Nanometer-scale Science and Technology
Room 101D - Session NS-TuM

Nanodiamonds, Thin Films and Electronics (8:20–10:00 am)/Health and Environmental Impact of Nanotechnology (11:00 am–12:20 pm)

Moderators: Trevor Wiley, Lawrence Livermore National Laboratory, Leonidas Ocola, Argonne National Laboratory

8:00am **NS-TuM1 Formation of Dynamic Topographic Patterns during Electron Beam Induced Etching of Diamond**, ***Aiden Martin,*** Lawrence Livermore National Laboratory*; A. Bahm,* FEI Company*; J. Bishop, I. Aharonovich, M. Toth,* University of Technology, Sydney

Spontaneous formation of complex geometric patterns is an interesting phenomenon that provides fundamental insights into underlying roles of symmetry breaking, anisotropy and non-linear interactions. Here we present dynamic, highly ordered topographic patterns on the surface of diamond that span multiple length scales and have a symmetry controlled by the chemical species of a precursor gas used in electron beam induced etching (EBIE).

We provide an anisotropic etch rate kinetics model that fully explains the observed patterns, and reveals an electron energy transfer pathway that has been over-looked by existing EBIE theory. We therefore propose a fundamental modification, whereby the critical role of energetic electrons is to transfer energy to surface atoms of the solid rather than to surface-adsorbed precursor molecules.

EBIE is a high resolution, direct-write nanofabrication technique in which a precursor gas and an electron beam are used to realize etching. A key advantage of EBIE is the ability to etch materials such as diamond that are resistant to conventional chemical etch processes, without introducing damage to the substrate as observed in ion sputtering techniques. As a result, EBIE has recently been used to fabricate components for photonic and electronic applications. Our findings can be harnessed to engineer specific surface patterns under various electron beam irradiation environments for controlled wetting, optical structuring and other emerging applications that require nano and micro-scale surface texturing.

A portion of this work was funded by FEI Company and the Australian Research Council (Project Number DP140102721). A portion of this work was performed under the auspices of the U.S. DOE by LLNL under Contract DE-AC52-07NA27344. I.A. is the recipient of an Australian Research Council Discovery Early Career Research Award (Project Number DE130100592).

8:20am **NS-TuM2 Towards a Gold Standard in Single Digit Detonation Nanodiamond**, *N.J. Nunn, O.A. Shenderova, M. Torelli,* Adamas Nanotechnologies, Inc.*;* ***Gary McGuire,*** International Technology Center

Aggregates of detonation nanodiamond have long been of interest for their numerous potential applications; however, no size of detonation nanodiamond (DND) is perhaps more elusive, yet technologically important, than sub 10 nanometer (or “single-digit”) primary particles. Primary particles of DND have a number of potential applications including drug delivery, seeding in microelelctronics, polymer nanocomposites, and lubricants. Nevertheless, the challenge associated with obtaining these particle from the initial 200-300nm aggregates of purified detonation soot has made them too expensive for widespread use. Even after overcoming the initial challenge of obtaining the primary particles, they are still often limited in their use due to the assortment of chemical functional groups found on their surface. Therefore, an additional challenge is to tailor the surface chemistry of the particles without sacrificing their size by promoting re-aggregation. A final challenge is to identify useful solvents where stability and size of the functionalized particles are preserved. Here we report our work in obtaining high yields of 5nm particles of DND, progress made toward functionalizing these particles with a number of useful chemical structures including: carboxyl, hydroxyl, amine, hydrophobic chains and the dispersion of these particles in a range of solvents such as DMSO, NMP, DMF, THF, Ethylene Glycol, Synthetic Oils, alcohols, and water.

9:20am **NS-TuM5 Field Emission Electron Source Based on UltraNanoCrystalline Diamond Films for Electron Accelerators Applications**, *S. Baryshev, S. Antipov, C. Jing,* Euclid TechLabs LLC*;* ***Anirudha Sumant,*** Argonne National Laboratory

Currently, commercially available electron sources for electron accelerators are photocathodes or thermionic cathodes. Both types puts limits onto the resulting duty cycle of an accelerator and adds into increasing its complexity, as they require additional accessories (lasers, pulser compressors etc.). Cold cathode field emission technology based on low work function metals and other materials is an attractive alternative to simplify the electron injector, however, field emission current stability and processing challenges associated with formation of an atomically sharp tip for these field emitters makes it difficult to adopt this technology for accelerator applications

