Advanced Ion Microscopy Focus Topic
Room 203B - Session HI+AS-ThM

Advanced Ion Microscopy & Surface Analysis

Moderators: Gregor Hlawacek, Helmholtz Zentrum Dresden-Rossendorf, Germany, Shida Tan, Intel Corporation

8:00am **HI+AS-ThM1 Pushing the Limits: Secondary Ion Mass Spectrometry with Helium Ion Microscopy*, Alex Belianinov,*** Oak Ridge National Laboratory*; S. Kim,* Pusan National University, South Korea*; M. Lorenz,* University of Tennessee Knoxville*; A.V. Ievlev, A. Trofimov, O.S. Ovchinnikova,* Oak Ridge National Laboratory **INVITED**

Material functionality is defined by structure and chemistry often at micro- and nano-scale. The effects are coupled; however, few methods exist that can simultaneously map both. This presents a challenge for material scientists. Functional materials are continuously increasing in complexity, and the number of studies devoted to designing new materials often overwhelms characterization capacity. Recently, attention has been devoted to offer hardware and software solutions in chemical imaging, where a blend of *in-situ* and *ex-situ* techniques are used to capture and describe material behavior using combinatorial data. However, many of the emerging techniques need to be carefully validated and contrasted against existing approaches.

This talk will cover the performance of the recently developed combinatorial Helium Ion Microscopy (HIM) and Secondary Ion Mass Spectrometry (SIMS) tool on a wide variety of conductive and insulating samples. While the HIM imaging and milling performance to explore the physical structure has been repeatedly demonstrated, questions on the effect, quality, and resolution of a Neon beam SIMS remain. Ion yields, chemical resolution, and charge compensation results and strategies will be presented and discussed.

Acknowledgement

This research was conducted at the Center for Nanophase Materials Sciences, which is a DOE Office of Science User Facility.

8:40am **HI+AS-ThM3 When HIM meets SIMS*, Tom Wirtz,*** Luxembourg Institute of Science and Technology (LIST), Luxembourg*; O. De Castro, J. Lovric,* Luxembourg Institute of Science and Technology (LIST)*; J.-N. Audinot,* Luxembourg Institute of Science and Technology (LIST), Luxembourg

In 2015, we first presented a Secondary Ion Mass Spectrometry (SIMS) system which we specifically developed for the Zeiss ORION NanoFab Helium Ion Microscope (HIM) [1]. This SIMS system is based on (i) specifically designed secondary ion extraction optics coupled with post-acceleration transfer optics, providing maximized extraction efficiency while keeping a finely focussed primary ion beam for highest lateral resolution, (ii) a compact floating double focusing magnetic sector mass spectrometer allowing operation in the DC mode at full transmission (and hence avoiding duty cycles like in TOF systems that either lead to very long acquisition times or, for a same acquisition time, intrinsically limit the sensitivity) and (iii) a specific detection system allowing the detection of several masses in parallel. We have demonstrated that our instrument is capable of producing (i) mass spectra with high mass resolution, (ii) very local depth profiles and (iii) elemental SIMS maps with lateral resolutions down to 12 nm [1-5]. Furthermore, HIM-SIMS opens the way for in-situ correlative imaging combining high resolution SE images with elemental and isotopic ratio maps from SIMS [2,3,6]. This approach allows SE images of exactly the same zone analysed with SIMS to be acquired easily and rapidly, followed by a fusion between the SE and SIMS data sets [6]. Moreover, thanks to its depth profiling capability of the SIMS add-on, it is now possible to follow the chemical composition in real time during nano-patterning in the HIM for applications such as end-pointing.

Here, we will review the instrument performance and present a number of examples taken from various fields of applications, with a special emphasis on 3D reconstructions in materials science (battery materials, solar cells, micro-electronics) and on correlative HIM-SIMS bioimaging.

