

Wednesday Morning, October 20, 2010

Surface Science

Room: Santa Ana - Session SS2-WeM

Electron, Photon and Ion Beam Induced Surface Modification

Moderator: J.A. Yarmoff, University of California, Riverside

8:00am **SS2-WeM1 Focused Electron Beam Induced Processing: Experiments, Simulations, and Applications**, *P.D. Rack*, University of Tennessee **INVITED**

The rapid and precise direct-write growth of nanoscale features by electron-beam-induced deposition (EBID) and etching (EBIE) requires the optimization of the growth parameters to maintain nanoscale feature dimensions. The tremendous and complex EBID/EBIE parameter space includes the precursor gas pressure, primary electron beam energy, electron beam current, surface diffusion rates of adsorbed precursor species, thermal effects on desorption, and the cascade of electron species produced by elastic and inelastic scattering processes. These variables affect the probability of precursor dissociation and hence determine the feature growth velocity and the size of the structure through a series of complex, coupled nonlinear interactions. In this presentation, a variety of experimental studies will be presented to demonstrate the various electron-gas, gas-solid, and electron-solid interactions that are germane to the electron beam induced processing technique. A dynamic computer simulation based on Monte-Carlo calculation sequences will then be described and compared to various experimental observations. Finally, several nanoscale device applications will be demonstrated.

8:40am **SS2-WeM3 Electron Beam Deposition for Nanofabrication: Insights from Surface Science**, *H. Fairbrother*, Johns Hopkins University, *J. Wnuk*, Princeton University, *J. Gorham*, National Institute of Standards and Technology, *S. Rosenberg*, Johns Hopkins University, *C.W. Hagen*, TU Delft, the Netherlands, *W. van Dorp*, University of Groningen, the Netherlands

Electron beam induced deposition (EBID) is attracting increased interest as a single-step, direct-write process capable of depositing free standing, nanometer-sized structures with high spatial resolution (≈ 1 nm). However, the largest single limitation of EBID is that the deposited metallic nanostructures typically contain unacceptable levels of organic contamination which adversely affects the material's properties, thereby limiting potential applications. A more detailed understanding of the electron stimulated, decomposition of EBID precursors is needed to rationalize the relationships between organometallic ligand architecture and the composition of the deposits. Such mechanistic detail will allow greater control over the composition and function of nanostructures deposited by EBID while providing the necessary rational design criteria to fashion new organometallic precursors. Other scientific issues associated with EBID include a lack of quantitative information on the fundamental surface dynamics and deposition processes as well as overcoming the challenges of implementing successful purification strategies. The application of surface analytical techniques enables changes in the metal oxidation state, surface and gas phase composition as well as structure and chemical composition that accompany electron interactions with organometallic precursors to be studied *in situ* and in real time. In addition, I will describe how these various electron stimulated processes can be studied to extract data on reaction cross-sections and kinetics, information that would facilitate the development and testing of predictive models that can accurately describe EBID. Mechanistic insights into purification strategies that can be obtained through surface analytical techniques are also detailed. Throughout, I will discuss unresolved challenges and opportunities associated with EBID.

9:00am **SS2-WeM4 Multi-Electron Effects in Low Energy Sr^+ Ion Scattering**, *X. He*, *J.A. Yarmoff*, University of California, Riverside

A system of many electrons can display emergent phenomena that cannot be extrapolated from the behavior of independent electrons. Non-adiabatic resonant charge transfer is used to reveal this multi-electron behavior by employing singly charged alkaline earth ions in a low energy ion scattering experiment. The spin of the single valence electron of such an ion behaves as a magnetic impurity that interacts with the continuum of many-body excitations in the metal, resulting in Kondo and mixed valence resonances near the Fermi energy.^{1,2} The occupation of these resonances is acutely sensitive to changes of surface temperature, which leads to an anomalous temperature dependence of the ion neutralization probability. We report a maximum in the neutralization probability near 600 K for 2-4 keV Sr^+ ions

scattered from polycrystalline gold. Correlated electron effects, which have traditionally been manifest at low temperature, are observable well above room temperature because the projectile's ionization level shifts and crosses the target's Fermi energy as it approaches the surface where the interaction between the localized and extended electrons is very strong. This interaction becomes more pronounced as the work function of the surface is lowered by Sr implantation into the near-surface region. Further study will involve well-characterized single crystal surfaces that will enable detailed investigation of the relationships between the formation of correlated electron states and the atomic structure of the solid.

