Thursday Morning, October 23, 2008

Surface Science
Room: 207 - Session SS1-ThM

Growth and Etching on Surfaces
Moderator: A.A. Baski, Virginia Commonwealth University

8:00am **SS1-ThM1 Step Etching and Restructuring on Cl_2-exposed, Cl-saturated Si(001)-(2x1)**, ***R.E. Butera***, *J.H. Weaver*, University of Illinois at Urbana-Champaign

We use scanning tunneling microscopy and density functional theory to investigate the etching of rebonded step atoms and the concomitant restructuring of the B-type step for Cl_2-exposed, Cl-saturated Si(001)-(2x1) at 675 K ≤ T_S ≤ 725 K. Previous studies have shown that these exposure conditions allow uptake beyond "saturation," providing inserted Cl moieties, Cl_i, that lead to novel etching patterns without regrowth structures. Using surfaces with narrow terraces, we show that Cl_i diffuses to the rebonded S_B step and our calculations identify a stable adsorption configuration that bridges the rebonded and non-rebonded step atoms. Step etching removes the rebonded step atoms and results in the formation of an atom-wide vacancy line (AVL) along the step. Step restructuring begins with AVL diffusion into the terrace and ends with step retreat by one dimer unit to reestablish the rebonded S_B step structure. We use theory and experiment to show that restructuring is driven by the reduction of step energies and adsorbate-adsorbate repulsion. These results identify the rebonded step structure as the most energetically favored step structure on Cl-terminated Si(001)-(2x1).

8:20am **SS1-ThM2 Ion Scattering from Au Nanoclusters formed by Buffer Layer Assisted Growth**, ***S. Balaz***, *J.A. Yarmoff*, University of California, Riverside

Ion scattering is used to probe the atomic and electronic structure of Au nanocrystals grown by Buffer Layer Assister Growth (BLAG). Amorphous solid water (ASW) was adsorbed as a buffer layer onto SiO2/Si(111) at liquid nitrogen temperature. Au was then evaporated onto the buffer layer to form nanoclusters. The samples were subsequently annealed to room temperature, causing the water to desorb and the clusters to deposit directly onto the substrate. Time-of-flight (TOF) spectroscopy was used to measure 2 keV 7Li+ and 39K+ ions scattered from Au atoms both at low temperature when the clusters reside atop the buffer layer, and after desorbing the water. Small Au depositions yielded a sharp single scattering peak that indicates single layer structures. Following larger depositions, multiple scattering features were present indicating the formation of multilayer nanoclusters. The neutral fraction of scattered K+, which provides an indication of the filled quantum states, starts at ~50% for small Au coverages and decreases with further deposition, indicating changes in the quantum state occupancy with cluster size.

8:40am **SS1-ThM3 Competition Between Particle Formation and Burrowing: Gold on Bismuth**, ***P. Swaminathan***, *J.S. Palmer*, *J.H. Weaver*, University of Illinois at Urbana-Champaign

We discuss Au nanoparticle formation on Bi films under conditions where burrowing of the formed Au particles into the film is competitive to growth. Burrowing occurs because the surface free energy of Bi is lower than that of Au, the Au-Bi interface energy is small, and the kinetics, in terms of high surface and grain boundary diffusion rates, are favorable. The negligible solid solubility of Au in Bi at low temperatures means that alloy formation effects can be neglected. By changing deposition temperatures and rate, we show the effect of burrowing on the final size distribution. These results are supported by kinetic Monte Carlo simulations that include atom impingement, surface diffusion, and burrowing rates as parameters. Burrowing broadens and splits the size distribution as small particles are removed from the surface continuously and those that remain grow to larger sizes by adatom capture. These results are important for systems where nanostructures are assembled on low surface energy substrates, and they specify the conditions where growth is affected by burrowing.

