Prairie Chapter of the AVS 2004 Annual Meeting
14 June 2004, Monday
Frederick Seitz Materials Research Laboratory,
University of Illinois at Urbana-Champaign

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Midwest Tungsten Service

Session Coordinator: David Xu (gxu@uiuc.edu),
Dept. of Materials Science, MC 246, 1304 W. Green street, Univ. of Illinois, Urbana, IL 61801

Meeting Organizers
Dr. Suneel Kodambaka (kodambaka@mrl.uiuc.edu) & Dr. Timothy Spila (tspila@uiuc.edu)
Dept. of Materials Science and the Frederick Seitz Materials Research Laboratory
University of Illinois, Urbana, IL 61801
## Program Outline

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<td>2:00 PM</td>
<td>Xiangdong Qin, Notre Dame: Site-Selective Abstraction in the Reaction of 5- to 20-eV O+ with a Self-Assembled Monolayer</td>
<td>Saw-Wai Hla, Ohio, Invited Talk: STM Single Atom/Molecule Manipulation and Molecular Self-Assembly</td>
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<td>David Chopp, Northwestern, Invited Talk</td>
<td>Jessica Benson, Ohio: Low Temperature STM Manipulation and Spectroscopy of Single Chlorophyll-a Molecules from Spinach</td>
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<td>Violeta Iancu, Ohio: Molecular recognition, self-assembly and electronic structure of Co-TBrPP on Cu(111): An LT-STM study</td>
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<td>Guangjun Xu, UIUC: Si Epitaxial Growth on Br-Si(100): How Steric Repulsive Interactions Dictate Overlayer Development</td>
<td>Praneeth Edirisinghe, UIC: Single Photon Ionization of a Derivatized Peptide Covalently Bound to a Surface</td>
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<td>Sanjay Khare, UIUC: Dislocation-Driven Surface Dynamics on Solids</td>
<td>Rongping Deng, UIC: Characterization of Ethylidene and Methylidyne on Pt(111) with Infrared Spectroscopy</td>
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<td>4:00 PM</td>
<td>Michal Ondrejcek, UIUC: Surface diffusion on Au(111) studied by LEEM</td>
<td>Carrie Crot, UIC: Probing the Conformation of Hydrated Molecular Adsorbates on Solid Interfaces Using Long Period X-ray Standing Wave Fluorescence</td>
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<td>Boquan Li, UIUC: Dynamic observation of Ag nanostructures on Si (100) surfaces</td>
<td>Peter Albrecht, UIUC: STM and Spectroscopy of Single-walled Carbon Nanotubes Directly Interfaced with Silicon Surfaces</td>
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<td>G. Antczak, UIUC: Long Jumps in Surface Diffusion: Ir and W on W(110)</td>
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*** Awards for Best Posters ***
### Organic & Inorganic Thin Films

**Room: 1003 FS-MRL**

**Session Chair: Julio Soares, FS-MRL**

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INVITED TALK 8:30 AM

DEFECT DYNAMICS, COMPLIANCE, AND GUIDED ASSEMBLY OF ALIGNED NANOSCALE POLYMER DOMAINS IN CONFINEMENT

Steven J. Sibener*
The James Franck Institute and Department of Chemistry
The University of Chicago, 5640 South Ellis Avenue
Chicago, IL 60637

This talk will present issues pertaining to defect mobility and thermal annealing, spatial alignment, and the prospect for functional decoration of diblock copolymer surface structures. The first stage of this effort has demonstrated that atomic force microscopy imaging can be used in a time-lapse manner to track the interactions of topological defects. Combining rules for various dislocation and disclination pairs have been established [1]. Next, efforts have been focused on inducing spatial alignment in phase-separated cylinders, initially with PS-b-PMMA and now with PS-b-PEP. Strong polymer alignment has been realized in annular structures [2] and on intentionally constructed lithographically generated grating substrates having selected depths and widths which guide the assembly of highly-aligned polymeric interfaces [3]. Most recently, we have refined our methods and pursued a thermodynamic route (as opposed to a method based on kinetic control) in which silicon nitride grating substrates are used to template the alignment of ultra-high aspect ratio cylindrical polymer domains [4,5]. The mechanism of alignment involves nucleation by PS preferentially wetting the channel sidewalls and is extended throughout the film by defect annihilation. These structures are rather tolerant to imperfections in substrate lithography due to dimensional compliance. Future activities in selective decoration of these thin-film materials will also be discussed. This top-down/bottom-up hierarchical assembly methodology can be applied to hybrid hard/soft condensed matter systems for a variety of applications in, for example, electronics, magnetic systems, optics, and sensors.

*It is with pleasure that I acknowledge my collaborators Jong-in Hahm, Seth Darling, Deepak Sundrani, Qin Zheng, Nataliya Yufa, Dong-Chang Lee, Vladimir Belyi, and Professors Luping Yu, Heinrich Jaeger, and Tom Witten. It is a pleasure to acknowledge funding from the University of Chicago NSF-MRSEC and the University of Chicago-Argonne National Laboratory Consortium for Nanoscience Research, as well as the AFOSR for financing instrumentation development.


