Advanced Ion Microscopy and Ion Beam Nano-engineering Focus Topic
Room B231-232 - Session HI+AS+CA-WeA

Advanced Ion Microscopy and Surface Analysis Applications

Moderators: Richard Livengood, Intel Corporation, USA, Armin Gölzhäuser, Bielefeld University, Germany

2:20pm **HI+AS+CA-WeA1 Analytical Capabilities on FIB Instruments using SIMS: Applications, Current Developments and Prospects**, ***Tom Wirtz,*** Luxembourg Institute of Science and Technology, Luxembourg*; J.-N. Audinot,* Luxembourg Institute of Science and Technology, Luxembourg, Luxembourg*; J. Lovric, O. De Castro,* Luxembourg Institute of Science and Technology, Luxembourg **INVITED**

Secondary Ion Mass Spectrometry (SIMS) is an extremely powerful technique for analyzing surfaces, owing in particular to its ability to detect all elements from H to U and to differentiate between isotopes, its excellent sensitivity and its high dynamic range. SIMS analyses can be performed in different analysis modes: acquisition of mass spectra, depth profiling, 2D and 3D imaging. Adding SIMS capability to FIB instruments offers a number of interesting possibilities, including highly sensitive analytics, in-situ process control during patterning and milling, highest resolution SIMS imaging (~10 nm), and direct correlation of SIMS data with data obtained with other analytical or imaging techniques on the same instrument, such as high resolution SE images or EDS spectra [1,2].

Past attempts of performing SIMS on FIB instruments were rather unsuccessful due to unattractive detection limits, which were due to (i) low ionization yields of sputtered particles, (ii) extraction optics with limited collection efficiency of secondary ions and (iii) mass spectrometers having low duty cycles and/or low transmission. In order to overcome these limitations, we have investigated the use of different primary ion species and of reactive gas flooding during FIB-SIMS and we have developed compact high-performance magnetic sector mass spectrometers operating in the DC mode with dedicated high-efficiency extraction optics. We installed such SIMS systems on different FIB based instruments, including the Helium Ion Microscope [3-5], a FIB-SEM DualBeam instrument and the npSCOPE instrument, which is an integrated Gas Field Ion Source enabled instrument combining SE, SIMS and STIM imaging with capabilities to analyse the sample under cryo-conditions.

Here, we will review the performance of the different instruments with a focus on new developments such as cryo-capabilities and new detectors allowing parallel detection of all masses, present a number of examples from various fields of applications (nanoparticles, battery materials, photovoltaics, micro-electronics, tissue and sub-cellular imaging in biology, geology,…) and give an outlook on new trends and prospects.

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

[2] 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

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

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

[5] T. Wirtz, O. De Castro, J.-N. Audinot, P. Philipp, Ann. Rev. Anal. Chem. 12 (2019)

3:00pm **HI+AS+CA-WeA3 Correlated Materials Characterization via Multimodal Chemical Imaging using HIM-SIMS**, *A. Belianinov,* Oak Ridge National Laboratory*; S. Kim,* Pusan National University, South Korea*; A. Trofimov,* ***Olga S. Ovchinnikova,*** Oak Ridge National Laboratory

Multimodal chemical imaging simultaneously offers high resolution chemical and physical information with nanoscale, and in select cases atomic, resolution. By coupling modalities that collect physical and chemical information, we can address a new set of scientific problems in biological systems, battery and fuel cell research, catalysis, pharmaceuticals, photovoltaics, medicine and many others. The combined multimodal platforms enable local correlation of material properties with chemical makeup, making fundamental questions in how chemistry and structure drive functionality approachable. The goal of multimodal imaging is to transcend the existing analytical capabilities for nanometer scale spatially resolved material characterization at interfaces through a unique merger of advanced microscopy, mass spectrometry and optical spectroscopy.Combining helium ion microscopy (HIM) and secondary ion mass spectrometry (SIMS) onto one platform has been demonstrated as a method for high resolution spot sampling and imaging of substrates. To advance this approach and to expand its capabilities I will present our results of multimodal chemical imaging using this technique on test substrates and show application of this approach for the multimodal analysis of perovskite (HOIPs) materials. I will discuss the performance metrics of the multimodal imaging system on conductive and non-conductive materials and discuss our results on understanding the chemical nature of ferroelastics twin domains in methylammonium lead triiodide (MAPbI3) perovskite using HIM-SIMS.

