to investigate modifier-crystal interactions at a molecular level. The results of these studies have provided tremendous insight into the mechanisms governing crystal inhibitors as well as the rational design of new compounds to replace less effective commercial analogues.
FLUORESCENCE LIFETIME IMAGING OF THE LASER INDUCED BIRTH OF CRYSTALS.

Presenting Author: Robert Pansu

Topic: Symposium on Nucleation in Microfluidics

Format: Contributed

Session: 1, 5

Date: 8/4/2021

Time (in MDT): 9:30:00 AM

Authors: Robert Bernard Pansu, CNRS, Gif sur Yvette, France Zhengyu Zhang, CentraleSupelec, Gif sur Yvette, France Jean-Frédéric Audibert, ENS Paris Saclay, Gif sur Yvette, France Anne Spasojevic de Biré, CentraleSupelec, Gif sur Yvette, France

DBDCS is an organic molecule that is more fluorescent as a crystal than in solution. The fluorescence lifetime and spectra are different for the different polymorphs.[1] We produce the crystals by an antisolvent precipitation. A saturated solution of DBDCS in 1,4-Dioxane is injected into a water solution inside a glass capillary 200µm in diameter.[2] We can study the spontaneous nucleation, but also the laser induced nucleation (NPLIN) by focussing a 1030nm, 400fs, pulsed laser into the flow.[3] When the crystals are larger than 3µm, we can detect them one by one. We measure their size, and identify their polymorph. In presence of a laser the nucleation rate is increased by a factor of ten. The growth rate and the distribution of the polymorph are not changed. NPLIN triggered the nucleation but with a minimal change in the products and mechanism. When the crystals are smaller, we can never the less map in the flow the fluorescence and its lifetime. We unravel and quantify the contribution of three different populations of emitters, using the principal component analysis. The liquid phase of DBDCS, that is produced by oiling out, is not fluorescent and not detected through cross polarizers. We can record the fluorescence produced at the NPLIN laser focal point and compared it with the one of the crystals. The dominant polymorph among the subcritical aggregates is not the one that will escape and grow.<br />


Solid-state studies of Active Pharmaceutical Ingredients (APIs) is critical in the development of pharmaceuticals [1]. A molecule can appear in different solid forms which significantly affect solubility, stability, process-ability or bioavailability. Solid form optimization is often achieved through screenings of salts, co-crystals, polymorphs or amorphous solid dispersions to provide the most appropriate properties. Classical methods for solid forms screening being time and product consuming, microfluidics approaches are more and more considered in both academic and industrial environments [2]. However, microfluidic experiments usually require a stock of saturated solution which consumes extra-compound and in which it can be hard to prevent undesired crystallization. Here, we describe a versatile tubing-based microfluidic platform and some applications to polymorphism screening and solubility measurements, in organic and aqueous solvents, directly from powder. The principle consists in flowing the solvent of interest through a cartridge containing the API powder, at low flow rates for the solvent to dissolve the compound until saturation is reached. Solubility measurements [3] are performed online with a UV-VIS detector, using successive dilutions to reach the linearity range of the detector. For polymorphism studies [4], microliter-droplets acting as independent crystallizers are generated. The system allows studying the impact of different supersaturations and temperatures of storage on crystal growth and polymorphism. Since small volumes favor single crystal growth, metastable phases can be “frozen” [5] and identified by Raman spectrometry. Secondly, the microfluidic tool is adapted to industrial needs, notably in terms of security, ease of use, and possible automation. In this purpose, the microfluidic principle is transferred toward a HPLC system. The powder cartridge is replaced by an emptied UPLC column to ease its filling and prevent powder volatility. Moreover, solubility measurement in biorelevant media, such as FaSSIF (fasted state simulated intestinal fluid), is assessed to integrate this set-up into a salt screening strategy in the pharmaceutical industry.
Abstract Book - ACCGE-22//OMVPE-20

CRYSTALLIZATION AND AGGREGATION IN CONTROLLED FLOW

Presenting Author: Dominique Maes

Topic: Symposium on Nucleation in Microfluidics

Format: Contributed

Session: 2, 3

Date: 8/4/2021

Time (in MDT): 11:00:00 AM

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In the first part of the lecture, we will elaborate on the effect of shear flow on crystallization. Both theory and experiments have indicated that flow affects the nucleation rate, the size of the emerging phase and polymorphism. To enable detailed quantitative studies on the influence of shear flow on nucleation and growth, we have developed a new microfluidic setup that creates a controlled constant shear flow profile in a solution. With the unique shear combined with the on-chip observation we can shed light on a variety of phase transitions that are influenced by flow. The first set of results indicate that shear rates promote nucleation and decrease solubility. A monotonically increasing nucleation rate was observed. Further, we will report on our study of the effect of confinement and controlled shear on polymorphism. The second part of the lecture deals with the use of acoustic waves in microfluidic chips to manipulate crystals and dense liquid phases, the precursors of crystals and aggregates, in flows.
Enhanced Control of Protein Crystallization in Droplet-Based Microfluidic Tubings

Presenting Author: Filipa Castro

Topic: Symposium on Nucleation in Microfluidics

Format: Contributed

Session: 2, 4

Date: 8/4/2021

Time (in MDT): 11:15:00 AM

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Protein crystallization is difficult to address mainly due to the specific structure of these molecules. Despite tremendous efforts in the field, there is still no comprehensive theory to guide the experimental design. Thereby, finding the appropriate crystallization conditions for a given protein largely relies on trial-and-error approaches, involving the performance of a significant number of experiments where numerous chemical and physical parameters are systematically tested. Progresses in automation and miniaturization have provided solutions for the faster screening of protein crystallization conditions with reduced protein consumption. However, they have suffered from poor hit rate and the upfront equipment of these systems is expensive and thus not accessible to most laboratories. In this context, droplet-based microfluidic tubings offer versatile, cheap and easy-to-use platforms for protein crystallization. The discrete volumes work as independent batch plug microreactors under identical conditions, where each microdroplet (dispersed phase) is generated within a second immiscible carrier fluid (continuous phase). This small scale allows a high degree of control over the crystallization conditions and performing several assays within a single experiment. In the present work, a Teflon tube arranged in a serpentine was used for the crystallization of two model proteins, lysozyme and insulin. In a first approach, lysozyme crystallization was conducted, where a phase diagram was derived, and the influence of droplet size and supersaturation on the size and number of crystals was assessed. Further, experimental and numerical approaches were combined to optimize the operating conditions in order to form monodisperse and stable droplets. The droplet volume effect became more important at lower supersaturations as the crystal number follows the droplet volume increase, while at higher supersaturations, the crystal number did not considerably vary with the droplet volume. Afterwards, insulin crystallization was studied, where both hanging-drop vapour diffusion and microfluidic tubings techniques were studied. At low protein concentrations, aggregates formation was observed during the hanging-drop experiments, while crystals with variable size were produced in the droplet-based microreactor. For this last approach, aggregates tend to appear at lower precipitant concentrations. In addition, crystal size seems to present a higher uniformity when produced in the droplet-based microreactor. This distinct behavior might be attributed to three main factors: supersaturation levels reached during the assays, time required to achieve homogeneous micromixing and interfacial effects. Ultimately, an operating regime map for each crystallization technique was derived.
HELICAL SELF-ASSEMBLED NANOCOMPOSITES