Contact info: s-sibener@uchicago.edu
Hyperthermal polyatomic ions have been used to deposit and modify a wide range of films. Cationic polymerization can induced at the gas-solid interface by ≤200 eV organic cations coincident on a surface with a thermal beam of organic monomers. This process, termed surface polymerization by ion assisted deposition (SPIAD), is used to produce a polythiophene film with terthiophene monomers and 100-200 eV thiophene ions on Si and indium tin oxide (ITO) substrates held under vacuum. Ion energy and ion to neutral ratio are varied to control film properties. Morphology has been so varied from well-organized lamellar grain to closely packed structure in films grown from mass-selected ions. Film photoluminescence is modulated in films produced from non-mass-selected ions. X-ray photoelectron spectroscopy shows an enhancement in film growth for SPIAD compared with either thiophene ion or terthiophene exposure alone. Mass spectrometry identifies multiple polythiophene species in the SPIAD film. Quartz crystal microbalance and infrared spectroscopy measurements are used to explain the overall role of ion energy and structure on the optical properties and growth rate of the film.


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9:30 AM: **Electronic Structure and Molecular Orientation of Conducting Polymer Films Produced via Surface Polymerization by Ion Assisted Deposition**

**S. Tepavcevic**, Y. Choi, M. Bissen, D. Wallace and L. Hanley

Department of Chemistry, University of Illinois at Chicago, Chicago, IL 60607-7061

Conducting polymer films are grown by mass-selected, hyperthermal organic cations coincident on a surface with a thermal beam of organic monomers, in a process termed surface polymerization by ion assisted deposition (SPIAD). SPIAD is applied here to create polymer films from thiophene ions and either α-terthiophene neutrals (3T SPIAD) or p-terphenyl neutrals (3P SPIAD). Mass spectrometry and x-ray photoelectron spectroscopy (XPS) verify the polymerization of both 3T and 3P SPIAD films. The electronic structure and molecular orientation of these films are probed by valence band XPS, ultraviolet photoelectron spectroscopy (UPS) and polarized near-edge x-ray absorption fine structure spectroscopy (NEXAFS). Valence band XPS and UPS of the 3T SPIAD films produced with 200 eV ions and an ion/neutral ratio 1/150 display similar spectral features as polythiophene films prepared electrochemically. A new state is observed 1 - 3 eV below the Fermi level in the 3T SPIAD film spectra which is not observed in films prepared by evaporation of 3T. This new state is attributed to an extended π bonding band along the conjugated aromatic chain of the polymerized 3T. Carbon K-edge NEXAFS probes the unoccupied π* and σ* bands of 3T SPIAD films which appear similar to those of the evaporated 3T film. Polarized NEXAFS show that the 3T SPIAD film is at least partially oriented with their molecular axes close to the normal of the substrate surface. The 3P SPIAD film prepared at 200 eV with an ion/neutral ratio 1/100 display more electron delocalization over the π bonding band compared with the 3P evaporated film. Polarized NEXAFS shows that as little or no orientation in the 3P SPIAD film, in contrast to the highly oriented 3P film.


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10:10 AM: **Effects of Sulfur Addition to Magnetron Sputtered a-C:H**

**Christina Freyman**, Northwestern University

Amorphous hydrogenated carbon films (a-C:H) have shown ultra low friction coefficients (μ<0.01) in dry nitrogen testing environments. The ultra low friction properties degrade with the addition of water vapor to the testing environment. In this work, we explore the effects of sulfur addition to magnetron sputtered a-C:H films on elastic modulus, hardness and tribological properties as a function of relative humidity in the testing environment. These studies show that with appropriate control of the film-substrate interface, sulfur addition of a few atomic percent is sufficient to reduce the adverse effect of humidity on friction.
The objective of this project is to monitor and control the growth process and the thermal stability of ultrathin tantalum nitride barrier nanostructures against copper diffusion in integrated circuits using real-time spectroscopic ellipsometry (RTSE). These studies are essential to transferability, scale-up, and reproducibility of new processes being developed to produce the next generation electronic nanodevices. Bilayer films of copper and tantalum nitride were produced using unbalanced magnetron sputtering. RTSE was used to monitor the growth of the film and obtain information about the interface regions based on effective medium approximations (EMAs) and a combined Drude-Lorentz model. Changes in the deposition rate and or refractive index were correlated to the growth mode of the material. Valuable information was deduced from analyzing the Drude term and includes information about microstructure, defect concentration, and the transport properties of conduction electrons. To verify the validity of the model architecture deduced from RTSE, the structural and chemical properties of the resulting films were characterized using X-Ray diffraction, Auger Electron Spectroscopy, and Rutherford Backscattering. The effectiveness of the diffusion barrier to stop the diffusion of copper into silicon was evaluated by annealing the bilayer samples up to 750 °C. RTSE was demonstrated to provide information about microstructural and phase transformations that occur during heat-treatments.

