Advanced Ion Microscopy Focus Topic
Room 7 & 8 - Session HI+NS+TR-ThA

Novel Beam Induced Surface Analysis and Nano-Patterning

Moderators: Anne Delobbe, Orsay Physics, Shinichi Ogawa, National Institute of Advanced Industrial Science and Technology (AIST)

2:20pm **HI+NS+TR-ThA-1 Multimodal Chemical Imaging of Nanoscale Interfacial Phenomena on a Combined HIM-SIMS Platform***, **Olga Ovchinnikova,*** Oak Ridge National Laboratory **INVITED**

The key to advancing energy materials is to understand and control the structure and chemistry at interfaces. However, significant gaps hamper chemical characterization available to study and fully comprehend interfaces and dynamic processes; partly due to the lack of breadth of necessary information, as well as its scattered nature among a multitude of necessary measurement platforms. Multimodal chemical imaging transcends existing analytical capabilities for nanometer scale spatially resolved interfacial studies, through a unique merger of advanced helium ion microscopy (HIM) and secondary ion mass spectrometry (SIMS) techniques. In this talk I will discuss how to visualize material transformations at interfaces, to correlate these changes with chemical composition, and to distil key performance-centric material parameters using a multimodal chemical imaging approach on a combined HIM-SIMS system. Particular attention will be focused on how to use the HIM-SIMS to study the role of ionic migration on the photovoltaic performance, or alternatively whether the ionic migration plays a positive or negative role in determining superior photovoltaic performance in organic-inorganic perovskites (HOIPs). I will discuss how synthesizing perovskite on custom substrates effect active chemical agents in materials and understand how interfaces in materials affect the local chemistry, specifically, key energy related parameters such as electron and ion motion and their re-distribution. Overall, multimodal chemical imaging on a combined HIM-SIMS platform offers the potential to unlock the mystery of active interface formation through intertwining data analytics, nanoscale elemental characterization, with imaging; to better grasp the physical properties of materials and the mechanistic physics-chemistry interplay behind their properties.

Acknowledgements

This work was conducted at the Center for Nanophase Materials Sciences, which is a Department of Energy (DOE) Office of Science User Facility

3:00pm **HI+NS+TR-ThA-3 Characterizing Surface Immobilized Antibodies using ToF-SIMS and Multivariate Analysis***, N Welch,* CSIRO Manufacturing, Australia*; R Madiona,* La Trobe University, Australia*; J Scoble, B Muir,* CSIRO Manufacturing, Australia*; **Paul Pigram,*** La Trobe University, Australia

Antibody attachment, orientation and function at the solid interface are critical for the sensitive detection of biomolecules during immunoassays. Correctly oriented antibodies with solution-facing antigen binding regions have improved antigen capture in comparison with randomly oriented antibodies. Direct characterization of oriented proteins with surface analysis methods still remains a challenge. Surface sensitive techniques, however, such as Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) provide information-rich data that can be used to probe antibody attachment, orientation, denaturation and related characteristics.

Diethylene glycol dimethyl ether plasma polymers (DGpp) functionalized with chromium (DGpp+Cr) have improved immunoassay performance that is indicative of preferential antibody orientation. ToF-SIMS data from proteolytic fragments of anti-EGFR antibody bound to DGpp and DGpp+Cr have been used to construct artificial neural network (ANN) and principal component analysis (PCA) models indicative of correctly oriented systems. Whole antibody samples (IgG) tested against each of the models indicate preferential antibody orientation on DGpp+Cr. Cross-reference between ANN and PCA models yield 20 mass fragments associated with $F(ab')_2$ region representing correct orientation, and 23 mass fragments associated with the Fc region representing incorrect orientation. The mass fragments have been compared with amino acid fragments and amino acid composition in $F(ab')_2$ and Fc regions. A ratio of the sum of the ToF-SIMS ion intensities from the $F(ab')_2$ fragments to the Fc fragments demonstrated a 50% increase in intensity for IgG on DGpp+Cr as compared to DGpp.

This systematic data analysis methodology offers new opportunities for the investigation of antibody orientation on a range of substrates. It also yields good results for the characterization of antibody denaturation and for determining limits of detection.

4:00pm **HI+NS+TR-ThA-6 Single-nanometer Functional Graphene Devices Patterned with Helium Ion Beam***, **Hiroshi Mizuta,** M Schmidt, T Kanzaki,* Japan Advanced Institute of Science and Technology (JAIST), Japan*; S Ogawa,* National Institute of Advanced Industrial Science and Technology (AIST), Japan*; M Muruganathan,* Japan Advanced Institute of Science and Technology (JAIST), Japan **INVITED**

The bombardment of specimen by accelerated ions causes implantation and surface sputtering. The latter can be employed to create structures with sub-10 nm dimensions. This precision is demonstrated in electrically contacted and suspended graphene layers by a Helium ion microscope (HIM). 5 nm wide monolayer graphene, suspended above a pore and milled by HIM, had been demonstrated [1]. However, the physical properties of such a ribbon cannot be investigated in such a device architecture due to lack of electrical contacts. Recently, we demonstrated a ~6 nm wide suspended GNR and reported on the room temperature electrical characteristics. A wide range of drain current, at which current suppression occurs, has been observed [2]. However, that device was based on exfoliated grapheme, which makes it necessary to individually design the structures, and the yield is typically small.