3:20pm **HI+AS+CA-WeA4 Compositional Characterization of Biogenic Nanoparticles using the ORION NanoFab with SIMS**, ***Christelle Guillermier***, *F. Khanom,* Carl Zeiss PCS, Inc.*; D. Medina,* Northeastern University*; J.-N. Audinot,* Luxembourg Institute of Science and Technology, Luxembourg

Over the past several years, the use of both nanoparticles and nanostructured surfaces have emerged as an alternative's solution to antibiotic resistant bacteria as they effectively decrease bacterial survival without being highly toxic to mammalian cells. These nanoparticles whose sizes span 10 nm to several hundred nm are composed of a variety of materials such as pure metals, metal oxides, and metalloids. Their chemical characterization however remains a challenge due to their small sizes. Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX) are the conventional analytical techniques of choice to determine the nanoparticles' morphology, size, and elemental composition. However, although sensitive enough to detect trace elements, SEM and EDX cannot provide elemental information for the smallest features on a bulk sample, or for the lightest elements.

The ORION NanoFab is an ion microscope that allows for high resolution secondary electron (SE) imaging with a He^+ focused ion beam that can be focused to a 0.5 nm probe size. The same instrument offers a Ne^+ ion beam with a focused probe size of 2 nm. Recently, this same platform has been configured with a custom-designed magnetic sector secondary ion mass spectrometer (SIMS). It allows for the detection of all periodic table elements including H and Li which EDS cannot easily detect. Importantly, SIMS with neon provides elemental imaging with spatial resolution smaller than 20 nm. The combination of high resolution He^+ imaging (0.5 nm) with Ne^+ SIMS elemental mapping yields a direct correlative technique particularly attractive for exploring nanoparticles and nanofeatures in general.

NanoFab-SIMS has already yielded information-rich images in diverse fields of applications. We will here illustrate its potential for the characterization of biogenic nanoparticles made by bacteria and plants.

4:20pm **HI+AS+CA-WeA7 Effects of Ion Irradiation on Two-Dimensional Targets: What is Different from Bulk Materials**, ***Arkady V. Krasheninnikov,*** Helmholtz-Zentrum Dresden-Rossendorf, Germany **INVITED**

Ion irradiation has successfully been used for introducing impurities and creating defects in two-dimensional (2D) materials in a controllable manner. Moreover, focused ion beams, especially when combined with in-situ or post-irradiation chemical treatments, can be employed for patterning and even cutting 2D systems with a high spatial resolution. The optimization of this process requires the complete microscopic understanding of the interaction of energetic ions with the low-dimensional targets.

In my presentation, I will dwell upon the multi-scale atomistic computer simulations of the impacts of ions onto free-standing (e.g., suspended on a TEM grid) and supported (deposited on various substrates) 2D materials, including graphene and transition metal dichalcogenides (TMDs), such as MoS2 and WS2. I will emphasize the differences between defect production under ion irradiation in 2D materials and bulk solids. The theoretical results will be augmented by the experimental data obtained by the coworkers. I will further present the results of multi-scale simulations of ion irradiation of free-standing [1] and supported [2] graphene and 2D TMDs, and demonstrate that depending on ion mass and energy, the defect production can be dominated by direct ion impacts, back scattered ions or atoms sputtered from the substrate [2]. Finally, I will touch upon the interaction of highly-charged [3] and swift heavy ions [4] with 2D systems and overview recent progress in modelling this using non-adiabatic approaches including time-dependent density functional theory and Ehrenfest dynamics [5].

