

Wednesday Morning, November 6, 2002

Nanometer Structures

Room: C-207 - Session NS-WeM

Nanostructured Materials

Moderator: W.N. Unertl, University of Maine

8:20am **NS-WeM1 Electronic Structure of Nitrogen Doped Ultrananocrystalline Diamond**, **J. Birrell**, University of Illinois at Urbana-Champaign, *O. Auciello, J.A. Carlisle, J.E. Gerbi, J.M. Gibson, D.M. Gruen*, Argonne National Laboratory

The local bonding structure of ultrananocrystalline diamond (UNCD) thin films synthesized using Ar/CH₄/N₂ microwave plasmas has been investigated using near-edge x-ray absorption fine structure (NEXAFS). These films exhibit a dramatic increase in electrical conductivity (up to 150 Ω⁻¹ cm⁻¹) as nitrogen gas is added to the plasma. Theoretical models predict that this is due to an increase in band gap states due to the presence of nitrogen at the grain boundaries. C 1s NEXAFS experiments have been performed to ascertain the ratio of sp²/sp³ bonded carbon in these films. It was found that, as nitrogen is added, the amount of sp²-bonded carbon increases by roughly %50 compared to the undoped films, but overall the films remain largely sp³-bonded. The sp³ σ* exciton, located at ~289 eV, diminishes in intensity, however, in spite of an observed increase in grain size with nitrogen content in the plasma. These results, as well as previous experiments using high resolution transmission electron microscopy, are used to explain the observed changes in the materials properties of nitrogen doped UNCD.

8:40am **NS-WeM2 Growth, Microstructure and Properties of Fullerene-Like Carbon Nitride Thin Solid Films Deposited by DC Magnetron Sputtering**, **Zs. Czigány**, *J. Neidhardt, I.F. Brunell, L. Hultman*, Linköping University, Sweden

Fullerene-like CN_x (x ≤ 0.2), as an inherently nanostructured material, were deposited as thin solid films by reactive magnetron sputtering of graphite in a nitrogen and argon discharge. The films were characterized by HRTEM, EELS, XPS and nanoindentation. Most fullerene allotrope synthesis is completed in the gas phase at high temperatures and the resulting material does not form a dense solid film. In comparison, the route to fullerene-like material presented here is by continuous surface nucleation and growth of curved basal planes at relatively low temperature. Plasma characterization revealed low flux of low energy species in the deposition flux with high portion of reactive complexes (e.g., CN, C₂N, C₂N₂). In the fullerene-like structures N substitutes for C and reduces the energy barrier to form pentagons in graphite sheets, thus inducing curvature of the basal planes. N also increases the reactivity of the neighboring C atoms, thus promoting sp³ cross-linking between C atoms in neighboring fullerene domains and provides solid CN_x films with high elasticity. TEM imaging of fullerene-like structures in a thin solid film form gives rise to difficulties compared to isolated fullerene features. Sample preparation methods for artefact-free specimens with thickness compatible with the characteristic feature size of fullerene-like domains will be discussed.

9:00am **NS-WeM3 Selective Oxidation of Faulted Halves of Si(111): (7x7) with Ozone**, **K. Miki**, NRI-AIST and NIMS, Japan, *T. Narushima, NRI-AIST, Japan, M. Kitajima, NIMS, Japan*

For nano-scale devices, an electronic isolation technique is desired since the working current is very small and therefore leakage through the substrate should be suppressed. In this paper we demonstrate a nano-scale selective reaction to realize this isolation technique. For this model case, we used an ozone radical to selectively oxidize one subunit of Si(111)-7x7. This surface has two different subunits; the faulted and unfaulted halves. Due to whether or not a stacking fault exists, the electronic states of the two halves differ, especially around 0.5 eV below Ef. This state is the backbond state of the adatoms. Therefore we could expect selective oxidation with some radicals on either the faulted or the unfaulted half. In conventional thermal oxidation, this possibility has already been denied, while ozone remains a possibility. We introduced highly concentrated ozone gas onto 7x7 reconstructed Si(111) surface in a UHV chamber in a split second. At room temperature, by means of scanning tunneling microscopy, it is found that the faulted sites are imaged as depressions at the sample bias of 0.8 V, but the other sites are mostly unchanged. This depression could be due to back bond oxidation. The reactive site of the oxygen changed with temperature, up to 873 K. As the substrate temperature increased, the chemical reaction selectivity disappeared. This may be due to diffusion of backbond oxygen atoms, which has a barrier height around 1eV. We intend to make 2.7 nm-size nano structure (unit size of 7x7) with atomic scale isolation of

backbond oxidation state. It is very useful because it does not involve processing at high temperature, which could induce damage, or disappearance, of nano structures.