Nitrogen incorporated ultrananocrystalline diamond (N) UNCD films developed at Argonne National Laboratory have demonstrated its remarkable field emission properties. The unique structure of atomically abrupt nitrogen-incorporated grain boundaries provides field emission sites with very high field enhancement and therefore eliminates the need to make sharp nano-tips thus drastically reducing processing steps to fabricate field emission source. More specifically, it delivers significant currents at electric gradients as low as ~10^5 V/cm, which is far below typical breakdown thresholds in many materials (>~10^6 V/cm), and has turn-on voltages as low as 2-5×10^4 V/cm, and have shown excellent emission current stability for extended time periods up to 1000 hrs. Small grain size and a unique grain boundary network ensure more uniform emission properties over large areas and smaller current load per emitting site (i.e., per grain boundary). Taking advantage of these unique properties of (N)UNCD, Euclid TechLabs in collaboration with Argonne conducted a case performance study of a thin film planar (N)UNCD field emitter in an radio frequency(RF) 1.3 GHz electron gun in an electron accelerator. The field emission cathode was a 100 nm thick (N)UNCD film grown on a 20 mm cathode plug. At surface gradients 45-65 MV/m, peak currents of 1-80 mA (0.3-25 mA/cm^2) were achieved. Imaging with two YAG screens confirmed emission from the planar (N)UNCD surface with beam emittance of 1.5 mm×mrad/mm-rms and longitudinal FWHM energy spread of 0.7% at 2 MeV[1]. The same technology could be adopted for industrial and scientific linear accelerators, both normal-conducting and superconducting, for isotope production for radiopharmacy; X-/gamma-ray production for medicine, non-destructive evaluation, well-logging; and materials processing.

References:

[1] S. V. Baryshev et al., Appl. Phys. Lett. 105, 203505 (2014).

9:40am **NS-TuM6 Time-resolved Small Angle X-ray Scattering during the Formation of Detonation Nanodiamond**, ***Michael Bagge-Hansen,*** *M. Nielsen, L. Lauderbach, R. Hodgin, S. Bastea, L. Fried, D. Hansen, C. May,* Lawrence Livermore National Laboratory*; T. Graber,* Washington State University*; B.J. Jensen, R. Gustavsen, D. Dattelbaum, E. Watkins, M. Firestone,* Los Alamos National Laboratory*; J. Ilavsky,* Argonne National Laboratory*; T. van Buuren, T.M. Willey,* Lawrence Livermore National Laboratory

Most commercial nanodiamond originates from detonation of high explosives, particularly from RDX/TNT mixtures. Models suggest that the phase, crystallinity, and morphology of carbon is strongly dependent on the type of high explosive used and the exact evolution of temperature and pressure conditions during the very early stages of detonation; however, characterization of carbon condensation under the extreme conditions present at 100 ns timescales has been technically challenging. Using time-resolved, synchrotron-based small-angle x-ray scattering, we present a comparative survey of early time carbon condensation from three CHNO high explosives: HNS, Comp B (60% RDX, 40% TNT), and DNTF. We also extend this study to post-mortem TEM analysis of recovered carbon condensates. At later times, the size of particles extracted from SAXS compares favorably with our microscopy results. At early times, models predict that this array of explosives should provide graphitic, nanodiamond, and liquid carbon phases, respectively; our analysis of time resolved SAXS is remarkably consistent with these computational predictions.

This work was performed under the auspices of the US DOE by LLNL under Contract DE-AC52-07NA27344.

11:00am **NS-TuM10 Transformations and Biological Impact of Emerging Energy Storage Nanomaterials**, ***Robert Hamers,*** University of Wisconsin-Madison **INVITED**

The rapid increase in mobile electronics and electric vehicle technologies is leading to a rapid escalation in the use of complex oxides as cathode materials in the lithium-ion batteries that power these devices. Economic factors are driving a trend toward mixed-oxide materials such as $Li_xNi_yMn_zCo_{1-y-z}O_2$ (“NMC”) that combine high performance with low cost. However, these materials also incorporate substantial amounts of metals

such as Ni and Co that may post environmental risk, and there is not current any national infrastructure for recycling of these materials. We have been investigating the transformation of these emerging nanomaterials and the resulting biological impact as revealed through acute and chronic mortality studies and gene expression studies using *Shewanella oneidensis* and *Daphnia magna* as model organisms. Further molecular-level insights are provided by detailed investigations of NMC interactions with supported lipid bilayers. Our results show that this class of materials induces toxic effects through multiple pathways; with Shewanella with effects can be attributed almost exclusively to the redox dissolution of the NMC to form Ni^{2+} and Co^{2+} ions in solution; in contrast, ion-equivalent controls cannot reproduce the effects observed with *Daphnia magna*. These results highlight the need to develop a mechanistic understanding of the transformation of nanomaterials in the environment and the resulting impacts. Some perspectives on potential strategies for redesign to reduce adverse biological impact will be presented.

11:40am **NS-TuM12 Bio-inspired Nanosystems for Healthcare Applications***, **Elena Rozhkova**,* Argonne National Laboratory **INVITED**

Nanotechnology offers efficient solutions for virtually all areas of science and technology spanning from energy to healthcare technologies. Owing to rapid development of synthesis, nanofabrication and characterization techniques today we are able to engineer advanced hybrid nanosystems from scratch, at atomic and molecular scale, through controlled assembly of nanoparticles and molecules toward practical devices. Biological phenomena such as self-assembly, electron transfer, photosynthesis and enzyme catalysis, and magnetic field sensing have been a source of inspiration for engineers and scientists. We are using both nature's blueprints and biostructure building blocks for developing smart nano-bio hybrids and devices and then interface them with living systems of various levels of complexity towards advancing modern therapeutic, sensing, imaging and diagnostic methods.

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