References:

[1] T. Wirtz, P. Philipp, J.-N. Audinot, D. Dowsett, S. Eswara, Nanotechnology 26 (2015) 434001

[2] T. Wirtz, D. Dowsett, P. Philipp, Helium Ion Microscopy, edited by G. Hlawacek, A. Gölzhäuser, Springer, 2017

[3] D. Dowsett, T. Wirtz, Anal. Chem. 89 (2017) 8957-8965

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[6] F. Vollnhals, J.-N. Audinot, T. Wirtz, M. Mercier-Bonin, I. Fourquaux, B. Schroeppel, U. Kraushaar, V. Lev-Ram, M. H. Ellisman, S. Eswara, Anal. Chem. 89 (2017) 10702-10710

9:00am **HI+AS-ThM4 Deciphering Chemical Nature of Ferroelastic Twin Domain in $MAPbI_3$ perovskite by Helium Ion Microscopy Secondary Ion Mass Spectrometry*, Yongtao Liu,*** University of Tennessee*; L. Collins,* Oak Ridge National Laboratory*; R. Proksch,* Asylum Research an Oxford Instruments Company*; S. Kim,* Oak Ridge National Laboratory*; B.R. Watson,* University of Tennessee*; B.L. Doughty,* Oak Ridge National Laboratory*; T.R. Calhoun, M. Ahmadi,* University of Tennessee*; A.V. Ievlev, S. Jesse, S. Retterer, A. Belianinov, K. Xiao, J. Huang, B.G. Sumpter, S.V. Kalinin,* Oak Ridge National Laboratory*; B.H. Hu,* University of Tennessee*; O.S. Ovchinnikova,* Center for Nanophase Materials Sciences, Oak Ridge National Laboratory

Hybrid organic-inorganic perovskites (HOIPs) have recently attracted attention due to its success in optoelectronics, largely due to power conversion efficiency, which has exceeded 20% in a short time. Recently, the appearance of twin domains in $MAPbI_3$ has been described ambiguously in a number of investigations. While all previous publications are limited in the descriptions of ferroelectric and/or ferroelastic nature, given (i) the correlation of defect chemistry and ferroelasticity, (ii) the coupling of ferroelectricity and ionic states, the chemistry of this twin domain can no longer be ignored. In earlier investigations, the twin domain size is revealed in the range of 100 nm- 400 nm, well in the detectability of helium ion microscopy secondary ion mass spectrometry (HIM-SIMS) (spatial resolution ~10 nm). Therefore, in this work, we correlate HIM-SIMS with multiple image techniques to unveil the chemical nature of the twin domain in $MAPbI_3$ perovskite.

Our scanning probe microscopy (SPM) studies indicate the variation of elasticity and energy dissipation between domains. Moreover, correlating SPM with scanning electron microscope (SEM), we observed smooth topography and twin domain contrast in SEM image, simultaneously, indicating the twinning contrast in SEM image is not due to morphology. These results allow us to suppose the chemical variation between twin domains, suggesting the need of clarifying the chemical difference between domains.

Using HIM-SIMS, which combines high-resolution imaging <0.25 nm of helium ion microscopy with the chemical sensitivity of secondary ion mass spectrometry (SIMS), we can detect ion distribution with a spatial resolution of 10 nm, allowing us to quantitatively explore the chemical composition of the twin domains (100 nm-400 nm). A HIM-SIMS using two gas field ionization sources (He^+ and Ne^+) was utilized for mass-selected chemical imaging of perovskite samples as well as identification of chemical species by spectrum collection in this study. In a positive mode measurement, $CH_3NH_3^+$ (m/z~32) chemical map shows that the $CH_3NH_3^+$concentration differs both in grains and twin domains, however, the Pb^+ (m/z~208) distributes uniformly. These results clarify that the chemical variation between domains originates from $CH_3NH_3^+$ segregation. For the most relevant for the optoelectronic applications of HOIPs, we have shown that this chemical variation affects HOIPs' interaction with light. Combining HIM-SIMS with multiple image techniques, this work offers insight into the fundamental behaviors of the twin domain in $MAPbI_3$, as well as a new line of investigative thought in these fascinating materials.