10:50 AM: UNDERSTANDING THICK DIELECTRIC FILMS: MOCVD (Ba$_{0.7}$Sr$_{0.3}$)Ti$_{1+y}$O$_{3+z}$ FILMS

S. Saha$^1$, D. Y. Kaufman$^2$, S. K. Streiffer$^3$, and O. Auciello$^3$

$^1$Materials Science Division and $^2$Energy Technology Division, Argonne National Laboratory, Argonne, IL

Despite significant progress over the last ten years, one of the outstanding issues in ferroelectric film science and technology is the lack of understanding of size and interface effects. While much of the effort in this area has concentrated on what happens as film thickness is reduced below 100nm, many applications require significant power-handling capability and thus film thicknesses approaching or even exceeding 1 μm. Interestingly, much can be learned concerning the behavior of film/electrode interfaces by exploring changes in behavior as film thickness is increased above twice the depletion length into this parameter range. With this framework in mind, we have investigated the leakage and dielectric properties of a thickness series (90-480 nm) of (100) fiber-textured MOCVD (Ba$_{0.7}$Sr$_{0.3}$)Ti$_{1+y}$O$_{3+z}$ (BST) thin films with well-controlled microstructure. The temperature and voltage dependencies of the permittivity were consistent with previous observations, where thinner films demonstrated a suppressed temperature and electric field response that transitioned to a more bulk-like response with increasing thickness. However, an unexpected positive temperature coefficient of resistance (PTCR) was observed in the leakage current behavior as film thickness was increased. To model the observed dielectric and leakage behavior, we have simulated the potential distribution in our films in a manner incorporating a temperature-dependent Landau-Ginzburg-Devonshire description of the nonlinear permittivity, along with considerations of space charge within the film and the image potential arising from the electrode/film contact. Our results clearly reveal an intrinsic contribution to the suppression of the dielectric constant in thinner BST films resulting solely from band-matching. The observed PTCR effect in our thicker films’ leakage behavior will be discussed in the light of the Schottky-Heywang model most widely used to explain PTCR behavior in bulk BaTiO$_3$ ceramics, with attention to how our films depart from that model. The implications of our results for the understanding of BST properties as a function of film thickness will be described.

11:10 AM: Integration of novel Cu-based electrodes with (Ba$_{x}$Sr$_{1-x}$)TiO$_3$ thin Films for application to high-frequency tunable devices


Argonne National Laboratory, Materials Science Division, Argonne, IL 60439

R.P.H. Chang

Northwestern University, Department of Materials Science and Engineering, Evanston, IL 60208*

R. Ramesh

University of Maryland, Department of Materials and Nuclear Engineering, College Park, MD 20742

Copper (Cu) has recently been introduced as an interconnect material in integrated sub-micron circuit technology, due to its low resistivity and high electro- and stress-migration resistance. The main problems inhibiting its application as electrode material in high-dielectric constant (κ) thin film based devices are the Cu oxidation and diffusion during the growth of the oxide layer at relatively high temperature in an oxygen-rich environment. To overcome the above problems, we have investigated the oxidation and diffusion resistance of heterostructured TiAl/Cu/Ta multilayers, which showed high
electrical conductance and excellent thermal stability in oxygen environment up to 600°C. Characterization of the layered structure using various analytical methods showed that two amorphous oxide layers were formed on both sides of the TiAl barrier after heating in oxygen, such that the oxide layer on the free surface of the TiAl layer correlates with a TiAlOₓ, while the oxide layer at the TiAl/Cu interface is an Al₂O₃-rich layer. This double amorphous barrier layer structure effectively prevents oxygen penetration towards the underlying Cu and Ta layers. Polycrystalline (BaₓSr₁₋ₓ)TiO₃ (BST) thin films were subsequently deposited on the Cu-based bottom electrode by RF magnetron sputtering to investigate the performance of BST/Cu-based capacitors for high-frequency devices. The thickness of the TiAl oxide layer and interface roughness play a critical role in the optimization of the electrical performance of the BST capacitors using Cu-based electrode. It was determined that low temperature (450°C) BST deposition followed by rapid thermal annealing (RTA) at 700°C in pure oxygen yield BST capacitors with Cu-based electrodes with good electrical properties for application to phase shifters and other high frequency devices. As a result, high permittivity (280), low dielectric loss (0.007), and low leakage current (<2×10⁻⁸ A/cm² at 100kV/cm) were achieved on the BST thin film capacitors using Cu-based electrodes.

* This work was supported by the US Department of Energy, BES-Materials Sciences, under Contract W-13-109-ENG-38; and NSF-MRSEC under Grant #DMR 00-80008 (University of Maryland).

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11:30 AM: In Situ TEM & Nanograind Gold

Khalid Hattar
University of Illinois

In situ transmission electron microscopy (TEM) has been used to study free-standing nanograind thin films produced by microlithography. This technique has allowed observation of the deformation and failure mechanism of nanograind gold, as well as grain growth and subsequent gold-silicon reaction. Additionally, a novel MEMS device has been fabricated that can accurately determine the stress-strain relationship of free-standing thin films during in situ TEM observation. The aim of this novel combination of MEMS and in situ TEM analysis is a better understanding of the deformation processes controlling mechanical properties of nanograind materials.