Presenting Author: Willem Noorduin

Topic: Symposium on Twisted Crystals

Format: Invited

Session: 1, 1

Date: 8/4/2021

Time (in MDT): 8:30:00 AM

Authors: Willem Noorduin, AMOLF, Amsterdam, Netherlands Lukas Helmbrecht, AMOLF, Amsterdam, Netherlands Melissa Tan, New York University, New York City, New York, United States Femius Koenderink, AMOLF, Amsterdam, Netherlands Ruslan Röhrich, AMOLF, Amsterdam, Netherlands Marloes Bistervels, AMOLF, Amsterdam, Netherlands Bruno Ortiz Kessels, AMOLF, Amsterdam, Netherlands Bart Kahr, New York University, New York City, New York, United States

Bottom-up assembly can organize simple building blocks into complex architectures with advanced functionalities. We explore this potential by assembling nanocomposites of barium carbonate/silica into double helices and investigate the optical properties using fluorescent Fourier and Mueller matrix microscopy. Helices doped with fluorescein direct light emission along the long axis of the structure. Furthermore, light transmission measured normal and parallel to the long axis exhibits twist sense-specific circular retardance and wave-guiding, respectively. The helices thus integrate highly directional emission with enantiomorph-specific polarization. This optical response emerges from the arrangement of nanoscopic mineral crystallites in the microscopic helix, and demonstrates how bottom-up assembly can achieve ordering across multiple length scales to form complex functional materials. Finally, we will present an outlook on how these nanocomposites can be further tuned to broaden the functionality potential of self-assembled forms.
TWISTED CRYSTALS OF DIKETOPYRROLOPYRROLES

Presenting Author: David Amabilino

Topic: Symposium on Twisted Crystals

Format: Invited

Session: 1, 3

Date: 8/4/2021

Time (in MDT): 9:00:00 AM

Authors:
CHIRAL TWISTED VAN DER WAALS NANOWIRES

Presenting Author: Eli Sutter

Topic: Symposium on Twisted Crystals

Format: Invited

Session: 1, 5

Date: 8/4/2021

Time (in MDT): 9:30:00 AM

Authors: Eli Sutter, University of Nebraska-Lincoln, Lincoln, Nebraska, United States Peter Sutter, University of Nebraska-Lincoln, Lincoln, Nebraska, United States

Van der Waals stacks with small misalignment between adjacent layers ('interlayer twist') are of interest due to electronic structure and correlated electron phenomena such as Mott insulating behavior and superconductivity, which are determined by both the atomic lattice and long-range superlattice potentials arising in interlayer moiré patterns. Conventionally, such twisted heterostructures involve a single planar interface between layers isolated by exfoliation and mechanically stacked in the desired orientation. We recently demonstrated a new class of materials—van der Waals nanowires of layered crystals—in which a tunable interlayer twist evolves naturally during synthesis.<sup>[1]</sup>

Synthesized by vapor-liquid-solid growth, nanowires of germanium sulfide, an anisotropic layered semiconductor, crystallize with layering along the wire axis<sup>[2]</sup> and have a strong propensity for forming axial screw dislocations. Nanometer-resolved electron diffraction shows that the resulting Eshelby twist causes a chiral structure in the van der Waals nanowires. The in-plane crystal axes progressively rotate along the wire, and germanium sulfide layers in adjacent turns of the helix naturally form an interlayer twist moiré pattern. The axial rotation and the twist are precisely tunable by varying the nanowire thickness, and even small interlayer twist angles are effectively stabilized by the axial dislocation. Using tailored growth protocols complex structures can be obtained that are impossible to realize in planar van der Waals stacks, including homojunctions between twisted (dislocated) and ordinary layered (dislocation-free) segments as well as continuously variable Eshelby twist translating into a seamless progression of helical moiré patterns.<sup>[3]</sup>

Combined electron diffraction and local (nanometer-scale) optoelectronic measurements using cathodoluminescence and electron-energy loss spectroscopy show the correlation between the interlayer twist and locally excited light emission/optical absorption that is due to progressive changes in the lattice orientation and in the interlayer moiré registry along the nanowires. These findings demonstrate an avenue for the scalable fabrication of van der Waals structures with defined twist angles for the emerging field of twistronics, in which interlayer moiré patterns are realized along a helical path on a nanowire instead of a planar interface.<br />

TWISTED ORGANIC SEMICONDUCTOR CRYSTALS

Presenting Author: Stephanie Lee

Topic: Symposium on Twisted Crystals

Format: Invited

Session: 2, 1

Date: 8/4/2021

Time (in MDT): 10:30:00 AM

Authors: stephlee@nyu.edu

Molecular crystals that twist as they grow are common but little known and introduce completely unexplored features to materials design. Here, we present growth-induced twists to molecular semiconductor crystals with the expectation that microstructure and continually precessing crystallographic orientations can modulate interactions with light, charge transport, and other optoelectronic processes. We have found that a variety of organic semiconductors and charge transfer complexes can be readily induced to grow from the melt as spherulites of tightly packed helicoidal fibrils. The twisting pitch can be controlled by the degree of undercooling after melting or through the incorporation of additives. Intriguingly, charge mobilities measured using field-effect transistor platforms have been found to increase with increasing extent of twisting. Photoluminescence intensity is also modulated by crystal twisting, with some orientations exhibiting stronger PL signal compared to others. These results indicate crystal twisting to be a promising strategy for modulating the performance of optoelectronic devices.
SUPERTWISTED SPIRALS OF LAYERED MATERIALS ENABLED BY GROWTH ON NON-EUCLIDEAN SURFACES

Presenting Author: Yuzhou Zhao

Topic: Symposium on Twisted Crystals

Format: Invited

Session: 2, 3

Date: 8/4/2021

Time (in MDT): 11:00:00 AM

Authors:
UNDERSTANDING THE DYNAMICS OF SEMICONDUCTOR NANOSTRUCTURE GROWTH WITH IN-SITU TEM

Presenting Author: Kimberly Thelander

Topic: Thin film growth, epitaxy, and superlattices

Format: Invited

Session: 3, 1

Date: 8/4/2021

Time (in MDT): 1:00:00 PM

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Nanostructures and nanoscale materials offer important opportunities in terms of unique and size-dependent properties as well as new crystal structures. In order to design new nanostructures according to specific needs, we need to understand how crystal growth occurs at an atomic scale, and how nanoscale processes and size effects lead to structures with unique properties. To address this we use atomically-resolved in-situ TEM to follow the nanoscale crystal growth process in real time. In this talk I will discuss recent investigations into the crystal growth of semiconductor nanostructures, including nanowires and nanoparticles, as well as hybrid metal-semiconductor structures. In particular I will discuss the structure and dynamics of metal-semiconductor interfaces, and how these influence the crystal growth process and properties of the resulting nanostructures. One focus area will be the interface between liquid metal and solid semiconductor, and how the structure and dynamics influence the formation of metastable crystal phases. The second focus area will be on solid-solid metal-semiconductor interfaces, and the potential to design specific interface structures of interest for example to photocatalytic applications.
INDIUM CONCENTRATION FLUCTUATIONS IN INGAN/GAN QUANTUM WELLS - THEIR HOMOGENIZATION AND DECOMPOSITION.