9:00am **SS1-ThM4 Optical Anisotropy Induced by Oblique Incidence Ion Bombardment of Ag(001)**, ***H. Wormeester***, *F. Everts*, *B. Poelsema*, University of Twente, The Netherlands

Oblique incidence ion sputtering has become a widely used method for the creation of highly regular patterns of lines and dots. On a Ag(001) surface oblique incidence sputtering creates a ripple pattern that exhibits plasmonic features. The photon energy of this plasmonic feature depends on the ripple periodicity. The development of these anisotropic features is measured in-situ with the optical technique Reflection Anisotropy Spectroscopy (RAS). The ion induced nanopatterns are prepared using 2 keV Ar ions with a flux of a few Ma/cm^2 in a temperature range of 300 - 420K. With RAS, a periodicity of ripples above 200 nm is measured by a shift in photon energy of the plasmon resonance. Features with a smaller periodicity show a plasmon resonance around 3.65 Ev. For very grazing incidence sputtering, 80° polar angle of incidence, only a resonance feature around 3.65 Ev is observed. High resolution LEED measurements after sputtering confirm the formation of 1D nanoripples. For a polar angle of incidence of the ion beam of 70° a shift in the maximum of the plasmon resonance feature is observed. These spectra can be well described within the Rayleigh-Rice description for scattering from a slightly rough surface. The formation of nanoripples, i.e. a 1D roughening of the surface perpendicular to the direction of the ion beam, suffices to describe the measured optical data. The evolution of the rms, wavelength and wavelength distribution of the ion bombardment induced nanoripples is obtained from in-situ measurements. For a polar angle of the ion beam of 61° we find that also the roughening in the direction along the nanorippels has to be taken into account to describe the optical spectra.

9:20am **SS1-ThM5 Producing Ultraflat Si(100) Surfaces with Aqueous Etching: STM and FTIR Yield Mechanistic Insights**, ***M.A. Hines***, Cornell University **INVITED**

The production of atomically flat Si(100) surfaces is a long-standing technological challenge, as Si(100) is the basis for today's microelectronic devices. From a chemist's standpoint, the study of etch morphologies yields fascinating insights into surface chemistry, as etching reactions literally write a record of their reactivity on the etched surface. We use a combination of STM and vibrational spectroscopy to show that a simple aqueous etchant can produce Si(100) surfaces of surprising and unprecedented smoothness. The etched surface is characterized by long rows of H-terminated silicon atoms. This structure is favored because it minimizes interadsorbate repulsion on the surface. A new technique for the analysis of surface infrared absorption spectra[1] is used to deconvolute the well-known vibrational spectrum of the etched H/Si(100) surface. This analysis yields a relatively simple picture of the structure of the etched surface -- a picture that is much simpler and much smoother than previous analyses. The significant effects of interadsorbate strain on the spectrum will also be discussed. Finally, the influence of gas evolution on the mesoscale roughness of etched surfaces will be discussed. Again, the fascinating patterns that form during etching yield new insights into the chemistry of etching.

[1] I. T. Clark, B. S. Aldinger, A. Gupta, and M. A. Hines, J. Chem. Phys. 128, 144711 (2008).

10:40am **SS1-ThM9 Focused Ion Beam (FIB) Patterning and Selective Decomposition of III-V Semiconductors**, ***K.A. Grossklaus***, *J.M. Millunchick*, University of Michigan

The use of focused ion beams (FIB) has been identified as a method by which III-V substrates may be modified in a variety of ways for subsequent film growth. Presented here are the initial results of research exploring the use of FIB to modify III-V semiconductor surfaces and directly mill 3-D square array and hole patterns. Studies thus far have examined the FIB response of GaAs, InAs, and InP wafer substrates, along with AlAs layers grown on GaAs substrates. Each of these materials has been found to respond differently to the ion beam. Through use of the FIB to chemically decompose selected sample areas, group III nanostructures have been produced in patterned areas on InAs, GaAs, and InP, while AlAs has been shown to be resistant to metal nanostructure formation. The appearance and distribution of these nanostructures has been found to depend on the ion dose used for patterning. Nanostructure size and distribution on InP in particular has been shown to vary with ion dose and time from milling. It has been shown that ridge-like features act as preferential sites for the self-assembly, providing a method for the regular placement of metallic nanostructures. The causes for the different FIB response of each material will be discussed relative to their different material properties and predicted ion beam response. Proposed routes for controlling or eliminating the formation of group III nanostructures and the results of preliminary attempts to do so will be presented. The FIB patterning conditions and the patterns created thus far will be discussed in terms of their suitability for the creation of modified substrates upon which low defect density lattice mismatched films may be grown. As part of this additional patterning types and geometries for future examination and film growth experiments will also be discussed.

