Advanced Ion Microscopy and Ion Beam Nano-engineering Focus Topic
Room 301 - Session HI+AS-ThM

Advanced Ion Microscopy & Surface Analysis

Moderators: Armin Golzhauser, Bielefeld University, Germany, **Shida Tan**, Intel Corporation

8:00am **HI+AS-ThM-1 Defect Engineering on the Atomic Scale with the Helium Ion Microscope***, **Frances I. Allen,*** UC Berkeley **INVITED**

The use of ion beams to tune the properties of materials through the introduction of defects is a well-established technique. In this area, focused ion beam microscopes have the advantage that they allow the researcher to irradiate materials locally in a highly controlled manner. Over the last 15 years, the Helium Ion Microscope (HIM) has been employed for a range of defect engineering applications, in particular concerning thin films and 2D materials. Properties tuned include electrical, magnetic, optical and thermal behavior, achieved by varying the concentration of defects and local disorder, controlled by varying the ion dose [1]. In the case of freestanding atomic monolayer materials, it has been shown that irradiation with helium (and neon) ions using the HIM in raster mode (as opposed to e.g. spot mode), can form single vacancy defects and vacancy defect clusters due to single-ion hits [2,3]. Such sub-nanometer pores have applications in gas separation [4] and for selective ion transport in liquid [5]. In this talk, I will discuss the fabrication of sub-nanometer pores in 2D materials using the HIM. I will present characterization results from Raman spectroscopy and high-resolution transmission electron microscopy, and will also discuss the merits of multi-step fabrication workflows in which vacancy "seeds" are first introduced into the 2D material by ion irradiation, that are then expanded into the final nanopores of desired size and shape by plasma treatment and/or electron beam irradiation.

[1] F. I. Allen 2021. "A Review of Defect Engineering, Ion Implantation, and Nanofabrication Using the Helium Ion Microscope." *Beilstein Journal of Nanotechnology* 12 (July): 633–64.

[2] K. Yoon, A. Rahnamoun, J. L. Swett, V. Iberi, D. A. Cullen, I. V. Vlassiouk, A. Belianinov, et al. 2016. "Atomistic-Scale Simulations of Defect Formation in Graphene under Noble Gas Ion Irradiation." *ACS Nano* 10 (9): 8376–84.

[3] P. Maguire, D. S. Fox, Y. Zhou, Q. Wang, M. O'Brien, J. Jadwiszczak, C. P. Cullen, et al. 2018. "Defect Sizing, Separation, and Substrate Effects in Ion-Irradiated Monolayer Two-Dimensional Materials." *Physical Review. B, Condensed Matter* 98 (13): 134109.

[4] J. Liu, L. Jin, F. I. Allen, Y. Gao, P. Ci, F. Kang, and J. Wu. 2021. "Selective Gas Permeation in Defect-Engineered Bilayer Graphene." *Nano Letters* 21 (5): 2183–90.

[5] A. Smolyanitsky, E. Paulechka, and K. Kroenlein. 2018. "Aqueous Ion Trapping and Transport in Graphene-Embedded 18-Crown-6 Ether Pores." *ACS Nano* 12 (7): 6677–84.

8:40am **HI+AS-ThM-3 Effects of Defects and Si Doping on Ion Motion in TaOx Bilayer Memristors***, **Matthew Flynn-Hepford,*** University of Tennessee Knoxville*; J. Keum, I. Kravchenko, S. Randolph, A. Ievlev, B. Sumpter,* Oak Ridge National Laboratory*; M. Marinella,* Arizona State University*; O. Ovchinnikova,* Oak Ridge National Laboratory

TaOx materials have promising properties for memristive applications such as long state retention time and consistent resistive switching.If the mechanism of the resistive switching can be controlled, these materials could be the foundation for the next generation of neuromorphic computing. A material design approach was implemented with the goal of lowering the operational voltage of these devices.Radial distribution functions (RDF) of the modeled TaOx materials with added defects and Si doping were used to predict the bonding strength of the materials.Experimentally, in order to increase ion mobility, defects were introduced into the active layer by He ion irradiation.Local strong bonding was induced in the form of local Si doping by Si irradiation, in an attempt to induce ion mobility channels where ion motion can be better controlled.In order to probe the mechanism of this resistive switching, conductive atomic force microscopy (c-AFM) and kelvin probe force microscopy (KPFM) were used to induce ion motion in the thin films and probe the change in surface potential, respectively.Specially resolved time-of-flight secondary ion mass spectroscopy (ToF-SIMS) was used to probe the chemical change in the film with applied tip bias.These c-AFM and KPFM experiments along with ToF-SIMS were used to probe the locally defected and Si-irradiated areas in order to better understand the effects of defects and Si doping on ion mobility in TaOx bilayer memristors.