Presenting Author: Ewa Grzanka

Topic: Thin film growth, epitaxy, and superlattices

Format: Invited

Session: 3, 3

Date: 8/4/2021

Time (in MDT): 1:30:00 PM

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Indium fluctuation are very often present inside InGaN Quantum Wells (QWs) grown by MOCVD method. It is known that amount and size of In fluctuation increase with In content in QWs, being a big problem especially in green emitters such Light Emitting Diodes (LED) and Laser Diodes (LD). Presence of Indium fluctuation inside QWs can contribute to shortening of optical devices lifetime, decreasing of their efficiency and significantly reduce temperatures at which QWs get decomposed. It is worth to mention that In fluctuation can be associated with point defects presence, especially complex VGa-In. During LED/LD structure growth it is important to properly establish p-type growth temperature since too high temperature leads to the decomposition of MQWs but too low temperature causes worsening of p-type conductivity. In this work we also show that at temperatures range of p-type layers growth, i.e. around 900-940oC, homogenization process of QWs, grown on sapphire template, take place. It leads to improvement of the properties of the emitted light - FWHM of the emitted spectra decrease and optical power increase. In case of the QWs grown on bulk GaN substrate we don’t observe homogenization phenomenon. As consequence, process of decomposition of the QWs take place at little bit higher temperature - around 20oC more, and degree of decomposition in short time become huge and decomposition of the subsequent QWs occurs faster than in case of sapphire template. All described above phenomenon were investigated using a combination of XRD, PL, EL, TEM. The visualization of the initial Indium fluctuations as well as homogenization and decomposition processes was presented thanks to SIMS research. Explanation of the above differences in homogenization and decomposition process is fact the bulk GaN substrate had much lower dislocation density compare to sapphire template. It is known that close to dislocation can be much more point defects than in some distance away from them and also In distribution in QWs is disturbed by threading dislocation. This mean that in case of QWs grown on bulk substrate distribution of In atoms and diffusion of point defects differ from that on sapphire template. However in case of bulk substrate, due to lower dislocation density they don’t constitute any border for decomposition and this process can occur without any disruptions or limitations. These results are very important for optimization of the MOVPE growth of deep blue and green emitters.
THERMODYNAMIC ANALYSIS OF HYBRID VAPOR PHASE EPITAXY (HYBVPE) OF AL<sub>1-X</sub>SC<sub>X</sub>N SINGLE-CRYSTALLINE PIEZOELECTRIC THIN FILMS

Presenting Author: Mina Moradnia

Topic: Thin film growth, epitaxy, and superlattices

Format: Contributed

Session: 3, 5

Date: 8/4/2021

Time (in MDT): 2:00:00 PM

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AlN is one of the primary candidates for a wide range of electro-acoustic and high-temperature applications. However, the low piezoelectric response and electrochemical coupling in AlN utilization make a restriction on its performance for high functional piezoelectric device applications. Therefore, there is a necessity to enhance the piezoelectric properties of AlN. Incorporation of scandium (Sc) from group IIIb transition metals into AlN structure indicates a tremendous increase in the piezoelectric coefficients of AlN-based materials up to three times. Magnetron reactive sputtering system using co-sputtering and compound target sputtering have been used in the semiconductor manufacturing process for epitaxial growth of AlScN. However, size limitation for high Sc content of compound targets, mass production limits, and difficulty in control of uniform Sc content across the whole area of large substrates cause difficulties to rely on this growth method. To overcome the restrictions, we consider the hydride vapor phase epitaxy (HVPE) as a more convenient growth method. The HVPE has excellent compatibility between supply control and mass production pursuing increase of the growth rate along with better control on composition of aluminum nitride alloy. We introduce a new epitaxial thin-film growth technique coined as “hybrid vapor phase epitaxy (HybVPE)”. In this technique, transition-metal-alloyed Group III-N single-crystalline thin films are epitaxially deposited on a suitable substrate by providing a mixture of various gases in a deposition/growth chamber. The precursors for the chemical reactions include vapor phase of group IIIb transition metals, chlorides (vapor phase) of group IIIa elements, and hydride of group V element (N). HybVPE method can give a promise to control the Sc content in a more controlled way compared to the sputtering growth method. Our thermodynamic calculations show the possibilities of Al<sub>1-x</sub>Sc<sub>x</sub>N solid compositions at various temperatures, III/V material input ratios, and carrier gases partial pressures in an aluminum source zone, scandium source zone and deposition/growth zone. We investigate the adjustment of a target solid composition ratio of Sc (x<sub>Sc</sub>) and Al (x<sub>Al</sub> = 1−x<sub>Sc</sub>) in AlScN thin film by changing relative input amounts of the Sc precursor (x' <sub>Sc</sub>) and Al precursor (x' <sub>Al</sub>) in the growth process. Based on the thermodynamic analysis, the driving force for the deposition P<sub>III</sub>−P<sub>III</sub>−ΔP<sub>Sc</sub> predicts that Sc doping content of up to 30% in the AlScN alloy can be controlled in the HybVPE method, which plays an important role to improve the piezoelectric properties of AlN alloy by HybVPE method.
In-situ observation of crystal growth of AlGaN with lattice relaxation on sputtered AlN and improvement of crystal quality

**Presenting Author:** Motoaki Iwaya

**Topic:** Thin film growth, epitaxy, and superlattices

**Format:** Invited

**Session:** 4, 1

**Date:** 8/4/2021

**Time (in MDT):** 3:00:00 PM

**Authors:** Moe Shimokawa1, Sho Iwayama1,2, Tetsuya Takeuchi1, Satoshi Kamiyama1, Hideto Miyake2

AlGaN-based UV light emitting devices are expected to be applied in many fields such as medical, sterilization and biotechnology. In order to realize these applications, it is essential to achieve high quality AlGaN crystals. In particular, high-quality lattice-relaxed AlGaN is indispensable for UV LEDs in the UV-B region. In this presentation, we will introduce a method to control the crystal growth of lattice-relaxed AlGaN and to improve its quality by using in-situ observation. We will also introduce the effect of the quality improvement on the devices.
GROWTH OF CHALCOGENIDE PEROVSKITE THIN FILMS BY MOLECULAR BEAM EPITAXY (MBE)

Presenting Author: Ida Sadeghi

Topic: Thin film growth, epitaxy, and superlattices

Format: Contributed

Session: 4, 3

Date: 8/4/2021

Time (in MDT): 3:30:00 PM

Authors: Ida Sadeghi, MIT, Cambridge, Massachusetts, United States  Kevin Ye, MIT, Cambridge, Massachusetts, United States  Michael Xu, MIT, Cambridge, Massachusetts, United States  James M. LeBeau, MIT, Cambridge, Massachusetts, United States  Rafael Jaramillo, MIT, Cambridge, Massachusetts, United States