Here, we report on the large-array processing of 100 nm wide monolayer CVD based suspended graphene structures by HIM. The structures are prepared by electron-beam lithography and thin-film processing. Before HIM milling, the graphene is released by buffered hydrofluoric acid etching and critical point drying. Annealing in H_2/Ar atmosphere is used to remove the resist contamination.

We will first discuss results of fabricating suspended GNRs with constriction milled with HIM (30 keV acceleration voltage, 1.1×10^{18} ion/cm^2). The GNRs with sub-10-nm constriction are successfully patterned, and the electrical conduction is measured as function of temperature. We will discuss the milling results and electrical characterization in detail along with their potential impact on the performance of graphene-NEMS-based single-molecular detection [3]. We will then report on the recent progress in preparing arrays of nanopores in graphene by HIM. 9x9 arrays with pitch of ~9 nm are successfully realized with a dose of 6.5×10^{18} ions/cm^2. Arrays of pores spanning a complete suspended ribbon with a pitch of ~18 nm are demonstrated as well, and we will discuss the impact of such periodic structure on the electrical and thermal (phononic) transport for nanoscale heat phonon engineering.

Acknowledgements: T. Iijima is acknowledged for the usage of the HIM at AIST SCR Station**.** This research was supported through the Grant-in-Aid for Scientific Research KAKENHI 25220904, 16K13650, 16K18090 from JSPS and COI program of the Japan Science Technology Agency.

References [1] D. Pickard and L. Scipioni, “Graphene Nano-Ribbon Patterning in the ORION® PLUS,” Zeiss application note, 2009. [2] M. E. Schmidt *et al*., 63rd JSAP Spring Meeting (2016) [3] J. Sun *et al*., Science Advances **2**(4), e1501518 (2016)

5:00pm **HI+NS+TR-ThA-9 Monte Carlo Simulation Study of Gas Assisted Focused Ion Beam Induced Etching***, **Kyle Mahady,** P Rack,* University of Tennessee*; S Tan,* Intel Corporation*; Y Greenzweig,* Intel Corporation, Israel*; R Livengood,* Intel Corporation*; A Raveh,* Intel Corporation, Israel

We present a simulation study of focused ion beam etching using a gas assist. The use of a precursor gas greatly enhances material removal rate when compared to ion beam sputtering, enabling features such as valleys to be etched with lower ion doses, and consequently less damage to the substrate. The basis of our study is a Monte Carlo based code for focused ion beam milling, which simulates the cumulative removal of material due to sputtering, and secondary electron emission, for various target compositions and structures. In this talk, we describe the gas assisted etching portion of the code, which simulates monolayer adsorption of XeF_2 to a SiO_2 substrate, and the reactions between adsorbed gas and surface atoms which lead to volatilization and material removal. We study the effect of etching parameters such as beam current and gas flux on the shape of etched valleys, and the influence of ion species such as Ne^+ and Ga^+, to characterize the underlying limitations on etching resolution. Simulations are compared against experimental results, for validation and to understand experimentally observed features.

5:20pm **HI+NS+TR-ThA-10 Direct Write of Complex 3-Dimensional Structures with Helium Ion Microscopy***, **Matthew Burch**, A Ievlev,* Oak Ridge National Laboratory*; M Stanford, B Lewis,* University of Tennessee*; X Sang, S Kim, J Fowlkes,* Oak Ridge National Laboratory*; P Rack,* University of Tennessee*; R Unocic, A Belianinov, O Ovchinikova,* Oak Ridge National Laboratory

The next generation of computing, the generation which will follow the end of Moore's law, will need materials processing and interconnects that exist in 3-dimensions. This need has led to multiple investigations into the fabrication of complex free standing 3-dimensional structures onto any substrate at the nano-scale. Several techniques are currently being developed to fabricate free-standing micro- and nano- level structures including two-beam photon lithography and focused electron beam induced deposition (FEBID). Recent advancements in FEBID has led to the ability to simulate and subsequently fabricate complex 3D-platinum structures from an organometallic precursor.

In this work, we demonstrate the ability of the helium ion microscope (HIM) to fabricate complex 3-dimensional structures using focused ion beam deposition (FIBID) at scales smaller than previously demonstrated with FEBID. Using modern day image analytics we demonstrate a method we've successfully utilize to investigate and understand some of the most important structure-growth parameters with FIBID and how that parameter space impacts the size and morphology of created structures. These parameters include beam current, organometallic gas volume, dwell time, etc., and how these impact a grown structures length, width, and possible growth angles.

We further investigate the composition and crystalline nature utilizing scanning transmission electron microscopy (STEM) and electron energy loss spectroscopy (EELS) in the prescence of different carrier gasses of nitrogen and oxygen. We show, that in general the morphology and chemistry is nearly identical between the two gasses, that there is a slight difference in the apparent crystalline nature between the two flow gasses.

Finally, we demonstrate the minimum size structures currently grown with FIBID and the complex nature of the way these structures can be grown. We also demonstrate the HIM's unique ability to direct write structures repeatedly and reliably on non-conductive using the HIM's unique charge compensation mechanisms.

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