9:20am **HI+AS-ThM5 Helium and Neon Ion Microscopy for Microbiological Applications*, Ilari Maasilta,*** University of Jyvaskyla, Finland **INVITED**

Imaging of microbial interactions has until now been based on well-established electron microscopy methods. In this talk I review our recent drive to study microbiological samples using a helium ion microscopy (HIM). The main focus will be given on bacterial colonies and interactions between bacteria and their viruses, bacteriophages, which we imaged in situ on agar plates [1]. Other recent biological applications will also be briefly discussed. In biological imaging, HIM has advantages over traditional scanning electron microscopy with its sub-nanometer resolution, increased surface sensitivity, and the possibility to image nonconductive samples. Furthermore, by controlling the He beam dose or by using heavier Ne ions, the HIM instrument provides the possibility to mill out material in the samples, allowing for subsurface imaging and in situ sectioning.

Here, we present the first HIM-images of bacterial colonies and phage–bacterium interactions are presented at different stages of the infection as they occur on an agar culture. The feasibility of neon and helium milling is also demonstrated to reveal the subsurface structures of bacterial colonies on agar substrate, and in some cases also structure inside individual bacteria after cross-sectioning. The study concludes that HIM offers great opportunities to advance the studies of microbial imaging, in particular in the area of interaction of viruses with cells, or interaction of cells with biological surfaces.

[1] M. Leppänen, L.-R. Sundberg, E. Laanto, G. Almeida, P. Papponen and I. J. Maasilta, Imaging bacterial colonies and phage–bacterium Interaction at sub-nanometer resolution using helium-ion microscopy, Adv. Biosystems 1, 1700070 (2017)

11:00am **HI+AS-ThM10 Characterization of Soot Particles by Helium Ion Microscopy***, **André Beyer**, D. Emmrich, M. Salamanca, L. Ruwe, H. Vieker, K. Kohse-Höinghaus, A. Gölzhäuser,* Bielefeld University, Germany

Complementary techniques for the characterization of soot particles are needed to gain insight into their formation processes. In this contribution, we focus on Helium Ion Microscopy (HIM) which allows high contrast imaging of soot particles with sizes down to 2 nm. Soot formation was realized with well-defined model flames from different fuel compositions. The particles were sampled on silicon substrates at different positons within the flame which allows choosing the particles degree of maturity. Large numbers of particles were recorded with a single HIM image in a relatively short time. A number of such images were combined to obtain meaningful particle size distributions. In addition, the following geometric properties of soot particles were evaluated: sphericity, circularity, and fractal dimension. Comparison with other experimental techniques as well as theoretical model calculations demonstrate the strength of the HIM characterization method [1-3].

[1] M. Schenk et al., ChemPhysChem 14, 3248 (2013).

[2] M. Schenk et al., Proc. Combust. Inst. 35, 1879 (2015).

[3] C. Betrancourt et al., Aerosol Science and Technology 51, 916 (2017).

11:20am **HI+AS-ThM11 Development of a Surface Science Spectra Submission Form for Low Energy Ion Scattering (LEIS)***, M.R. Linford, **Tahereh Gholian Avval**,* Brigham Young University*; H.H. Brongersma, T. Grehl,* IONTOF GmbH, Germany

Historically, Surface Science Spectra (SSS) has been an important archive for X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), and time-of-flight secondary ion mass spectrometry (ToF-SIMS) data; this detailed, peer-reviewed database now consists of thousands of submissions and spectra that represent these techniques. Thus, SSS has been and continues to be a valuable resource to the surface community. Recently, SSS has begun to expand the surface/material techniques it covers. For example, it now accepts spectroscopic ellipsometry submissions on the optical properties of materials. It is anticipated that submissions in this area will slowly increase so that SSS will become a valuable source of information in this area as well.

In this presentation we discuss the development of an SSS submission form for low energy ion scattering (LEIS). Fields in the form that will be discussed include the abstract, introduction, data, and conclusions. In an SSS submission, the provenance of the sample is carefully documented. A detailed description is also required of the equipment used and of all of its relevant operating parameters – the nature of its beams, the beam energies, the analyzer geometry, etc. The original data collected by the submitter must be supplied, and representative examples of it must be plotted.