Chemical intuition, first-principles calculations, and recent experimental results suggest that chalcogenide perovskites are an outstanding class of semiconductors. Chalcogenide perovskites feature the large dielectric response familiar in oxide perovskites, but also have band gap in the VIS-IR and strong light absorption [1]. Preliminary results suggest that chalcogenide perovskites feature excellent excited-state charge transport properties familiar in halide perovskites, while also being thermally-stable and comprised of abundant and non-toxic elements. Nearly all experimental results on chalcogenide perovskites to-date were obtained on powder samples and microscopic single crystals, and thin film synthesis is in its infancy. The history of complex oxide science teaches us that advances in fundamental understanding and development for applications will hinge on the availability of high-quality, controllable thin film synthesis, and that the best film quality and control is achieved by molecular beam epitaxy (MBE). Here we report the first epitaxial synthesis of chalcogenide perovskite thin films by single-step gas-source MBE: BaZrS\(_3\) films on (001)-oriented LaAlO\(_3\) substrates. The composition is confirmed by X-ray fluorescence and X-ray photoelectron spectroscopy: films are stoichiometric and oxygen-free at the film-substrate interface. The perovskite phase is confirmed by X-ray diffraction (XRD) and Raman spectroscopy. The films are atomically-smooth over large areas, as evidenced by reflection high-energy electron diffraction (RHEED) measured during growth, and by atomic-force microscopy (AFM) and scanning electron microscopy (SEM) data acquired after growth. Scanning transmission electron microscopy (STEM) shows an atomically-abrupt substrate/film (oxide/sulfide) interface with no chemical interdiffusion. RHEED, XRD, and STEM reveal two, competing epitaxial growth mechanisms: direct rotated-cube-on-cube growth, and strain-relaxed growth with a self-assembled buffer layer. The film color, spectroscopic ellipsometry, and photoluminescence spectroscopy demonstrate that the films have strong light absorption with direct band gap near 1.9 eV. This work sets the stage for developing chalcogenide perovskites as a family of semiconductor alloys with properties that can be tuned with strain and composition in high-quality epitaxial thin films, as has been long-established for other semiconductor materials, while also displaying rich solid-state chemistry and physics familiar in complex oxides. Our methods also represent a revival of gas-source chalcogenide MBE, with potential for impact on research on chalcogenide perovskites and other sulfur- and selenium-containing compounds.[1] R. Jaramillo, J. Ravichandran, APL Materials 7(10) (2019) 100902.
COMBINATORIAL SUBSTRATE EPITAXY OF METASTABLE COMPLEX OXIDES

Presenting Author: Catherine Zhou

Topic: Thin film growth, epitaxy, and superlattices

Format: Contributed

Session: 4, 4

Date: 8/4/2021

Time (in MDT): 3:45:00 PM

Authors: Catherine Zhou, Carnegie Mellon University, Pittsburgh, Pennsylvania, United States  Paul Salvador, Carnegie Mellon University, Pittsburgh, Pennsylvania, United States

Combinatorial substrate epitaxy (CSE) is a high-throughput thin film growth method developed to explore the epitaxial stability of complex oxides over all of substrate orientation space within a single deposition on polycrystalline substrates. Compared to the limited variety of commercial single crystal substrates, polycrystalline substrates are synthesized in-house in a wide range of compositions and structures, which greatly increases the search throughput for new materials as thin films. Across different complex oxide thin film materials grown using CSE, such as Ruddlesden-Popper Ca$_2$MnO$_4$, anatase and rutile TiO$_2$, 110-layered RE$_2$Ti$_2$O$_7$ perovskites, and hexagonal and cubic (AE)MnO$_3$ perovskites, similar observations are made that support the use of CSE as an appropriate method for the growth and stabilization of these materials. The results show that 1) grain-over-grain epitaxy occurs for most orientations of the substrate, 2) only a small number of orientation relationships exist between substrate and film, 3) similar results of the growth of complex oxide films are obtained using CSE as are obtained using single crystals, and 4) metastable and new complex oxides can be stabilized using CSE. To demonstrate this approach, we focus on the polytypic competition between stable hexagonal and metastable cubic SrMnO$_3$ on polycrystalline SrTiO$_3$ substrates. To explore the epitaxial phase stability of SrMnO$_3$ phase is stable over all SrTiO$_3$ substrate orientations, the metastable hexagonal phase was stabilized on non-basal plane orientations of a hexagonal SrMnO$_3$ substrate. This offers the possibility for the application of CSE to grow metastable hexagonal materials on hexagonal substrates. Electron backscatter diffraction and dictionary indexing are used to collect and analyze the local phase and orientation of each grain. It was determined that the eutactic OR, one that aligns nearly close-packed planes and directions, holds true regardless of substrate surface orientation, phase, and deposition conditions. In fact, this OR is observed for many CSE experiments involving other complex oxides. The ubiquity of the eutactic OR indicates that the interface energy is generally lower for the eutactic OR than for all other possible ORs.
TRENCH FILLING WITH PHOSPHORUS-DOPED MONOCRYSTALLINE AND POLYCRYSTALLINE SILICON

Presenting Author: Justine Lespiaux

Topic: Thin film growth, epitaxy, and superlattices

Format: Contributed

Session: 4, 5

Date: 8/4/2021

Time (in MDT): 4:00:00 PM

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The use of Selective Epitaxial Growth (SEG) in deep cavities faces multiple issues such as growth inhomogeneities along sidewalls or defect formation. Those defects are mainly voids which are due to a premature closing of the top of trenches during the deposition process, degrading the electrical performances of the devices. In this work, the main objective was to develop void-free processes to fill two kinds of trenches: i) low aspect ratio rectangular trenches in Si (1:6) (illustrated in Fig.1 prior filling), to be filled with lowly doped monocrystalline Si:P and (ii) high aspect ratio trenches or needles in Si or with a SiO<sub>2</sub> liner (1:16), to be filled with highly doped monocrystalline or polycrystalline Si:P, in a Reduced Pressure - Chemical Vapour Deposition (RP-CVD) reactor. Previous studies suggested the use of a SiH<sub>2</sub>Cl<sub>2</sub> (DCS) + PH<sub>3</sub> + HCl chemistry, with an optimization of the DCS/HCl mass-flow ratio (MFR) to conformally fill large and high aspect ratio trenches with monocrystalline Si:P (c-Si:P) while preventing overgrowth at the trench entrance and voids at the bottom. Current studies were first of all conducted on blanket wafers in order to choose the best strategy for varying DCS/HCl MFRs. Two trends were highlighted depending on the PH<sub>3</sub> partial pressure (P(PH<sub>3</sub>)<sub>3</sub>): lower than 10<sup>-5</sup>Torr, the dopant concentration increased solely with the phosphine flow and did not depend on the HCl flow for P<sub>3</sub>+<sub>3</sub> ions concentration in the 10<sup>-17</sup>cm<sup>3</sup> to 10<sup>-18</sup>cm<sup>3</sup> range. For PH<sub>3</sub> partial pressures higher than 10<sup>-5</sup>Torr and thus higher doping levels (between 3x10<sup>18</sup>cm<sup>3</sup> and 2x10<sup>19</sup>cm<sup>3</sup>), the P<sub>3</sub>+<sub>3</sub> ions concentration increased with the PH<sub>3</sub><sub>3</sub> flow and decreased with the HCl flow. The filling of 1:6 aspect ratio trenches by monocrystalline Si:P was achieved thanks to a three steps process with various DCS/HCl MFRs (Fig.2). Good crystalline quality with a good dopant uniformity was obtained but some small voids were still present (Fig.3). Further optimizations are required to completely suppress them. Preliminary assessments of the P atomic concentration in trenches, conducted by SIMS, showed a rather flat phosphorous depth profiles, illustrating the uniformity achievable with such a sequential process. Meanwhile, the filling of 1:16 aspect ratio trenches or needles by poly-Si:P was successfully achieved at 10 Torr with a SiH<sub>4</sub> + PH<sub>3</sub>
chemistry, provided that the deposition temperature, 750°C, was low enough to avoid the formation of large poly-Si:P grains, notably at the entrance (Fig.4).
THE IMPACT OF INTERFACIAL GROWTH SEQUENCE ON THE SURFACE MORPHOLOGY AND RADIATIVE EFFICIENCY OF INGAAS/GAASP MULTIPLE QUANTUM WELLS

**Presenting Author:** Maui Hino

**Topic:** Thin film growth, epitaxy, and superlattices

**Format:** Poster

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InGaAs/GaAsP multiple quantum wells (MQWs) are applied to opto-electronic devices and high radiative efficiency of MQWs improves the performance of devices. In InGaAs/GaAsP strain-balanced MQWs, crystal defects are often generated at the heterointerface between an InGaAs well and a GaAsP barrier with compressive and tensile strain, respectively. Accordingly, the growth sequence for the heterointerface is important to enhance the radiative efficiency. Insertion of a GaAs interlayer to the heterointerface is thought to be effective because GaAs without strain can mitigate the strain between InGaAs and GaAsP layers. However, it is not yet clear how the thickness and the growth sequence of the GaAs interlayer affect the radiative recombination efficiency of carriers inside MQWs.