1. M. Ghorbani-Asl, S. Kretschmer, D.E. Spearot, and A. V. Krasheninnikov, 2D Materials 4 (2017) 025078.

2. S. Kretschmer, M. Maslov, S. Ghaderzadeh, M. Ghorbani-Asl, G. Hlawacek, and A. V. Krasheninnikov, ACS Applied Materials & Interfaces 10 (2018) 30827.

3. R. A. Wilhelm, E. Gruber, J. Schwestka, R. Kozubek, T.I. Madeira, J.P. Marques, J. Kobus, A. V. Krasheninnikov, M. Schleberger, and F. Aumayr, Phys. Rev. Lett. 119 (2017) 103401.

4. R. Kozubek, M. Tripathi, M. Ghorbani-Asl, S. Kretschmer, L. Madauß, E. Pollmann, M. O'Brien, N. McEvoy, U. Ludacka, T. Susi, G.S. Duesberg, R.A. Wilhelm, A. V. Krasheninnikov, J. Kotakoski, and M. Schleberger J. Phys. Chem. Lett. 10 (2019) 904.

5. A. Ojanperä, A. V. Krasheninnikov, and M. Puska, Phys. Rev. B 89 (2014) 035120.

5:00pm **HI+AS+CA-WeA9 Effects of He Ion Irradiation on Gold Nanoclusters: a Molecular Dynamics Study**, ***Sadegh Ghaderzadeh***, *M. Ghorbani-Asl, S. Kretschmer, G. Hlawacek,* Helmholtz-Zentrum Dresden Rossendorf, Germany*; A.V. Krasheninnikov,* Helmholtz-Zentrum Dresden-Rossendorf, Germany

The interpretation of helium ion microscopy (HIM) images of crystalline metal clusters requires microscopic understanding of the effects of He ion irradiation on the system, including energy deposition and associated heating, as well as channeling patterns. While channeling in bulk metals has been studied at length, there is no quantitative data for small clusters. We carry out molecular dynamics simulations to investigate the behavior of gold nano-particles with diameters of 5-15 nmunder 30 keV He ion irradiation. We show that impacts of the ions can give rise to substantial heating of the clusters through deposition of energy into electronic degrees of freedom, but it does not affect channeling, as clusters cool down between consecutive impact of the ions under typical imaging conditions. At the same time, high temperatures and small cluster sizes should give rise to fast annealing of defects so that the system remains crystalline. Our results show that ion-channeling occurs not only in the principal low-index, but also in the intermediate directions. The strengths of different channels are specified, and their correlations with sputtering-yield and damage production is discussed, along with size-dependence of these properties. The effects of planar defects, such as stacking faults on channeling were also investigated.

Finally, we discuss the implications of our results for the analysis of HIM images of metal clusters.

5:20pm **HI+AS+CA-WeA10 Low Damage Imaging of Polymers with the Helium Ion Microscope**, ***Doug Wei,*** Carl Zeiss, RMS, Inc.*; J.A. Notte,* Carl Zeiss PCS, Inc.*; A. Stratulat,* Carl Zeiss Microscopy, Ltd., UK

Polymers present a combination of challenges for high magnification imaging with the conventional SEM or FIB. Because they are electrically insulating, polymers are susceptible to charge accumulation and can produce imaging artifacts. Or worse, the implanted charge and surface charge can generate fields large enough to induce catastrophic dielectric breakdown. The interaction of the primary beam with the chemical bonds can cause radiolysis, cross-linking, and chain scissions which alter their morphology and other properties. Ion beams of relatively heavy species (Ga and Xe) can cause appreciable sputtering especially at high magnifications. In some cases, the sputtering can be preferential for light atoms, causing disproportionate hydrogen loss. Further difficulties include heating effects, since the typical polymers are good thermal insulators. Compounding matters, they are often temperature sensitive and can be damaged at even modest temperature rises ~ 50 deg C.