¹H. X. Shao, P. Nordlander, and D. C. Langreth, *Phys. Rev. Lett.* **77**, 948 (1996).

²J. Merino and J. B. Marston, *Phys. Rev. B* **58**, 6982 (1998).

9:20am **SS2-WeM5 Parallel Scanning Near-Field Photolithography: The Snomipede**, *E. ul Haq*, University of Sheffield, UK, *Z. Liu*, University of Nottingham, UK, *S. Alang Ahmad*, University of Sheffield, UK, *Y. Zhang*, University of Glasgow, Ireland, *L.S. Wong*, University of Manchester, UK, *J.K. Hobbs*, *G.J. Leggett*, University of Sheffield, UK, *J. Micklefield*, University of Manchester, UK, *C.J. Roberts*, University of Nottingham, UK, *J.M.R. Weaver*, University of Glasgow, UK

There has been enormous interest in the organisation of molecules at interfaces with nanometre spatial resolution, but important challenges still remain to be addressed. Of the established techniques, electron beam lithography is expensive, and requires exposure under vacuum, while scanning probe methods are slow and (with few exceptions) do not permit fabrication over large areas. Here, a new approach is described that yields arbitrary pattern fabrication over macroscopic areas. Scanning near-field photolithography enables the arbitrary fabrication of molecular structures as small as 9 nm ($\lambda/30$). We have developed a parallel near-field lithography device that fuses scanning near-field optical techniques with the 'Millipede' concept of massively parallel serial fabrication: a 'Snomipede'. Two Snomipede designs will be described, one based around the use of a liquid crystal spatial light modulator to direct diffraction-limited spots into an array of sixteen cantilevers with hollow, pyramidal tips, and the other based around the use of a Brewster angle zone plate, coupled to a digital mirror array, to direct the light spots. Their use for nanopatterning will be demonstrated by patterning siloxanes self-assembled monolayers formed from amino siloxanes molecules with a photocleavable protecting group. Structures with line widths of 100 nm have been formed in parallel over regions over 1 mm wide. Resulting structures have been derivatised with initiators for atom transfer radical polymerisation, from which biocompatible brushes have been grown. The potential of the Snomipede for reactive processing at the nanoscale will be demonstrated by fabricating 70 nm structures in photoresist using a probe array submerged under water.

9:40am **SS2-WeM6 Understanding the Effects of Radiation on the Cerium Oxide Thin Films by Experiment and Simulation**, *A. Kumar*, University of Central Florida, *V. Shuthanandan*, *R. Devanathan*, *S. Kuchibhatla*, *S. Thevuthasan*, Pacific Northwest National Laboratory, *S. Seal*, University of Central Florida

The damaging effect of radiation in applications such as immobilization of toxic radionuclides, fission and fusion reactors, and radiation therapy has attracted considerable scientific interest. The search for radiation tolerant materials has revealed that fluorite structural derivatives, such as zirconia and cerium oxide, have the ability to accommodate high energy radiation induced defects. Particularly for biomedical applications, cerium oxide is of more interest because not only it can prevent the damage from radiation but also it has the ability to quench free radicals and reactive oxygen species produced as the result of high energy radiation by regenerative switching between the +3 and +4 valence states of cerium. However the underlying mechanisms of radiation interaction and the resulting physicochemical and structural changes of cerium oxide are not well understood. In order to gain a fundamental understanding of radiation tolerance of cerium oxide nanostructures, we explored the behavior of single and polycrystalline ceria under radiation. High quality single and poly crystalline nanoceria thin films were grown on YSZ and sapphire respectively by using oxygen plasma assisted molecular beam epitaxy and exposed to 2 MeV He^+ radiation at fluences extending over three order of magnitude (10^{14} to 10^{17} ions/cm²) using the ion beam accelerator at EMSL, in Pacific Northwest National Laboratory. The chemical changes occurring in the thin films due to radiation exposure were characterized *in situ* by x-ray photoelectron spectroscopy (XPS). The experimentally observed changes in valence state were correlated by simulating the nanoceria thin film by molecular dynamics and studying the displacement cascades produced by cerium and oxygen as primary knock on atom. The structural evolution of nanoceria

thin films due to radiation exposure will be discussed in detail with implications for the use of cerium oxide as a radiation tolerant material.