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### Nanoscale Processing & Devices

**Room: 280 FS-MRL**

**Session chair: Sanjay V. Khare, FS-MRL**

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INVITED TALK 8:50 AM

‘Soft’ Materials and Nanopatterning Techniques for Electronics

John Rogers
University of Illinois

Organic materials have a strong potential to play important roles in future electronic and photonic systems. Additive printing and lamination techniques can be used directly with these classes of ‘soft’ materials to fabricate unusual devices with dimensions deep into the nanometer regime. This talk describes the operational aspects of organic transistors and light emitting diodes that are built using these techniques with small molecule organics (single crystals and polycrystalline thin films), polymers and arrays of single walled carbon nanotubes as the active materials. It provides examples of working prototypes, such as flexible paperlike displays, that demonstrate some promising applications.
We are interested in using individual carbon nanotubes as the scaffold for chemical and biological sensing. To grow individual electrically-contacted carbon nanotubes, we use optical and electron-beam lithography to define electrical contacts, and then selectively deposit catalyst at the locations where nanotubes are desired. Using a home-built DC plasma-enhances CVD system, we can grow aligned carbon nanotubes at specified locations. By carefully controlling the conditions, it is possible to grow electrodes that are modified with individual carbon nanotubes. In order to characterize these individual nanotubes in an electrochemical cell, we protect the electrical contacts from the solution by using an electron beam patterned resist. This talk will describe our ongoing work in fabricating nanotube-based biological sensing systems.

10:10 AM: Spatially resolved electroluminescence from operating organic light-emitting diodes using conductive atomic force microscopy

L. S. C. Pingree, B. J. Scott, T. J. Marks, and M. C. Hersam
Department of Materials Science and Engineering, Northwestern University, Evanston, IL 60208-3108
http://www.hersam-group.northwestern.edu/

The advancement of materials characterization tools enables detailed studies of complex organic/inorganic systems at the nanoscale. The results of these studies subsequently allow improved materials development and process optimization. In this paper, organic light-emitting diodes (OLEDs) serve as a testbed to demonstrate the utility and the necessity of this strategy. The miniaturization of OLEDs, with potential applications in ultrahigh density displays and other novel optoelectronic devices, has placed an emphasis on the need to limit the effects of “dark spots” or non-emissive regions in the material. The effects of small non-emissive regions become enhanced as these devices decrease in size and can lead to significant device-to-device non-uniformities. To study this phenomenon and develop a strategy to limit its effects, we have developed an experimental approach for spatially mapping and correlating, with nanometer scale resolution, topology, current, quantum efficiency, and electroluminescence characteristics of operating OLEDs. Previous attempts to study light emission from these materials include the use of electroluminescence microscopy, near-field scanning optical microscopy, conductive atomic force microscopy (cAFM), and scanning tunneling microscopy. However, none of these techniques have previously been able to simultaneously probe topology, current-voltage response, and electroluminescence-voltage response of a functioning OLED device at the nanometer scale. By combining cAFM with light collection optics and a photomultiplier tube, our newly developed cAFM electroluminescence technique achieves this goal.

Both spectroscopic and spatial mapping data have been collected by our technique on 8 micron by 8 micron OLED pixel arrays. The spectroscopic data demonstrates the expected OLED behavior, with a turn on voltage of 7.5 V, initial detectable light emission at 9.5 V, and external quantum efficiency of 0.3%, which agrees with comparable millimeter scale OLED devices. In spatial mapping mode, simultaneous topography, current, and light emission images are acquired on the OLED pixel array at a fixed applied bias. These images illustrate clear spatial variations in the electroluminescence. Although the OLED pixels were fabricated simultaneously and nominally have the same structure, the magnitude of the current and the photon emission differs by up to 60% for neighboring OLEDs in a single array. One possible interpretation of these data is that dark spots have formed on the sub-10 micron length scale. Since the pixels with attenuated photon emission also show reduced current flow, the reduced photon emission cannot be solely attributed to a local reduction in external quantum efficiency, but rather to variations in growth conditions.

Besides device-to-device non-uniformities, clear response variations are observed within a given OLED, demonstrating enhanced performance characteristics upon the initial turn-on of the device. In this manner, our cAFM electroluminescence technique not only provides spatially dependent information but also time-dependent device behavior.

10:30 AM: A Cryogenic Variable Temperature Ultra-High Vacuum STM Optimized for Nanofabrication and Characterization of Individual Molecules on Silicon Surfaces

N. L. Yoder, E. T. Foley, N. P. Guisinger, and M. C. Hersam
Department of Materials Science and Engineering, Northwestern University
http://www.hersam-group.northwestern.edu/

A new cryogenic variable temperature ultra-high vacuum (UHV) scanning tunneling microscope (STM) has been designed and constructed. The cooling scheme consists of two gold-plated copper thermal shrouds that enclose the STM and the spring suspension stage [1]. The resulting isothermal environment allows the STM and the sample to be cooled down to a base temperature of 9 K. Variable temperature control up to 300 K is achieved through active heaters mounted on the roofs

8:30 AM: Fabrication and Characterization of Nanotube-based Sensing Elements

Sarah Baker, Matt Marcus, and Robert J. Hamers
University of Wisconsin-Madison

We are interested in using individual carbon nanotubes as the scaffold for chemical and biological sensing. To grow individual electrically-contacted carbon nanotubes, we use optical and electron-beam lithography to define electrical contacts, and then selectively deposit catalyst at the locations where nanotubes are desired. Using a home-built DC plasma-enhances CVD system, we can grow aligned carbon nanotubes at specified locations. By carefully controlling the conditions, it is possible to grow electrodes that are modified with individual carbon nanotubes. In order to characterize these individual nanotubes in an electrochemical cell, we protect the electrical contacts from the solution by using an electron beam patterned resist. This talk will describe our ongoing work in fabricating nanotube-based biological sensing systems.
of the thermal shrouds. The STM is based on a concentric piezotube design that is controlled with digital signal processor based feedback control electronics [2]. The STM and control electronics are optimized for differential tunneling conductance spectroscopy and atomically precise nanopatterning such as feedback controlled lithography [3]. Furthermore, the STM design allows for millimeter-scale coarse translation of the tip and the sample down to 9 K. The base temperature of the UHV chamber is 10⁻¹¹ Torr at room temperature, thus enabling atomically pristine imaging of reactive surfaces such as silicon.