9:20am **NS-WeM4 Dynamics of Br-Si(100)-(2x1): Surface Modification in the Absence of Desorption**, **E. Graugnard**, *G. Xu, V. Petrova, K.S. Nakayama, J.H. Weaver*, University of Illinois at Urbana-Champaign

The dynamics of surface modification of Si(100)-(2x1) with Br has been studied using variable temperature scanning tunneling microscopy (STM). A clean surface was saturated with Br at room temperature and then heated on the STM stage to 700 K, where no surface modification was expected. To our surprise, we found that the surface was, in fact, modified after heating for several hours. From sequential images of the same area, we were able to observe the formation and growth of novel defect structures, which consist of parallel atom vacancy lines separated by a single dimer row and could grow to be 120 nm in length. The formation of these vacancy lines was accompanied by Si adatom transfer onto the terrace, where regrowth dimers could form. The vacancy lines were often terminated at regrowth chains or dimer vacancy pits. We observed diffusion of regrowth features, but diffusion was limited to regions of the terrace where there were no vacancy structures. Thus, regrowth islands formed on defect-free areas of the terrace, and these islands limited the growth of the defect lines. As the surface roughened, the dynamics of the features became increasingly complicated with the atom vacancy lines converting into dimer vacancy lines and vice versa. The formation mechanisms and dynamics of these surface structures will be discussed.

9:40am **NS-WeM5 Surface, Bulk and Interfacial Analysis of Self-assembled Nano-phase Particle (SNAP) Films**, **L.S. Kasten**, AFRL/MLBT (UDRI), Wright-Patterson AFB, *V.N. Balbyshev, AFRL/MLBT (UTC), Wright-Patterson AFB, D.J. Gaspar*, Pacific Northwest National Laboratory, **M.S. Donley**, AFRL/MLBT, Wright-Patterson AFB

The chemistry, structure, and morphology of Self-assembled Nanophase Particle (SNAP) coatings were investigated using a variety of surface analysis methods. A new method of forming functionalized silica nanoparticles in-situ in an aqueous sol-gel process, and then crosslinking the nanoparticles to form a thin film, is an excellent example of a nanoscience approach to coatings. Results will be presented on the surface morphology, structure, surface chemistry, and chemical structure of SNAP films. The surface chemistry of the films was investigated using X-ray photoelectron spectroscopy (XPS), grazing angle XPS, and Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS). The surface morphology of films was examined using Atomic Force Microscopy (AFM), while X-ray Diffraction (XRD) was used to investigate film structure. The chemical structure and adhesion mechanism of SNAP coatings were also investigated via TOF-SIMS. Very little chemical difference between the outermost surface and bulk regions is seen, while the adhesion mechanism is related to the nature of the cross-linking agent. The results of these analyses will be discussed in detail and a model of the proposed chemical structure will be presented.

10:20am **NS-WeM7 Electronic Structure of Ag/Cu Striped Nanostructures**, **J. Lobo**, **E.G. Michel**, Universidad Autonoma de Madrid, Spain, *A. Bachmann*, Universitaet Osnabrueck, Germany, *S. Speller*, Katholieke Universiteit Nijmegen, The Netherlands, *L. Roca*, LURE-CNRS, France, *J. Kuntze, J.E. Ortega*, Donostia International Physics Center and Centro Mixto CSIC/UPV, Spain

The deposition of Ag on a stepped Cu surface gives rise to a periodic faceting of the surface.¹ The superstructure obtained is a very regular distribution of Cu and Ag stripes, with a lateral width in the range of 50-100 Å. The electronic band structure of this nanostructure has been studied using angle-resolved photoemission, for a range of Ag coverages between 0 and 1.2 ML. The photoemission experiments have been performed at the SU8 undulator beam line at LURE (Orsay, France). Surface states at Ag/Cu one-dimensional striped nanostructures are decoupled into Ag- and Cu-like stripe states. A model potential scaled from the infinite system explains the results. As a consequence, both Cu-like and Ag-like states display the characteristic periodicities of the corresponding facet plane. Furthermore, Cu-like stripe states exhibit the same terrace quantum-size effects observed in the infinite Cu(111) vicinal crystals.

¹ A. R. Bachmann, A. Mugarza, J. E. Ortega, and S. Speller, Phys. Rev. B 64, 153409 (2001).

10:40am **NS-WeM8 Patterned Anodization on Aluminum Surfaces, J. Yan, V. Goparaju, P. Atanasov, G. López, The University of New Mexico**

Nanoporous aluminum oxide (AAO), highly ordered arrays of uniform and straight pores with tunable features, can be formed through anodization of aluminum in an acid solution. Through-hole AAO membranes have recently been explored as an alternative to conventional lithographic techniques to achieve high resolution, to fabricate fine patterns over a large area, and to minimize costs. The inherent fragility of AAO membranes, however, limits their integration into established microfabrication process. To address this issue, we pre-patterned bulk aluminum sheets and vacuum-evaporated thin aluminum films on glass with silica through a sol-gel process or chemical vapor deposition. After a two-step anodization, we observed highly ordered, uniform and straight nanopores on uncovered areas, and no pores were observed for the covered areas after silica had been removed, thus providing intermittent aluminum supports to the fragile nanoporous AAO. This work allows facile incorporation of AAO in a robust form into microdevices for microelectronics, microfluidics and integrated optics.

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