10:40am SS2-WeM9 Methyl Radical Velocity Distributions from Ketone Photooxidation on TiO₂(110), D. Wilson, M. White, Stony Brook University

The velocity distributions of methyl radical desorption from a photoinduced reaction of three ketones (acetaldehyde, acetone, and acetophenone (coadsorbed with O₂)) on TiO₂(110) was studied to determine the mechanism of reaction for these model systems. The data was collected using a pump-probe Time-of-Flight (TOF) method. The firing delay time between pump (initiates surface chemistry) and probe (ionizes desorbing neutrals) can be varied over a wide time range to map the velocities of the desorbing methyl species. Excitation occurs using 3.7 eV photons followed by ionization using 13.05 eV photons. Differences in the velocity distributions are observed and potential explanations of these differences is explained.

11:00am SS2-WeM10 Laser Nitriding for Niobium Superconducting Radio-Frequency Accelerator Cavities, S. Singaravelu, Old Dominion University, J.M. Klopff, G. Krafft, Jefferson Lab, M.J. Kelley, College of William & Mary

Particle accelerators are a key tool for scientific research ranging from fundamental studies of matter to analytical studies at light sources. Cost-for-performance is critical, both in terms of initial capital outlay and ongoing operating expense, especially for electricity. It depends on the niobium superconducting radiofrequency (SRF) accelerator cavities at the heart of most of these machines.

Presently Nb SRF cavities operate near 1.9 K, well (*and expensively*) below the 4.2 K atmospheric boiling point of liquid He. Transforming the 40 nm thick active interior surface layer from Nb to delta NbN (T_c = 17 K instead of 9.2 K) appears to be a promising approach. Traditional furnace nitriding appears to have not been successful for this. Further, exposing a complete SRF cavity to the time-temperature history required for nitriding risks mechanical distortion.

Gas laser nitriding instead has been applied successfully to other metals [P.Schaaf, Prog. Mat. Sci. 47 (2002) 1]. The beam dimensions and thermal diffusion length permit modeling in one dimension to predict the time course of the surface temperature for a range of per-pulse energy densities. As with the earlier work, we chose conditions just sufficient for boiling as a reference point.

We used a Spectra Physics HIPPO nanosecond laser (l = 1064 nm, E_{max} = 0.392 mJ, beam spot @ 34 microns, PRF = 15 – 30 kHz) to obtain an incident fluence of 1.73 - 2.15 J/cm² for each laser pulse at the target. The target was a 50 mm diameter SRF-grade Nb disk maintained in a nitrogen atmosphere at a pressure of 550 – 625 torr and rotated at a constant speed of 9 rpm.

The materials were examined by scanning electron microscopy (SEM), electron probe microanalysis (EPMA) and x-ray diffraction (XRD). The SEM images show a sharp transition with fluence from a smooth, undulating topography to significant roughening, interpreted here as the onset of ablation. EPMA measurements of N/Nb atom ratio as a function of depth found a constant value to depths greater than the SRF active layer thickness. Certain irradiation conditions resulted in values consistent with formation of delta NbN. Under certain irradiation conditions, XRD data were consistent only with delta NbN on top of Nb metal.

Funding: authored by Jefferson Science Associates LLC under US DOE Contract De-AC05-06OR23177. We are indebted to Prof. P. Schaaf (Goettingen) for the simulation code and helpful discussions.