9:00am **HI+AS-ThM-4 Advantages of Using Helium Ion Microscopy for Morphological Analysis of $BiScO_3$-$PbTiO_3$ Piezoelectric Ceramics***, S. Chen, A. Bunevich, Y. Yuan,* ***Karen Kavanagh****, Z. Ye,* Simon Fraser University, Canada

Piezoelectric materials can convert mechanical energy into electrical and vice versa. Imaging by Scanning Electron Microscopy (SEM) is commonly used for initial morphological analysis of the grain size, uniformity and porosity, properties that correlate with the piezoelectric quality of interest. However, piezoelectric ceramic is highly insulating, requiring a conductive coating to inhibit charging while imaging through secondary electron collection in most SEMs. Thus, SEM images may not be representative of the sample surface. We have found that there are numerous advantages to using Helium Ion Microscopy (HIM) instead. In a HIM, a positively-charged focussed He ion beam is used to excite secondary electrons, with sample charging neutralized by a simultaneous, large-area electron flood gun. Samples are analysed directly without any surface modification, enabling rapid comparisons of a sintered batch for selection of the best quality ceramic for electrical testing. Higher resolution is achieved for better images of grain boundaries and textural irregularities that are not visible by SEM. In this talk, we will compare SEM and HIM secondary electron images of various compositions of $BiScO_3$-$PbTiO_3$ ceramics, a high temperature piezoelectric material. We will show examples of nanometer-wide ceramic grain boundaries and triple points that were not visible using SEM. Grain boundaries are regions of changes in the lattice structure that have significant implications for piezo and other electronic properties. We have found HIM images to show surface topography and regions of dramatically different contrast that are invisible in the SEM. Furthermore, the lack of conductive coating allows us to see variations in the grain boundary itself, which may explain why piezoelectric properties fluctuate with region in a single sample. Ceramics with large grains (> 20 mm) and flat surfaces correlated with high ferroelectricity at 200°C, with a P_{max} = 282 mC/cm^2. These samples were also more physically robust and able to be poled at higher temperatures and voltages than previous samples of the same composition, improving their piezoelectric properties. Incorporating HIM into the design and synthesis process allows us to quantify the effects of factors such as sintering temperature and die conditions on the physical quality of the ceramic, which ultimately determines its electronic properties and the feasibility of material commercialization.

Acknowledgments

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9:20am **HI+AS-ThM-5 Low-Energy Ion Implantation - Range Comparisons between Theory and Experiment***, **Michael Titze,*** Sandia National Laboratories*; J. Poplawsky,* Oak Ridge National Laboratory*; A. Belianinov, E. Bielejec,* Sandia National Laboratories

The continued decrease in size of microelectronic devices has created a need for shallower implanted dopant layers. With the recent discovery of two-dimensional (2D) materials, the ultimate limit for shallow layer implant is incorporating material into a single monolayer. Multi-specie focused ion beams (FIB) can operate with a variety of ion species and enable direct-write implantation of specific ions tailored for an exact application. Prior to any ion irradiation experiment, the range of ions in the material needs to be calculated, often predicted by using freely available Stopping and Range of Ions in Matter (SRIM) simulation.