In addition to the details of the instrument design, this paper will present initial data that confirms the overall system performance. In particular, degenerately doped Si(100) surfaces have been imaged at 300 K, 80 K, and 9 K with atomic resolution. Furthermore, feedback controlled lithography has been performed to create atomically precise templates of individual dangling bonds on the Si(100)-2×1:H surface. Preliminary spectroscopic data for isolated cyclopentene molecules on clean Si(100)-2×1 surfaces will also be discussed. At 80 K, isolated cyclopentene molecules show spatially resolved contrast in differential tunneling conductance images compared to the surrounding silicon substrate for sample biases between −2.5 V and −2.8 V. For voltages above and below this range, however, the molecules do not exhibit any differential tunneling conductance contrast with the background substrate. The paper will conclude by discussing the prospects of differential tunneling conductance imaging as a technique for performing chemical spectroscopy at the individual molecule level on silicon surfaces.

interfacial layers. At higher frequencies binding can be detected through a field effect induced in the diamond. The field effect mechanism allows us to directly detect biological molecules based on the different molecular charges. Complementary measurements on n-type and p-type silicon confirm the overall picture of the transduction process. Our results suggest the possibility of fabricating biological FET devices on diamond thin films.

11:10 AM: Molecular Monolayers on Single Crystal and Nanocrystalline Diamond Surfaces

Beth M. Nichols, James E. Butler, John N. Russell, Jr., and Robert J. Hamers
University of Wisconsin-Madison

The chemical stability and electronic properties of diamond make it an attractive substrate for chemical and biological sensing. Recent studies have demonstrated the ability to covalently functionalize nanocrystalline diamond surfaces with molecules bearing a terminal vinyl (C=CH) group via a photochemical process under ambient conditions. Here, we report studies of the properties of monolayer films formed on single-crystal diamond(111) and on polycrystalline diamond thin films by this process. XPS measurements on diamond(111) surfaces functionalized with molecules bearing a vinyl group at one end and a fluorine-protected amine group at the other show that the F/C ratio saturates after ~12 hours of reaction, suggesting a self-terminating monolayer. To prove that the molecules are aligned vertically on the surface, we measured the angular dependence of the apparent F/C ratio; this measurement shows that the F atoms are preferentially located at the exposed surface. We find that single-crystal and nanocrystalline samples have similar reaction rates, thereby eliminating the potential role of grain boundaries or graphitic impurities. To characterize the electronic properties, we measured valence-band photoemission spectra and work functions of clean, H-terminated, and molecularly-functionalized diamond(111) surfaces. Our results indicate that the molecular-modified samples have work functions comparable to the annealed, clean C(111) surface, and substantially higher than the H-terminated sample. We will discuss these results and the relationship between the chemical structure, electronic structure, and photochemical functionalization of diamond surfaces.

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<td>Tochko Tzvetkov, Notre Dame</td>
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<td>3:20 PM</td>
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<td>Si Epitaxial Growth on Br-Si(100): How Steric Repulsive Interactions Dictate Overlayer Development</td>
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<td>G. Antczak, UIUC</td>
<td>Long Jumps in Surface Diffusion: Ir and W on W(110)</td>
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INVITED TALK 2:40 PM

David Chopp
Engineering Sciences and Applied Mathematics Department,
Northwestern University, Evanston, IL 60208
The reaction of hyperthermal (5-20 eV) O$^+$ with alkanethiolate self-assembled monolayers (SAM) is studied under UHV conditions. To learn about the site-specificity to hydrogen abstraction in this system, we deposit SAM layers for which the hydrogen atoms located on the C-12, C-11, or C-10 positions of 1-dodecanethiol are substituted with deuterium atoms. By comparing the yields of OH to OD emerging from these three isotopomers, we find that hyperthermal O$^+$ initially abstracts only H(D)-atoms bound to the top two carbon atoms within the SAM layer. Continued bombardment with O$^+$ ions significantly disorders the structure of the SAM.

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**2:20 PM: Structural Damage of Self-Assembled Monolayers Induced by 5-eV O$^+$ Bombardment**

**T. Tzvetkov, X. Qin and D.C. Jacobs**  
Department of Chemistry and Biochemistry, University of Notre Dame

Self-Assembled Monolayers (SAM) of decanethiol/Au(111) are bombarded with 5-eV O$^+$ ions in UHV. XPS reveals that the carbon content of the SAM decreases, while the oxygen content increases with O$^+$ dose. STM images of ion-exposed and unexposed regions of the SAM are compared. The SAM layer exhibits greater disorder after only modest doses of 5-eV O$^+$ ions. Initially, ion-induced damage occurs predominantly near domain boundaries, surface steps, and vacancies. In contrast, large defect-free surface domains show considerable stability against 5-eV O$^+$ bombardment. A mechanism for degradation of the SAM by low-energy O$^+$ ions is proposed.