To clarify this issue by photoluminescence (PL), 10 periods of InGaAs/GaAsP MQWs were inserted in the core surrounded by InGaP clad layers. The structure was grown by metal organic vapor phase epitaxy (MOVPE). A GaAs interlayer was inserted either above or below an InGaAs layer. Reference MQWs without interlayers were prepared as well. As shown in the figure, the PL intensity from MQWs increased monotonically with the thickness of GaAs interlayers below InGaAs, while the PL intensity from MQWs with 0.5-nm-thick interlayers above InGaAs decreased by 39% compared with the reference MQWs, accompanied by the shift of the luminescence peak to longer wavelength, which indicates the segregation of indium on the InGaAs surface. Further increase in the GaAs thickness above InGaAs recovered and enhanced PL intensity.

To consider the mechanism of the behavior of luminescence intensity above, 7 samples were prepared by MOVPE: a GaAs interlayer with varied thickness was inserted either above or below an InGaAs well. The InGaAs surface was slightly 3D-island-like and the growth of 0.5 nm GaAs on it further roughened the GaAs surface as shown in the figure. The increased thickness of GaAs above InGaAs led to smooth surface because of the surface planarization by GaAs growth. In contrast, the surface of GaAs below InGaAs was smooth and step-like at any GaAs thickness. The results indicate that the 3D-like GaAs surface above InGaAs and beneath the GaAsP may introduce crystal defects that degrade the luminescence intensity of MQWs, and it is crucial to avoid the 3D-like surface of the GaAs interlayer on InGaAs. For this purpose, graded indium content at the latter stage of InGaAs growth and H<sub>2</sub> purge after InGaAs growth are seemingly effective because they...
would suppress indium segregation.
STEPS AS A TOOL FOR SELF-ORGANIZATION OF NANOISLANDS DURING STEP-FLOW GROWTH OF A MULTICOMPONENT CRYSTAL

Presenting Author: Alexey Redkov

Topic: Thin film growth, epitaxy, and superlattices

Format: Poster

Session: ,

Date:

Time (in MDT):

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One of the growth regimes, at which most high-quality crystals grow is the step flow-regime taking place at low supersaturations. It is well studied both theoretically and experimentally for single-component crystals and thin films, like Si and Ge, however, there are many white spots in its theoretical description of this regime in context of multicomponent systems, which are highly in demand in current industry (GaN, SiC, different perovskites, etc.). Many effects determined by the presence of several components are not studied yet. In this work we present our recent theoretical studies on the phenomena taking place at multicomponent crystal growth, for example, the influence of the surface vacancies, the nucleation of islands of pure components on the terraces between the multicomponent steps (e.g. Ga islands during GaN growth), etc. It was experimentally observed earlier many times, but there are only a few papers on theoretical consideration of this processes in multicomponent systems [1,2]. We derive an analytical criterion, at which growth conditions precipitation of single-component nanoislands at the terraces between the steps can take place, and at which it is impossible. We study interaction of such nanoislands with the steps, and show to which consequences and instabilities this interaction can lead to. The main difference between the multicomponent system and the single-component, is that in the single-component one, the step kinetics and nucleation of nanoislands are both determined by the surface supersaturation of this single component, there is no degree of freedom. On contrary, in multicomponent systems the velocity of multicomponent steps and nucleation of single-component islands can be controlled independently via adjusting fluxes, and one can use the steps to control the single-component island population and growth kinetics. We show how these effects can be used in crystal engineering – both for in-situ formation of ordered 3D-structures in the volume of the crystal, and for formation of ordered arrays of nanowires. Acknowledgments A.V. Redkov thanks the Russian Science Foundation (grant # 21-72-00032) for the support of this work.


DEVELOPMENT OF MOLYBDENUM<sub>1</sub>-X TUNGSTEN<sub>X</sub>SULFUR<sub>2</sub> 2D THIN FILMS BY SPIN COATING

Presenting Author: Ellis Spickermann

Topic: Thin film growth, epitaxy, and superlattices

Format: Poster

Session: ,

Date: 

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Two-dimensional materials are attractive for next generation logic and memory for Beyond Moore’s Law Computing. The multitude of 2D materials in regard to composition, crystal structure and layer thickness leads to a variety of material properties, including semiconducting, metallic, insulating, superconducting and magnetic, covering all of the components necessary to address voltage, interconnect, energy and dimensional scaling issues in Front-end and Back-end microelectronics nanomanufacturing. For 2D materials to be technologically competitive, it is imperative to develop a manufacturable low temperature thin film deposition approach that can be directly integrated into Back-end of the line microelectronic processes. To circumvent such high temperature processing limitation of 2D materials, we have developed a low temperature spin coating process for the growth of transition metal dichalcogens 2D thin films.<br />

Here, we will discuss the development of alloyed thin films of molybdenum tungsten disulfide [Mo<sub>1</sub>-xW<x>S<sub>2</sub>] across the composition range by preparing solutions for spin coating with varying Mo:W and Mo/W:S ratios. Mo<sub>1</sub>-xW<x>S<sub>2</sub> alloys are known to have promising electronic properties including a potentially tunable band gap based on layering and composition, causing their efficient and controllable synthesis approach to be of great interest. Ammonium Tetrathiomolybdate [(NH<sub>4</sub>)<sub>2</sub>MoS<sub>4</sub>] and Ammonium Tetrathiotungstate [(NH<sub>4</sub>)<sub>2</sub>WS<sub>4</sub>] were used as source materials for the transition metals, while Thioacetamide [CH<sub>3</sub>CSNH<sub>2</sub>] was utilized as a source of additional sulfur. All solutions were dissolved in Dichlorobenzene (DCB) and drop casted onto sapphire and silicon. Solutions were spin coated at 200ºC followed by a post anneal to improve the crystal quality of the films. The microstructure of the samples was investigated by scanning electron microscopy and x-ray diffraction. The crystal quality of the samples was correlated to the 2D thin film composition extracted from Raman measurement and X-ray Photoelectron Spectroscopy (XPS). The ability to achieve uniform crystalline monolayer and few layer films with oriented domains from single source solutions will be the turning point to realize and implement these materials more broadly in device applications.
THE STANDARD FOR RELAXOR-BASED SINGLE CRYSTALS FOR TRANSDUCER AND ACTUATOR APPLICATIONS - ACCELERATING THE TRANSITION OF PIEZOCRYSTALS