11:00am SS1-ThM10 Electron Induced Deposition of Amorphous Carbon Nitride Films

H. Fairbrother, *J.M. Gorham*, *J.D. Wnuk*, Johns Hopkins University

Nitrogen doped carbonaceous films have attracted intense experimental and theoretical interest due to the beneficial effects that nitrogen incorporation has on the wear resistance, adhesion characteristics and optical/electronic properties of amorphous carbonaceous films. Motivated by a desire (i) to understand the structure of amorphous carbon nitride films deposited by electron beam induced deposition (EBID) and (ii) to better understand the role that electrons play in moderating the microstructure and film growth of plasma deposited nitrogen doped carbonaceous films, we have studied the deposition of amorphous carbon nitride films from a 1,2-diaminopropane precursor molecule exposed to low energy (< 5keV) electrons. Our experimental approach involved initially depositing nanometer-scaled thin films of the precursor at low temperatures under ultra-high vacuum (UHV) conditions. The influence of electron irradiation on the chemical composition and bonding within the deposited film was then probed using reflection absorption infrared spectroscopy (RAIRS) in combination with x-ray photoelectron spectroscopy (XPS), while complementary data of the gas phase species evolved during electron irradiation were studied with mass spectrometry (MS). The electron stimulated decomposition of adsorbed 1,2-diaminopropane proceeded with the loss of both C-H and N-H bonds and the formation of an amorphous carbon nitride film. Upon more prolonged electron beam irradiation, nitrile ($C\equiv N$) species were formed. This observation suggests that electrons may play an important role in moderating the chemical structure of plasma deposited carbon nitride films. Hydrogen was the principal gas phase product evolved during film deposition. The loss of C-H and N-H bonds from the film, as well as the hydrogen evolution, were modeled by a first-order kinetic process with a rate constant that increases linearly with electron fluence. This information obtained under UHV conditions will also be compared with data obtained from the growth kinetics and structure of amorphous carbon nitride films grown using EBID of vapor phase 1,2-diaminopropane, studied using a combination of auger electron spectroscopy and atomic force microscopy. Results will also be presented on the role that the incident electron energy and the substrate exert in determining reaction rates and growth kinetics.

11:20am SS1-ThM11 Low Energy Electron Induced Decomposition of Adsorbed Methylcyclopentadienylplatinum(IV)-trimethyl

J.D. Wnuk, *J.M. Gorham*, Johns Hopkins University, *W.F. Van Dorp*, Rutgers, the State University of New Jersey, *C.W. Hagen*, Delft University of Technology, The Netherlands, *T.E. Madey*, Rutgers, the State University of New Jersey, *D.H. Fairbrother*, Johns Hopkins University