SRIM simulations are in excellent agreement with experiment for high energy light ions, however, for low energy heavy ions, discrepancies between SRIM and observed experimental values have been reported. We use Rutherford backscattering spectrometry (RBS), Secondary ion mass spectrometry (SIMS) and Atom-probe tomography (APT) to measure the depth of heavy ions in silicon following FIB implantation with energies from 1 – 150 keV. The resolution limit of RBS and SIMS is on the order of nanometers, comparable to the implantation depth for few keV ion implants, requiring the use of APT for measuring lowest energy implants because APT is capable of almost angstrom resolution in the 100 direction of single crystalline Si. The difference between SRIM and experimental result is < 10 nm for all investigated ion energies, however due to the low overall range of the ions, the relative error is larger for lower ion energies with 1 keV as the minimum energy investigated showing > 500 % relative discrepancy.

This work was performed, in part, at the Center for Integrated Nanotechnologies, an Office of Science User Facility operated for the U.S. Department of Energy (DOE) Office of Science. 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. DOE's National Nuclear Security Administration under contract DE-NA-0003525. The views expressed in the article do not necessarily represent the views of the U.S. DOE or the United States Government.APT research was supported by the Center for Nanophase Materials Sciences (CNMS), which is a US Department of Energy, Office of Science User Facility at Oak Ridge National Laboratory.

11:00am **HI+AS-ThM-10 Correlative Microscopy Using HIM and HIM/SIMS***,* ***Florian Vollnhals,*** Institute for Nanotechnology and Correlative Microscopy - INAM, Germany*; G. Sarau,* Fraunhofer Institute for Ceramics Technology and Systems - IKTS, Germany*; A. Kraus,* Institute for Nanotechnology and Correlative Microscopy - INAM, Germany*; S. Christiansen,* Fraunhofer Institute for Ceramics Technology and Systems - IKTS, Germany **INVITED**

The Helium Ion Microscope (HIM) has changed the world of charged particle microscopy [1]. The attainable spot sizes have enabled advances in imaging as well as nanotechnological applications such as ion beam lithography, nanopatterning or material modification.

An area that has been challenging for HIM, especially in comparison to scanning electron microscopy (SEM), is sample analysis beyond secondary electron (SE) imaging. While most SEMs are equipped with some form of X-ray detection systems (e.g., EDX) for chemical analysis, and many more analytical modes available for further characterization of physical or chemical sample properties, such capabilities have been limited for HIM [3].

The HIM community has made considerable efforts to improve this situation by introducing ion beam specific detection tools like Rutherford backscattering (RBS), Scanning Transmission Helium Ion Microscopy (STHIM) or Secondary Ion Mass Spectrometry (SIMS) using the neon ion beam provided by the latest generation ORION NanoFab HIM [2].

In HIM-SIMS, the focused ion beam is scanned across and thus sputters the surface, resulting in the emission of atoms and ions. The ions are collected and guided to a mass analyzer, allowing for the detection of ions and small clusters ranging from light elements like hydrogen, lithium and boron to heavy elements like Lead. Especially the detection of lithium is a valuable new tool for battery research.

Recently, the SIMS detection system developed by Wirtz et al. at Luxembourg Institute of Technology (LIST) has been upgraded from four individual detectors into a prototype focal plane detector within the npSCOPE project (npscope.eu, funded by the European Commission), allowing for the detection of many masses in parallel, which is beneficial for many applications for which a compositional analysis is required [3].

In addition to the detector development efforts at LIST, a focus has been set on the development of workflows for correlative microscopy using the HIM in a context of additional analytical modalities. The correlation of high resolution HIM and HIM-SIMS imaging with complementary analytical modalities like atomic force microscopy, optical or Raman microscopy to allow for new insights and overcome some of the limitations of the individual tools [4].

This contribution aims at showcasing applications of HIM-SIMS and offers some insights into correlative microscopy workflows involving the HIM.

[1] Ward et al., J. Vac. Sci. Technol. B 24 (2006) 2871

[2] Wirtz et al., Annu. Rev. Anal. Chem. 12 (2019) 523

[3] Audinot et al., Reports Prog. Phys. 84 (2021) 105901

[4] Vollnhals et al., Anal. Chem. 89 (2017) 10702

11:40am **HI+AS-ThM-12 Electronic vs. Nuclear Sputtering of Coronene***,* ***Lars Breuer****, T. Heckhoff, M. Herder,* University of Duisburg-Essen, Germany*; H. Tian, N. Winograd,* The Pennsylvania State University*; A. Wucher,* University of Duisburg-Essen, Germany