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**3:20 PM: Si Epitaxial Growth on Br-Si(100): How Steric Repulsive Interactions Dictate Overlayer Development**

**G. J. Xu** and J. H. Weaver  
Dept. of Materials Science and Frederick Seitz Materials Research Laboratory, University of Illinois, Urbana, IL 61801

Scanning tunneling microscopy results show the consequences of Si adatom deposition onto Br-saturated Si(100)-(2x1). Those adatoms undergo an exchange reaction with Br but they are immobile at room temperature. In the low coverage regime, annealing to 650 K leads to dimerization, limited ordering, and the formation of short Si chains. Adatom capture by those chains produces features of even and odd numbers of atoms. Annealing at 700 K eliminates the odd chains, but diffusion is highly constrained by Br site blocking. With increased Si coverage, there is further nucleation of chains and chain growth. The local patterning of the Si chains reveals the influence of the strong steric repulsive interactions of Br as out-of-phase structures were favored over in-phase structures around any given chain. Eventually, those interactions favor adlayer (3x2) patches rather than (2x1) islands. Second layer chains appear after the deposition of ~0.3 ML, with layer-2 nucleation at antiphase domain boundaries of layer-1. Bromine loss was observed, even at 650 K, and it is probably tied to the dynamics of atom exchange involved with Si diffusion on a saturated surface.

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**3:40 PM: Dislocation-Driven Surface Dynamics on Solids**

**S.V. Khare**, S. Kodambaka, J. Bareño, K. Ohmori, W. Święch, I. Petrov, and J.E. Greene  
Frederick Seitz Materials Research Laboratory and the Dept. of Materials Science, University of Illinois, Urbana, IL

Using low-energy electron microscopy, we investigate the near-equilibrium dynamics of surface-terminated dislocations. We observe, in real time, the thermally-driven (1500-1700 K) nucleation and shape-preserving growth of spiral steps rotating at constant temperature-dependent angular velocities (ω) around cores of dislocations terminating on TiN(111) in the absence of applied external stress or net mass change. We measure ω as a function of spiral geometry, Nω partial pressure, annealing time, and temperature. We find that ω is independent of the local environment and ambient, and decreases linearly with time. From the temperature-dependent ω data, we obtain an activation barrier of 4.9±0.3 eV for the growth of spirals. This phenomenon, attributed to point-defect migration from the bulk to the surface along dislocation lines, is both qualitatively and quantitatively different from step curvature-driven surface dynamics and "standard" Burton-Cabrera-Frank (BCF) spiral growth [Nature 429, 49 (2004)]. Our results demonstrate that dislocation-mediated surface roughening can occur even in the absence of deposition or evaporation, and provide fundamental insights into mechanisms controlling nanostructural stability. We expect that this process is general and that it occurs in other materials.
4:00 PM: Surface diffusion on Au(111) studied by LEEM

M. Ondrejcek, W. Swiech, M. Rajappan and C.P. Flynn
Department of Physics and Materials Research Laboratory, University of Illinois, Urbana, IL

We describe investigations of equilibrium step structure and step fluctuations on Au(111) in the temperature range 850-1270K using low energy electron microscopy (LEEM). From capillary wave analysis we obtained fluctuation amplitudes and relaxation times for Fourier components of the step edge displacement as functions of wave number $q$. We observe a crossover from surface to bulk diffusion phenomena which should occur in the step dynamics on most metal surfaces at sufficiently high temperatures. The relaxation rates $\tau(q)^{-1}$ at $\sim 0.65$ ps$^{-1}$ vary accurately with wavevector $q$ as $q^3$, showing that surface diffusion on the terraces drives. Bulk vacancy diffusion becomes the dominant relaxation mechanism at high temperatures with $\tau(q)^{-1} \sim q^2$. Surface mass (self) diffusion coefficient is obtained from the relaxation rates. The temperature dependence of the step stiffnesses determined as $\sim 0.15$ eV/nm for Au(111) along closed packed direction is very weak in the temperature interval measured. The quantitative results will be discussed and compared with values for other closed packed surfaces [1][2].

This research is supported by DOE grants DEFG02-02ER46011 and DEFG02-91-ER45439 through the Center for Microanalyses of Materials, University of Illinois.


e-mail: ondrejce@uic.edu

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4:20 PM: Dynamic observation of Ag nanostructures on Si (100) surfaces

B.Q. Li, W. Swiech and J.M. Zuo
Frederick Seitz Materials Research Laboratory and the Department of Materials Science, University of Illinois, 104 South Goodwin Avenue, Urbana, Illinois 61801

Understanding the mechanisms and kinetics involved in the growth and stability of metallic nanostructures formed on semiconductor surfaces is of fundamental importance in the burgeoning area of nanotechnology. Here we report on the growth dynamics and stability of Ag nanostructures on H-terminated-Si(100) surfaces investigated using real time low energy electron microscopy (LEEM) and transmission electron microscopy (TEM). Ag wires, typically 50 nm in width and several microns in length, can be formed under favorable deposition/annealing conditions. Dynamic LEEM observation demonstrates that the length of a Ag nanowire increases with the annealing time before saturation, at which the nearby Ag clusters are consumed. Further annealing results in the Ag wires to decay, predominantly along the wire direction, suggesting a detachment-limited decay mechanism. We also studied the competition between Ag wires and compact islands. Our results show that compact islands are more stable than wires. TEM study shows that the Ag nanowires grow along Si [110] or [1-10] direction. The epitaxial relationship is Ag(100)//Si(100) and Ag[011]//Si[011].