Electron beam induced deposition (EBID) of volatile organometallic precursors has emerged as an effective and versatile route to creating 2-D and 3-D metallic nanostructures. In an effort to better elucidate the process by which these structures are formed, we have studied the effect of low energy (500eV) electrons on sub-monolayer coverages of methylcyclopentadienylplatinum(IV)-trimethyl ($MeCpPtMe_3$) adsorbed onto gold substrates in situ under ultra-high vacuum conditions using a combination of mass spectrometry, reflection absorption infrared spectroscopy (RAIRS) and x-ray photoelectron spectroscopy (XPS). Electron beam irradiation produces a carbonaceous film that contains Pt atoms in an oxidation state which is intermediate between metallic Pt and the parent Pt(IV) species. XPS analysis of the Pt(4f) region indicates that the conversion of Pt species follows first order kinetics, with a rate constant proportional to the target current. Electron stimulated decomposition of adsorbed $MeCpPt(IV)Me_3$ is also accompanied by the evolution of gas phase methane and hydrogen as well as the loss of the C-H bonds associated with the parent $MeCpPt(IV)Me_3$ compound. The kinetics of methane and hydrogen production and the loss of C-H groups from the adsorbate layer can all be described by first order kinetics, with calculated reaction cross-sections comparable to the XPS-measured value. In conjunction, XPS, RAIRS and MS data suggests that a single electron event is responsible for decomposition of the parent compound and the formation of the platinum containing carbonaceous film. Electron beam irradiation also results in a reproducible change in the film's Pt/C ratio, whose magnitude is consistent with the idea that electron beam decomposition is initiated by a single $Pt\text{-}CH_3$ bond cleavage event. The average cross-section for the electron stimulated decomposition of adsorbed $MeCpPt(IV)Me_3$ via the different pathways at a specific electron beam energy of 500 eV is measured to be $1.5x10^{-16}$ cm^{-2}. Results from this study, carried out under well-defined reaction conditions where changes in the gas phase composition and the film's surface composition can be monitored simultaneously, provide new insights into the EBID process.

11:40am SS1-ThM12 A Study of the Surface Chemistry and Cross Sections for Electron Induced Dissociation using Temperature Programmed Desorption

W.F. Van Dorp, Delft University of Technology, The Netherlands, *S. Zalkind*, *B. Yakshinksiy*, *T.E. Madey*, Rutgers, the State University of New Jersey, *J.D. Wnuk*, *J.M. Gorham*, *H. Fairbrother*, Johns Hopkins University, *C.W. Hagen*, Delft University of Technology, The Netherlands

Electron beam-induced deposition (EBID) is a technique where adsorbed precursor molecules are dissociated by a focused beam of electrons to define metallic or semi-conducting patterns. Control over the process has developed to the extent that the amount of deposited material can be controlled (nearly) to the level of single molecules.[1] However, the purity of the deposits is not yet well controlled due to lack of knowledge of the precise nature of the precursor dissociation. Therefore, we study the adsorption behaviour of $(CH_3)_3\text{-}Pt\text{-}C_5H_4CH_3$ (a typical EBID precursor) and the dissociation cross section as a function of incident electron energy using Temperature Programmed Desorption (TPD).[2,3] TPD experiments using a Au(110) sample as substrate indicate that the first monolayer in contact with the substrate has a higher desorption temperature than condensed multilayers. The adsorption energy for the monolayer in contact with the Au is estimated to be 55 kJ/mol. The desorption behaviour in the first monolayer is first order and multilayers do not form until after the first monolayer has formed; the precursor desorbs molecularly. The precursor desorbs (nearly) completely below 0 °C. To study the adsorption behaviour in a condition more typical of an EBID experiment, we deposited a several nm thick carbon/Pt containing layer on the sample. TPD measurements using this "realistic" surface show that the desorption behaviour is similar to that on clean Au(110). The peaks have their maxima in the same range of temperatures, although the peaks are wider. Using this "realistic" C/Pt surface, we studied the effect of broad beam electron irradiation on the TPD spectrum of a single monolayer of precursor. As the total electron dose increases, the area under the TPD peak for m/z = 289 decreases. Cross sections for dissociation can be calculated from the reduction in the area under the TPD peak and are about 10^{-16} cm^2 for electron energies between 40 eV and 3 keV, comparable to those for electron induced dissociation in the gas phase.

---

[1] W.F. van Dorp, C.W. Hagen, P.A. Crozier, P. Kruit, Nanotechnology 19 (2008) 225305.

[2] N.S. Faradzhev, C.C. Perry, D.O. Kusmierek, D.H. Fairbrother, T.E. Madey, J. Chem. Phys. 121 (2004) 8547.

[3] C. C. Perry, N. S. Faradzhev, D. H. Fairbrother, T. E. Madey, Int. Rev. Phys. Chem. 23 (2004) 289.

Authors Index

Bold page numbers indicate the presenter