11:20am SS2-WeM11 A Model for the Hydroaffinity OH(1x1)-Si(100) and SiO₂ via Ion Beam Analysis (IBA), Tapping Mode Atomic Force Microscopy (TMAFM) and Surface Energy Analysis from Contact Angle Analysis, Q.B. Xing, N. Herbots, M.A. Hart, R.J. Culbertson, J.D. Bradley, Arizona State University

The hydroaffinity of Si-based surfaces is investigated as a function of surface defect density, topography and electrical carrier concentration via either doping and/or point defect concentration. Surface energy and the resulting hydrophobic or hydrophilic behavior of two surfaces of application for wafer bonding, OH(1x1)-Si(100) and beta-cristobalite SiO₂. A series samples are implanted with increasing doses, annealed to obtain a uniform dopant depth profile in the first 10 nm. Their electrical activation is measured via substitutional fraction detected by ion channeling and sheet resistance measurements.

A combination of ion channeling, 4.265 ± 0.035 MeV ¹²C(alpha, alpha;)¹²C, 3.05 ± 0.005 ¹⁶O(alpha, alpha)¹⁶O MeV Nuclear Resonance and 2.8 MeV Hydrogen Recoil Detection are used for high resolution compositional depth profiling of the first 10 nm of the surface. Tapping

Mode Atomic Force Microscopy (TMAFM) provides statistical analysis of the topography of these Si-based surfaces at a length scale ranging from a few nm to several μm. Extended atomic terraces with low edges and defects density on OH(1x1)Si(100) and crystalline silicates such as beta-cristobalite and alpha-quartz can render an insulating surface hydrophobic, while small scale roughness and surface defects makes it more hydrophilic. The water affinity and surface energy is measured using the Sessile Drop method and the Young-Dupré analysis as a function of topographical, compositional and micro-structural surface analysis using TMAFM, IBA combined with ion channeling and X-ray diffraction respectively. This correlation explains the behavior of water condensation at the liquid/air interface of intraocular implants during vitreoretinal surgery after cataract extraction and intraocular lens (IOL) implantation.

Polymer adsorption on surfaces alters their hydroaffinity, can control condensation on silicone IOL's [1] and enable for hermetic bonding in silica-based sensors in medical electronic implants [2]

[1] US Patent pending: "Molecular films for controlling hydrophobic, hydrophilic, optical, condensation and geometric properties of silicone implants surfaces, including intraocular lenses used in cataract surgeries." Inventor(s): N. Herbots, J. D. Bradley, M. Hart, D. A. Sell, S. Whaley, Q. Bradley (November 09, 2009)

[2] US Patent Pending: "Methods for Wafer Bonding, and for Nucleating Bonding Nanophases". Inventor(s): N. Herbots, J. D. Bradley, M. Hart, D. A. Sell, S. Whaley, R. J. Culbertson (April 30, 2010)

11:40am SS2-WeM12 UV Induced Work Function Changes of Metal Oxide Surfaces, M. Conrad, S. Gutmann, M.M. Beerbom, R. Schlaf, University of South Florida

The work function of a number of metal oxide thin films was measured using low intensity x-ray and ultraviolet photoemission spectroscopy (LIXPS, UPS).

Our experiments revealed that UPS based work function measurements of a variety of metal oxide surfaces previously exposed to the ambient or in contact with water vapor caused an immediate work function reduction of the order of 0.5 eV. This artifact was demonstrated using LIXPS work function measurements, which expose the sample surface to only a small fraction of the radiation flux encountered during UPS measurements. This enabled the measurement of the work function prior to the UPS characterization, revealing the UPS-related work function reduction. LIXPS measurement performed after the UPS measurements showed that sample charging effects can be ruled out as causes of the work function reduction, and that the work function change is permanent. These results suggest that a photochemical hydroxylation of the surface through photodissociation of water molecules occurs during the UPS measurement, which results in a surface dipole reducing the work function. Additional experiments investigated the influence of standard XPS measurements as well as LIXPS measurements on the work function. These experiments demonstrated that XPS measurements also cause a work function reduction similar to UPS measurements, albeit during a longer exposure time frame. In contrast, LIXPS measurements do not result in a significant work function reduction, i.e. can be used as a reliable work function characterization tool for oxide surfaces.

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