Electronic sputtering induced by swift heavy ion (SHI) irradiation of solids has been suggested as a relatively soft desorption mechanism for intact molecules in Secondary Ion Mass Spectrometry (SIMS). In order to evaluate the prospects of this "MeV-SIMS" technique as compared to the standard SIMS methodology utilizing nuclear sputtering with projectile energies in the keV range, we have performed a case study using time-of-flight (ToF) mass spectrometry to detect both ionized and neutral particles sputtered from a coronene film. In particular, secondary ion and neutral mass spectra obtained under 4.8 MeV/u Ca, Bi and Au ion impact were compared with those measured under irradiation with keV Ar, C_{60} and Ar_{1500} ions. While secondary ions were directly detected using a reflectron ToF spectrometer, sputtered neutral particles were post-ionized using two different laser photoionization schemes, namely vacuum ultraviolet single photon ionization at 157 nm and infrared strong field ionization at wavelengths between 800 and 1300 nm, respectively. The measured spectra are interpreted in terms of partial sputter yields, fragmentation patterns, emission velocity distributions and ionization probabilities with emphasis on the emission and/or formation of intact molecular ions.

The obtained data clearly demonstrate that the MeV-induced electronic sputtering process results in much cleaner molecule spectra than the keV-induced nuclear sputtering process even if cluster projectiles are used in the keV experiment. In particular for the Ca SHI and SPI post-ionization, the measured spectra are completely dominated by unfragmented neutral coronene molecules detected at m/z 300, followed by some fragmentation via the loss of one or more hydrogen atoms. Interestingly, the spectra measured under SHI impact are even cleaner than those measured under thermal evaporation conditions, thereby illustrating a fundamental difference between macroscopic thermal evaporation and the electronic sputtering process. Comparing the secondary neutral and ion spectra, one finds an ionization probability of the intact molecule of the order of 1 % under SHI impact, which may be slightly higher than that measured under keV C_{60}^+ ion impact (several 10^{-3}). Apart from the hugely different fragmentation characteristics, no significant difference is found between SHI and keV cluster ion impact regarding the emission velocity distributions of the emitted molecules, thereby indicating that the measured signals largely represent the respective partial sputter yields.

12:00pm **HI+AS-ThM-13 Scanning Transmission Helium Ion Microscopy-How Does It Compare to TEM?***,* ***Annalena Wolff,*** Caltech*; R. Fieth,* QUT, Australia

This work explores the HIM's analysis capabilities of unstained biological samples using a self-built dark field scanning transmission ion microscopy holder. For thin enough samples, such as thin sections of biological specimen on TEM grids, the high energy helium ions can penetrate through the sample. While the ion transverses through the thin foil, it undergoes collisions with the sample atoms and is deflected. The ion exits the sample at a deflection angle which is specimen thickness, ion energy as well as sample material dependent. The deflection angle can be determined using Monte Carlo simulations. The freeware program Stopping and Range of Ions in Matter was used in this work. This effect can be used to design a dark field scanning transmission ion microscopy holder (DF-STIM). The holder design is based on a previously reported experiment [1]. In principle, ions, which are deflected by a specific angle hit a metal conversion plate, which is mounted at a specified distance h below the sample. Here, the transmitted ions create a secondary electron signal which can be collected by the HIM's Everhart-Thonley Detector. Ions which are deflected less than the acceptance angle enter a hole in the holder which his located directly below the specimen. This hole acts as a Faraday cup. For this case, no secondary electron signal is created. For biological samples, areas with higher carbon density create signal while areas with lower carbon density create less signal and can this be distinguished in the DF STIM image.

The DF STIM holder is tested by imaging stained and unstained biological samples and the results are compared to TEM measurements.

[1] Emmrich D, Wolff A, Meyerbröker N, Lindner JKN, Beyer A, Gölzhäuser A. Scanning transmission helium ion microscopy on carbon nanomembranes. Beilstein J Nanotechnol. 2021 Feb 26;12:222-231. doi: 10.3762/bjnano.12.18. PMID: 33728240; PMCID: PMC7934706.

[2] Dr. Crystal Cooper is thanked for the many useful discussions and the sample preparation suggestions.

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