Presenting Author: Lynn Ewart

Topic: Third Symposium on Ferroelectric Crystals and Textured Ceramics

Format: Invited

Session: 4, 1

Date: 8/2/2021

Time (in MDT): 3:00:00 PM

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Standards and their development process accelerate the maturation and implementation of materials technologies. Piezoelectric single crystals (piezocrystals) offer significant technical advantages in numerous device applications, including naval sonar and medical ultrasound transducers, and their exploitation is currently underway. To accelerate the transition of piezocrystals from the research arena into commercial devices, an Institute of Electrical and Electronics Engineers – Standards Association (IEEE-SA) working group with international participation spent nine years drafting an appropriate standard to support the materials research and device design communities who use or want to use piezocrystals and taking it through the ballot process. In December 2017, IEEE-SA published the group’s work: IEEE Std 1859-2017: Standard for Relaxor-Based Single Crystals for Transducer and Actuator Applications.<br />
IEEE Std 1859-2017 covers the physical and electromechanical requirements for [001]-poled lead magnesium niobate-lead titanate (PMNT) and lead zinc niobate-lead titanate (PZNT). The focus of the standard is on three compositions from each of the PMNT and PZNT systems. The central content is the eight properties provided for each composition: free relative dielectric permittivity ($K_{33}^T$), dielectric loss tangent (tanδ), temperature of the first anomalous event in free relative dielectric permittivity ($T_{RT}$), rod extensional coupling factor ($k_{33}$), transversely poled length extensional coupling factor ($k_{31}$), longitudinal mode piezoelectric coefficient ($d_{33}$), transversely poled length extensional mode ($d_{31}$), elastic compliance at constant electric displacement ($s_{33}^{D}$). A committee is continuing the work of the IEEE-SA working group through the development of technical extensions to the existing standard. The topics under discussion include additional data for binary compositions of piezocrystals and approaches to standardizing ternary piezocrystals. As with all standards development work, anyone who has interest in the topic is welcome to join the discussions of the committee. This presentation will discuss the standard, the underlying contributions of the committee, and the extensions of the standard, including to ternary piezocrystals, that are underway.
MN PIN-PMN-PT PIEZOCRYSTAL FOR POWER ULTRASONICS APPLICATIONS

Presenting Author: Sandy Cochran

Topic: Third Symposium on Ferroelectric Crystals and Textured Ceramics

Format: Invited

Session: 4, 3

Date: 8/2/2021

Time (in MDT): 3:30:00 PM

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Commercial growth processes for affordable relaxor-based single crystal materials now produce material that has transformed the performance of ultrasound imaging transducers in recent years. Exemplified by Generation (Gen.) I Pb(Mg$_{1/3}$Nb$_{2/3}$O$_3$)-PbTiO$_3$ (PMN-PT) these offer the transducer designer unsurpassed electromechanical coupling coefficient, $k_{33} > 0.9$. When configured as tall, narrow pillars or planks, this delivers a higher sensitivity - bandwidth product. Later Gen. II Pb(In$_{1/2}$Nb$_{1/2}$O$_3$)-Pb(Mg$_{1/3}$Nb$_{2/3}$O$_3$)-PbTiO$_3$ (PIN-PMN-PT) piezocrystals have almost the same performance but higher phase transition temperatures, aiding manufacturing. These piezocrystals are well-established for low average power applications but surgical tools, underwater projectors and other power ultrasonics transducers demand higher figures of merit (FOMs) e.g. $FOM = k_{eff-ij}^2 Q_{ij}$, where $k_{eff-ij}$ is the effective coupling coefficient for excitation in direction $i$ and actuation in direction $j$ and $Q_{ij}$ is the mechanical quality factor. These require Gen. III piezocrystals, e.g. Mn:PIN-PMN-PT, bringing greater difficulties in crystal growth. Hence deeper understanding is needed to justify further investment and three relevant advances are described here.

Piezocrystal characterization for transducer design is usually performed with electrical impedance spectroscopy on samples of different geometries. However, Gen. III material is in short supply and needs characterization at the elevated pressures found in common device configurations and the temperatures experienced during high drive. Hence, new processes based on single cubic samples have been developed, additionally utilizing information from resonant ultrasound spectroscopy. Furthermore, for piezoelectric modes such as $d_{33}$, $d_{32}$ and $d_{36}$ there is a need to compare fundamental energy density, agnostic to geometry. We have thus developed a general coupling coefficient, $k_{G}$, rather than the previous mode-specific coefficients, $k_{eff-ij}$. Finally, power ultrasonics applications often require materials to be driven in non-linear regimes and comparison is thus needed between existing, hard piezoelectric ceramics and Gen. III piezocrystal. This is being explored with $d_{33}$-mode devices, which have shown that non-linear effects such as frequency shifts and dynamic softening are more pronounced in the piezocrystal. We conclude that Gen. III piezocrystal has potential
benefits in power ultrasonics but that further work is required. In our labs, this will include exploration of phase transitions in a closed-cycle refrigerator with optical access for all-optical characterization and use of state of the art optical and Laué exploration of material in multi-domain wafers. Our ultimate goal is to determine how to gain the maximum benefit from Gen. III material in practical configurations for power ultrasonics applications.
“GEN III” PIEZOELECTRIC PMN-PZT SINGLE CRYSTALS (D<sub>33</sub> > 4,000 PC/N) FOR PIEZOELECTRIC SENSOR AND ACTUATOR APPLICATIONS

Presenting Author: Ho-Yong LEE

Topic: Third Symposium on Ferroelectric Crystals and Textured Ceramics

Format: Invited

Session: 4, 5

Date: 8/2/2021

Time (in MDT): 4:00:00 PM

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“Gen III” Piezoelectric PMN-PZT Single Crystals (d<sub>33</sub> > 4,000 pC/N) for Piezoelectric Sensor and Actuator Application Hyun-Jae Joo<sup>1</sup>, Moon-Chan Kim<sup>1</sup>, Ho-Yong Lee<sup>1,2</sup>, Sunmoon University, Asan, South Korea<br />

Crystallographically engineered Relaxor-PT single crystals, specifically PMN-PT (Generation I) and PIN-PMN-PT/PMN-PZT (Generation II), offer much higher piezoelectric and electromechanical coupling coefficients (d<sub>33</sub> > 1,500 pC/N, k<sub>33</sub> > 0.9), when compared to polycrystalline PZT-5H ceramics (d<sub>33</sub> > 600 pC/N, k<sub>33</sub> > 0.75). Recently Ceracomp Co., Ltd. (<u>www.ceracomp.com</u>) has developed the solid-state single crystal growth (SSCG) technique and successfully fabricated Gen III PMN-PZT single crystals modified with acceptors or donors. The piezoelectric constants (d<sub>33</sub>) of (001) Gen III PMN-PZT single crystals were measured to be higher than 4,000 pC/N and thus about two times higher than those of PMN-PT/PZN-PT (Gen I) and PIN-PMN-PT/PMN-PZT (Gen II) single crystals. The Gen III PMN-PZT single crystals have been firstly applied to single crystal-epoxy composites, ultrasonic transducers, piezoelectric sensors, and piezoelectric actuators. In this presentation, we will introduce the development of high performance piezoelectric sensors and actuators by using the Gen III PMN-PZT single crystals, as shown in Fig. 1. Fig. 1. “Gen III” piezoelectric PMN-PZT single crystals (d<sub>33</sub> > 4,000 pC/N), single crystal-epoxy composites, SFC (Single crystal Flexible Composite), sensors and actuators<br />

![Image](http://files.abstractsonline.com/CTRL/F1/6/605/19C/D7C/4E8/8BD/483/C08/406/202/43/g1219_1.jpg)
SINGLE-CRYSTAL-LIKE PIEZOELECTRIC PROPERTIES AND IMPROVED TEMPERATURE STABILITY IN TEXTURED RELAXOR-PBTO3 FERROELECTRIC CERAMICS