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4:40 PM: Long Jumps in Surface Diffusion: Ir and W on W(110)*

G. Antczak, G. Ehrlich
Materials Research Laboratory, University of Illinois at Urbana-Champaign

We have intensively investigated the migration of iridium and tungsten atoms on the W(110) surface using field ion microscopy. The basic single jump on such a surface proceeds between nearest-neighbor sites in the <111> directions. In our work we in addition consider three types of long jumps: double jumps in the <111> direction, vertical jumps in the <110> direction and horizontal jumps along the <100>. We measured the distribution of displacements at temperatures in the range 300-370 K; at each temperature at least 1200 observation were made. From a comparison of the experimental distribution with Monte Carlo simulations, we found that at temperatures higher than 340 K long jumps play a significant role in the surface diffusion of tungsten as well as of iridium adatoms. Occurrence of long jumps diminishes the role of single jumps, and at temperatures around 370 K long jumps start to play the leading role. A comparison of Ir and W results is presented and a model for diffusion is proposed.

* Supported by the Department of Energy under Grant No. DEFG02-96ER45439 to the Materials Research Laboratory, and by the Petroleum Research Fund, under Grant ACS PRF No. 36919-AC5.

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## Molecular Electronics & Spectroscopy

**Room: 280 FS-MRL**

**Session chair: Koji Nakayama, FS-MRL**

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<td>2:40 PM</td>
<td>Jessica Benson, Ohio: Low Temperature STM Manipulation and Spectroscopy of Single Chlorophyll-a Molecules from Spinach</td>
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<td>3:00 PM</td>
<td>Violeta Iancu, Ohio: Molecular recognition, self-assembly and electronic structure of Co-TBrPP on Cu(111): An LT-STM study</td>
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<td>Praneeth Edirisimghe, UIC: Single Photon Ionization of a Derivatized Peptide Covalently Bound to a Surface</td>
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<td>Carrie Crot, UIC: Probing the Conformation of Hydrated Molecular Adsorbates on Solid Interfaces Using Long Period X-ray Standing Wave Fluorescence</td>
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<tr>
<td>4:20 PM</td>
<td>Peter Albrecht, UIUC: STM and Spectroscopy of Single-walled Carbon Nanotubes Directly Interfaced with Silicon Surfaces</td>
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The fascinating advances in STM single atom/molecule manipulation allow scientists to fabricate artificial atomic-scale structures, to study local quantum phenomena or to probe physical/chemical properties of matter at a spatial limit [1]. Using a variety of cutting-edge STM single atom/molecule manipulation schemes in combination with single molecule conductance and vibrational tunneling spectroscopy measurements, we examine the mechanical stability, electronic properties and chemical reactivity of single molecules and self-assembled molecular films on metallic surfaces. Molecules of study include bio-nano molecules like chlorophyll-a, spin-active molecules like Co-TBPP and molecular wires like sexi-phenyl. The extraction of single atoms from the native substrate using the STM-tip and construction of various atomic scale structures on an atom-by-atom basis will also be presented by showing STM movies.

2:40 PM: Low Temperature STM Manipulation & Spectroscopy of Single Chlorophyll-a Molecules from Spinach

Jessica J. Benson, Violeta Iancu, Aparna Deshpande, Saw-Wai Hla
Quantitative Biology Institute, Physics and Astronomy Department, Ohio University, Athens, OH 45701, USA

Single chlorophyll-a, a molecule produced from ‘Spinach’, adsorbed on a Cu(111) surface has been investigated by using an ultra-high-vacuum low-temperature scanning-tunneling-microscope (UHV-LT-STM) at liquid helium temperatures. The tunneling I-V and dI/dV spectroscopy techniques are used to probe the electronic properties of the chlorophyll-a molecules. These spectroscopic investigations elucidate properties of the single molecule such as the band gap and additional molecular orbital states. Studies are carried out both on isolated single molecules and on self-assembled molecular layers. Mechanical stability of the chlorophyll-a molecule is examined by using lateral manipulation techniques with the STM tip (1). In this procedure, the STM tip is placed in close proximity to the molecule (just a few angstrom separation) to increase the tip-molecule interaction. Then the tip is laterally moved across the surface, which results in pulling of the chlorophyll-a molecule to relocate to the corresponding STM-tip height signals. Our results highlight that the Spinach molecule is mechanically stable and that it is a promising candidate for environmental friendly nano-electronic device applications.


3:00 PM: Molecular recognition, self-assembly & electronic structure of Co-TBrPP on Cu(111): A LT-STM study

Violeta Iancu, Aparna Deshpande, Saw-Wai Hla
Nanoscale and Quantum Phenomena Institute, Physics and Astronomy Department, Ohio University, Athens, OH-45701

Porphyrin based compounds are stable compounds that have been studied extensively lately for their potential applications as electronic components in memory or/and logic circuits. We have carried out a low temperature STM study on a porphyrin based molecule, 5,10,15,20-Tetrakis-(4-bromophenyl)-porphyrin-Co (II) (Co-TBrPP), adsorbed on a Cu(111) surface. Electronic and vibrational spectra of Co-TBrPP molecules and of their self-assembled layers have been determined by means of dI/dV and d²I/dV² tunneling spectroscopy (STS) at liquid helium temperatures. The conductance spectra reveal the position of both the occupied and unoccupied electronic levels in the molecule with respect to the Fermi level. Electronic properties of molecules are important for the design of new molecular electronic devices.