Finally, we will show sample submissions based on this new form that should have been submitted for publication by AVS 2018. These will include LEIS submissions of CaF_2, SrO, and Al_2O_3 reference materials

11:40am **HI+AS-ThM12 Time of Flight Backscatter and Secondary Ion Mass Spectrometry in the Helium Ion Microscope***, **Nico Klingner**, R. Heller, G. Hlawacek, J. von Borany, S. Facsko,* Helmholtz Zentrum Dresden-Rossendorf, Germany

Existing Gas Field Ion Source (GFIS) based focused ion beam (FIB) tools suffer from the lack of a well integrated analytic method that can enrich the highly detailed morphological images with materials contrast. While Helium Ion Microscopy (HIM) technology is relatively young several efforts have been made to add such an analytic capability to the technique. So far, ionoluminescence, backscattering spectrometry (BS), and secondary ion mass spectrometry (SIMS) using a magnetic sector or time of flight (TOF) setups have been demonstrated.

After a brief introduction to HIM itself and a summary of the existing approaches I will focus on our own time of flight based analytic approaches. TOF-HIM is enabled by using a fast blanking electronics to chop the primary beam into pulses with a minimal length of only 20 ns. In combination with a multichannel-plate based stop detector this enables TOF backscatter spectrometry (TOF-BS) using He ions at an energy of only 30 keV. The achieved lateral resolution is 54 nm and represents a world record for spatially resolved backscattering spectrometry.

Finally a dedicated extraction optics for positive and negative secondary ions has been designed and tested. The setup can be operated in point and shoot mode to obtain high resolution SIMS data or in imaging mode to obtain lateral resolved maps of the sample surface composition. First experiments revealed a very high relative transmission of up to 76% which is crucial to collect enough signal from nanoparticles prior to their complete removal by ion sputtering. The mass resolution of 200 is sufficient for many life science applications that rely on the isotope identification of light elements (e.g.: C, N). The lateral resolution of 8 nm has been evaluated using the knife edge method and a 75%/25% criterion which represents a world record for spatially resolved secondary ion images.

12:00pm **HI+AS-ThM13 Helium and Neon Focused Ion Beam Hard Mask Lithography on Atomic Layer Deposition Films***, **Matthew Hunt**,* California Institute of Technology*; J. Yang,* University of Texas at Austin*; S.A. Wood, O.J. Painter,* California Institute of Technology

A hard mask lithography technique has been developed wherein a helium or neon focused ion beam (FIB) is used to directly etch a pattern into a thin, atomic layer deposition (ALD) film before then transferring the pattern into the underlying material using a reactive ion etch (RIE). The technique takes advantage of small He-FIB and Ne-FIB probe sizes, capable of directly etching patterns with feature sizes on the order of 1s and 10s of nanometers, respectively, while sidestepping several negative consequences associated with direct etch, namely that low sputter rates prevent large-area patterning from being carried out efficiently, with straight sidewalls, and/or without inducing substrate swelling. An example of the technique is presented here in which (1) 4-10 nm of ALD aluminum-oxide is applied as the hard mask on a 60 nm thick film of aluminum, (2) a <10 pC/um Ne-FIB dose is used to pattern lines that barely etch through the hard mask, and (3) a $Cl_2/CH_4/H_2$ RIE is used to etch the underlying aluminum in 10s of seconds. Neon FIB writing time is reduced by a factor of 20 or more compared to directly etching through the full 60 nm aluminum film. Nanowires as thin as 25 nm are produced with straight sidewalls on 70 nm pitch. This example is being utilized to make superconducting quantum circuit components, e.g. 4 mm long nanocoil inductors that fit into a (20x20) um^2 area. The technique has potentially wide-ranging nanofabrication applications given its amenability to different ALD/substrate material sets and compatibility with both He- and Ne-FIB.

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