However, some of the newly available light ion beams (H, He, Li) offer unique advantages that help to circumvent the problems traditionally encountered when imaging polymers. First, the charging effects are greatly diminished compared to the SEM. In part, this is because the incident ion is likely neutralized as it enters the sample, and remains in a mostly neutral state as it penetrates deeply. This leaves only a net surface charge, which is overall positive and made more so by the ejection of secondary electrons from the surface. This is easily resolved using a collection of low energy electrons provided by a flood gun. The light ion beams also have relatively low sputtering rates compared to the heavier ions. Their interactions are primarily with the electrons of the sample. So while they can affect bonding, they are much less likely to cause sputtering. The light ions will generally be implanted deeply, often hundreds of nanometers under the surface, and helium in particular is known to diffuse out over time. Thermal effects are also much reduced with the light ion beams compared to heavier ions or the SEM. The ion's initial kinetic energy is converted to random thermal energy over a relatively large volume. And much of the transferred energy goes to the electrons in the sample, and their relatively long mean free path helps to dissipate this energy into a larger volume.

Numerous imaging examples will be provided from a variety of polymers using the helium beam from the Zeiss ORION NanoFab. These serve as representative examples of the unique sample interaction of light ions and the advantages they offer for imaging polymers.

5:40pm **HI+AS+CA-WeA11 Imaging of Biological Cells with Helium-Ion Microscopy**, ***Natalie Frese***, *A. Beyer, C. Kaltschmidt, B. Kaltschmidt,* Bielefeld University, Germany*; A. Thomas,* Institute for Metallic Materials Dresden, Germany*; W. Parak,* University of Hamburg, Germany*; A. Gölzhäuser,* Bielefeld University, Germany

Studies from the last decade have shown that helium-ion microscopy (HIM) is suitable for studying biological samples. In particular, cell membranes can be imaged by HIM without metallic coatings, which could lead to disturbance of the surface. In this contribution, we give two examples of biological cells imaged by HIM: (i) mouse hippocampal neurons on patterned surfaces for neuronal networks and (ii) human cells treated with colloidal nanoparticles [1, 2]. Both examples benefit from the high resolution imaging of uncoated, biological materials by HIM, as for (i) the cell adherence to patterned surfaces could be imaged and for (ii) cell morphology images indicated harmful effects of colloidal nanoparticles to cells.

[1] M. Schürmann et al., PLoS ONE 13(2), e0192647 (2018)

[2] X. Ma et al., ACS Nano 11(8), 7807-7820 (2017)

6:00pm **HI+AS+CA-WeA12 Channeling in the Helium Ion Microscope**, ***Hussein Hijazi***, *C. Feldman, R. Thorpe, M. Li, T. Gustafsson,* Rutgers University*; D. Barbacci, A. Schultz,* Ionwerks

The helium ion microscope (HIM) has become a unique tool for modern materials science due to its high lateral resolution for imaging, high spatial resolution and nano-scale analysis. For crystalline materials, the incident beam may undergo ion channeling, which strongly modifies all of the basic ion-solid interactions associated with these HIM functions. Here, a 30 keV He^+ beam was used for RBS channeling in a W(111) crystal using a novel time of flight (HIM/TOF) detector developed at Rutgers University to extract critical channeling parameters. Measurements of the minimum backscattering yield (χ_{min}), surface peak (SP), and critical angle, are compared to several theoretical estimates. The results illustrate the advantage of using channeling in a backscattering mode to characterize crystalline materials with the HIM, as the backscattering intensity modifications are far greater for scattered ions than for secondary electrons. This case of "ideal" channeling with the HIM now provides a basis for analysis of more complex materials such as polycrystalline materials and textured structures, and quantifies the role of HIM induced materials modification in crystalline materials.

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