Presenting Author: Yunfei Chang

Topic: Third Symposium on Ferroelectric Crystals and Textured Ceramics

Format: Invited

Session: 4, 1

Date: 8/3/2021

Time (in MDT): 3:00:00 PM

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High-performance piezoelectrics are highly in demand for various electronic applications including ultrasonic transducers, multilayer actuators, smart sensors and energy harvesters. Despite the presence of high Lotgering factor $F_{001}$, a substantial performance gap still exists between relaxor-$\text{PbTiO}_3$ textured ceramics and single crystals in terms of piezoelectric properties. In this work, [001]-textured Pb(Yb$_{1/2}$Nb$_{1/2}$)O$_3$-$\text{Pb(Mg}_{1/3}\text{Nb}_{2/3})_3$-$\text{PbTiO}_3$ (PYN-PMN-PT) ceramics with $F_{001} \sim 99\%$ were synthesized by liquid-phase-assisted templated grain growth, where single-crystal-like properties, i.e., large electrostrain $S_{max}/E_{max} \sim 1830 \text{ pm V}^{-1}$ ($E_{max}=20 \text{ kV/cm}$), giant piezoelectric figure of merit $d_{33} \times g_{33} \sim 61.3 \times 10^{-12} \text{ m}^2 \text{ N}^{-1}$ and high electromechanical coupling $k_{33} \sim 0.90$ were simultaneously achieved. Interestingly, the achieved $S_{max}/E_{max}$ and $d_{33} \times g_{33}$ values correspond to ~180% enhancements as compared to the regularly textured ceramics with $F_{001} \sim 96\%$. Combined with phase-field simulation and texture characterization results, we attributed the enhanced piezoelectric performance to the effective control of grain orientation features and domain miniaturization. Besides, textured PYN-PMN-PT ceramics demonstrated remarkably improved temperature stability of piezoelectric strain, being mainly associated with the thermally stabilized phase and stable domain response over a broad temperature range. This work provides guidelines for developing high-performance functional ceramics in the future, and expands application fields of textured ceramics to high-performance electronic devices.
TEXTURED FERROELECTRIC CERAMICS WITH HIGH ELECTROMECHANICAL COUPLING FACTORS OVER A BROAD TEMPERATURE RANGE

Presenting Author: Fei Li

Topic: Third Symposium on Ferroelectric Crystals and Textured Ceramics

Format: Invited

Session: 4, 3

Date: 8/3/2021

Time (in MDT): 3:30:00 PM

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Textured Ferroelectric Ceramics with High Electromechanical Coupling Factors over a Broad Temperature Range

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Piezoelectric devices have been employed in numerous fields, such as medical ultrasonic transducers, where the ferroelectric materials are the heart of the devices. Generally speaking, the figure-of-merits of ferroelectrics for transducer applications are electromechanical coupling factor and the thermal stability/usage temperature range. Relaxor-PbTiO<sub>3</sub> ferroelectric crystals show much improved electromechanical coupling factor (88~93%) when compared to their ceramic counterparts (65~78%), by taking advantage of the strong anisotropy of crystals. However, only few relaxor-PT systems, such as Pb(Mg<sub>1/3</sub>Nb<sub>2/3</sub>)O<sub>3</sub>-PbTiO<sub>3</sub> and Pb(In<sub>1/2</sub>Nb<sub>1/2</sub>)O<sub>3</sub>-Pb(Mg<sub>1/3</sub>Nb<sub>2/3</sub>)O<sub>3</sub>-PbTiO<sub>3</sub>, can be grown into single crystals, whose temperature usage range is limited by their rhombohedral-tetragonal phase
transition temperatures ($T_{rt}$), being around 60~120°C. Here, we developed template-grain-growth approach to fabricate $<001>$-textured Pb(In$_{1/2}$Nb$_{1/2}$)O$_3$-Pb(Sc$_{1/2}$Nb$_{1/2}$)O$_3$-PbTiO$_3$ (PIN-PSN-PT) ceramics with a high level of refractory component Sc$_2$O$_3$, which has an ability to increase the $T_{rt}$ of the system but make it very difficult to be grown into crystal from the melt. The high $k_{33}$ of 85%~90% and greatly increased $T_{rt}$ of 160~200°C were simultaneously achieved in the newly designed textured ceramics. In addition to the increased $T_{rt}$, the textured PIN-PSN-PT ceramics show many other advantages over relaxor-PT crystals, including high composition uniformity and low manufacturing cost. The above merits will make the textured PIN-PSN-PT ceramics alternatives of single crystals, benefiting numerous advanced piezoelectric devices, ranging from acoustic transducers to actuators.
GROWTH AND CHARACTERIZATION OF PMN-PT CRYSTALS BY VERTICAL GRADIENT FREEZE (VGF) TECHNOLOGY

Presenting Author: Guojian Wang

Topic: Third Symposium on Ferroelectric Crystals and Textured Ceramics

Format: Contributed

Session: 4, 5

Date: 8/3/2021

Time (in MDT): 4:00:00 PM

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Relaxor ferroelectric Lead Magnesium Niobate-Lead Titanate (PMN-PT) crystal has been used in various applications such as medical ultrasound imaging, SONAR, micro-actuation and energy harvesting due to its high electromechanical coupling coefficient and high piezoelectric coefficient. The high cost of PMN-PT stems from low crystal growth yield and limits the wider its application. Vertical gradient freeze(VGF) is a crystal method requiring relatively simple equipment and producing high quality crystals with low dislocation densities and less impurity striations and facets. This method has been extensively used to grow semiconductor and optical crystals. Here, we reported the growth of $\phi$3” PMN-PT crystals. The crystal structure, dielectric and piezoelectric properties of grown crystals were studied. Prospects of growing $\phi$6” and larger will also be discussed. This project is supported by Office of Naval Research (ONR) Contract N00014-18-C-1031 and N00014-21-C-1037.
GROWTH AND CHARACTERIZATION OF A NEW BISMUTH-BASED HIGH CURIE TEMPERATURE PIEZO-/FERROELECTRIC (1-X)PbTiO<sub>3</sub>-XBi(Zn<sub>2/3</sub>Ta<sub>1/3</sub>)O<sub>3</sub> SINGLE CRYSTALS

**Presenting Author:** Yi Yuan

**Topic:** Third Symposium on Ferroelectric Crystals and Textured Ceramics

**Format:** Contributed

**Session:** 4, 6

**Date:** 8/3/2021

**Time (in MDT):** 4:15:00 PM

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With the increasing demand for high-temperature and high-performance piezoelectrics for electromechanical transduction applications in MEMS systems, automotive industry, and aerospace industry, materials which can function well at high temperatures are highly desired in those applications. Many bismuth-based perovskites were found to enhance the polarization and thus the Curie temperature when forming solid solution with PbTiO<sub>3</sub>. In this work, the single crystals of a new solid solution between Bi-based complex perovskite and lead titanate, (1-X)PbTiO<sub>3</sub>-XBi(Zn<sub>2/3</sub>Ta<sub>1/3</sub>)O<sub>3</sub>, with the nominal composition of 0.80PbTiO<sub>3</sub>-0.20Bi(Zn<sub>2/3</sub>Ta<sub>1/3</sub>)O<sub>3</sub>, have been successfully grown by high-temperature solution method. Single crystals with dimensions of 5-20mm have been obtained. X-ray diffraction measurements show that the grown single crystals possess the perovskite structure with a tetragonal symmetry. The natural growth direction of the single crystals was found to be in the <001> direction. Dielectric measurements of the single crystals revealed a high Curie temperature of 480 degree. Ferroelectric P-E loop characterization shows a high coercive field (<i>E_C</i> > 30kV/cm) for this single crystal system. The domain structure of the (001)-oriented single crystal was examined by polarized light microscopy. The high coercive electric field, as well as the high remanent polarization of the PbTiO<sub>3</sub>-Bi(Zn<sub>2/3</sub>Ta<sub>1/3</sub>)O<sub>3</sub> single crystals make them a promising candidate for applications in high-power electromechanical transducers that can be operated in a wide temperature range.
The benefits of single crystals for piezoelectric applications are now well known, with ultrahigh piezoelectric coefficients, coupling and strain reported in relaxor-PbTiO$_3$ systems. Environmental concerns and regulations have since sparked a new change in direction for research of piezoelectric single crystals with the demand for high performing, lead-free alternatives. Single crystal growth processes in (K,Na)NbO$_3$, (Na,Bi)TiO$_3$–BaTiO$_3$ and BaTiO$_3$ have been heavily investigated, showing some promise for use in specific applications. In high-end applications, where state of the art piezoelectric materials are required, the property advantages of single crystals outweigh the associated costs. For further utilisation of single crystals in industry, the production costs must be reduced, and crystal sizes increased, to be more comparable with polycrystalline ceramics. Bulk ferroelectric single crystals are grown using various techniques by taking advantage of the diffusion, nucleation and subsequent growth during the phase transformation from a liquid to solid (flux, Bridgman, Czochralski, top seeded solution growth, etc.) or solid to solid (solid-state crystal growth). While the liquid phase growth methods are the most researched and established processes for the development of single crystals, there are limitations for their use, especially for lead-free systems. The lower growth temperatures of the solid-state crystal growth (SSCG) method is useful for compositions with a mixture of volatile and refractory constituents, such as those in (K,Na)NbO$_3$ and (Na,Bi)TiO$_3$–BaTiO$_3$. Compared to the melt growth techniques, SSCG does not require expensive platinum crucibles and can be utilised in muffle furnaces and is considered a cheaper alternative. Recent success in the rapid growth of centimetre-sized (K,Na)NbO$_3$ single crystals using SSCG has highlighted the need to explore this technique further. Optimisation and control of the growth behaviour, as well as overcoming the issues of high porosity and leakage currents will enable lead-free single crystals to become commercially viable in the near future.
VISIBLE-LIGHT ACTIVATION OF FERROELECTRIC PHOTOVOLTAICS

Presenting Author: Yuji Noguchi

Topic: Third Symposium on Ferroelectric Crystals and Textured Ceramics

Format: Invited

Session: 4, 3

Date: 8/4/2021

Time (in MDT): 3:30:00 PM

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Similar to titanium dioxide, a typical photocatalyst, the oxide ferroelectrics suffered from the band-gap problem, namely, photons with energies greater than the bandgap ($E_g$) can generate electron-hole pairs that deliver the robust PV effect. Our group reported the gap-state engineering\(^1\) that mid-gap states act as a scaffold for visible-light activation of the PV response in BiFeO\(_3\). However, this materials design was still restricted by the materials $E_g$, i.e., the photon energies greater than the half of $E_g$ was required for generating electron-hole pairs.\(^2\) The motivation of our study was quite simple; how transition metal cations that can have multiple valence states influence the PV effects. We chose iron doped barium titanate (Fe-BaTiO\(_3\)), where the valence state of iron, Fe\(^{3+}\) and Fe\(^{2+}\), was reported to be controlled by a high-temperature annealing. At first, we anticipated that a higher concentration of Fe\(^{2+}\) that creates a donor state induce larger photocurrents. The experimental results were qualitatively consistent with this expectation, but the reduced sample exhibited extraordinary large photocurrents. This result cannot be explained solely by the role of Fe\(^{2+}\). The subsequent experimental and theoretical investigations\(^2\) revealed that the coexisting of Fe\(^{3+}\) and Fe\(^{2+}\) provided the robust PV effect. As shown in Fig. 1, the Fe\(^{2+}\) and Fe\(^{3+}\) coexisting state, namely the polar lattice with the Fe\(^{2+}\) and Fe\(^{3+}\) domains having the donor and acceptor states, respectively, undergoes electron and hole injections under light illumination. Visible light with energies much smaller than $E_g$ can, in principle, induces electron-hole pair generation, which is accompanied by the redox reactions of iron both in the domains.\(^1\) Matsuo, H., Noguchi, Y. & Miyayama, M. Gap-state engineering of visible-light-active ferroelectrics for photovoltaic applications. \(\langle i \rangle\) Nat. Commun. 8, 207 (2017).\(^2\) Noguchi, Y., Taniguchi, Y., Inoue, R. & Miyayama, M. Successive redox-mediated visible-light ferrophotovoltaics. \(\langle i \rangle\) Nat. Commun. 11, 1–10 (2020).
Abstract Book - ACCGE-22//OMVPE-20

ROOM-TEMPERATURE SYNTHESIS, GROWTH MECHANISMS, AND OPTOELECTRONIC PROPERTIES OF ORGANIC-INORGANIC HYBRID HALIDE PEROVSKITE
CH<sub>3</sub>NH<sub>3</sub>PbX<sub>3</sub> (X= I, Br, and Cl) SINGLE CRYSTALS

Presenting Author: MARYAM BARI

Topic: Third Symposium on Ferroelectric Crystals and Textured Ceramics

Format: Contributed

Session: 4, 5

Date: 8/4/2021

Time (in MDT): 4:00:00 PM

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Single crystals of the organic-inorganic halide perovskites are well needed in order to fully explore their potential in optoelectronic applications and to gain a fundamental understanding of their intrinsic properties. In addition, they exhibit superior optoelectronic performance and higher intrinsic/environmental stability compared to their polycrystalline counterparts. Previously, inverse temperature crystallization (ITC) was used to grow halide perovskite crystals at high temperatures (» 100 °C). Here, we develop an effective synthetic technique by which the CH3NH3PbX3 (X= I, Br, and Cl) crystals are grown in polar solvents at room temperature (except for CH3NH3PbI3 grown at 45 °C) in a relatively short time. A constant supersaturation during the crystal growth is created to produce large single crystals, which is achieved during room temperature crystallization (RTC) through controlled solvent evaporation. We investigate the effects of the temperature and supersaturation level on the nucleation kinetics of CH3NH3PbCl3 as an example and propose and compare the different growth pathways. The crystal structural analysis, steady-state absorption, photoluminescence, and charge-transport properties demonstrate excellent long-term stability (over 2 years) of the RTC-grown CH3NH3PbX3 (X= Br, Cl) crystals against environmental degradation and moisture. Surprisingly, the charge-transport characteristics and trap densities obtained for the RTC-grown crystals are comparable to those of the single crystals grown by the previous methods. In particular, the RTC-grown MAPbI3 crystal exhibits an ultra-high carrier mobility μ of 410 cm2V-1s-1 and an ultra-long diffusion length LD of 10.75 μm, suggesting that it could be a promising material for high-performance optoelectronic devices. This work presents a general strategy for designing, controlling, and optimizing the growth of high-quality halide perovskite crystals, which is an important step forward toward realizing high-end and stable optoelectronic devices such as nonlinear absorbers, photocatalyst, and micro-electromechanical actuators.