This work is financially supported by the US-DOE grant DE-FG02-02ER46012 and NSF-NIRT grant DMR-0304314.

3:20 PM: Single Photon Ionization of a Derivatized Peptide Covalently Bound to a Surface

Praneeth D. Edirisingle, Syed S. Lateef, Carrie Crot, and Luke Hanley
Department of Chemistry, University of Illinois at Chicago, Chicago, IL 60607-7061
Jerry F. Moore, Wallis F. Calaway, and Michael J. Pellin
Materials Science Division, Argonne National Laboratory, Argonne, IL 60439

Covalently bound peptides, proteins, and other biomolecules are widely used for microarrays, microfluidic channels, cell growth surfaces, and biosensors. Detection of these surface bound species by matrix assisted laser desorption ionization or secondary ion mass spectrometry (SIMS) is often complicated by low ionization yields and/or high fragmentation. Single photon ionization is one method that shows great promise for enhancing ionization yields with a minimum of fragmentation. The fluorine excimer laser is an intense laboratory source of vacuum ultraviolet radiation, but the 7.87 eV photons it generates are lower in energy than the ionization potential of many target species. A method is described here whereby derivatization of peptides with the Fmoc group allows efficient fluorine laser single photon ionization of the entire labeled peptide. Various Fmoc labeled peptides are covalently bound to oxidized Si(100) wafers via maleimide coupling to surface bound aminopropyltriethoxysilane. Physisorbed films of Fmoc labeled peptides, unlabelled peptides, and various amino acids are prepared by drying a solution thereof onto the silicon wafer. Both covalently bound and physisorbed peptides are analyzed by laser desorption photoionization (LDPI) mass spectrometry. Only the Fmoc labelled peptides form large ions identified as common peptide fragments bound to either Fmoc or the surface linker. Unlabelled peptides and amino acids do not form large representative ions. Electronic structure calculations performed with Gaussian 98 indicate the Fmoc label is behaving as an ionization tag for the entire peptide, lowering the ionization potential of the complex below the 7.87 eV photon energy. This method should allow detection of many molecular species covalently or electrostatically bound to surfaces.
An ultrahigh-vacuum scanning tunneling microscope (UHV-STM) is used to elucidate the fundamental electronic properties and chemical interactions intrinsic to single-walled carbon nanotubes (SWNTs) directly interfaced with silicon surfaces. Atomically-resolved topographic imaging, combined with local density of states (LDOS) information ascertained by scanning tunneling spectroscopy (STS), make the UHV-STM an ideal instrument for correlating atomistic structural features and chemical phenomena with their electronic signatures. We have developed a novel UHV dry contact transfer (DCT) technique to fabricate an atomically pristine interface between SWNTs and silicon [1], circumventing the need for ambient solution-based deposition of SWNTs. All of our experiments to date suggest that the UHV DCT scheme results in
the transfer of predominantly isolated SWNTs, rather than cumbersome bundles or catalyst particles, to the silicon surface. This fortuitous outcome enables sensitive STM measurements that are unperturbed by tube-tube interactions arising within a rope.

Results to be presented include UHV-STM topographic and current images conveying simultaneous atomic resolution of SWNTs and the proximal Si substrate. Figure 1 shows a 10×10 nm² STM topograph rendered in three dimensions. Furthermore, STS is able to identify spectroscopic features corresponding to both semiconducting and metallic SWNTs inside of the substrate band gap [1]. We will report on new results from Current Image Tunneling Spectroscopy (CITS), where a dI/dV-V characteristic is measured at each pixel of a topographic image to generate real-space maps of the electronic structure of the hybrid SWNT/Si surface.

The H-terminated Si(100) surface lends itself to nanolithographic patterning via the atomically-precise desorption of H by the STM tip [2,3]. One can then exploit the chemical contrast between the highly reactive Si dangling bonds and the relatively inert H-passivated background to engineer the local environment at an arbitrary position along the SWNT. The 30×30 nm² STM topograph presented as Fig. 2(a) shows a ~4-nm-wide, ~25-nm-long stripe of depassivated Si intercepting an isolated SWNT [4]. Patterning conditions (+7 V sample bias, 0.1 nA, 10⁻¹¹ C/nm dose) were not interrupted when the electron current intercepted the adsorbed SWNT approximately halfway through the nanolithography routine. The atomic corrugation of the SWNT lattice is noticeably enhanced within the section in close proximity to the patterned Si dangling bonds, clearly elucidated by the 22×22 nm² STM topograph shown as Fig. 2(b). CITS may provide significant insight into local changes in the chemical and electronic interactions at the SWNT/Si interface (e.g., a transition from physisorption to chemisorption). Maltezopoulos and coworkers have recently observed confined states in extended metallic SWNTs on Au/mica surfaces, which they attribute to backscattering by impurities and/or defect sites [5]. This suggests the possibility for templating spatially-localized electronic states along the length of a SWNT adsorbed onto Si(100)-2×1:H by the selective desorption of H.

We will also present detailed STM topographic and spectroscopic data for SWNTs on clean Si(100) and formulate comparisons with previous data obtained for SWNTs on H-passivated Si(100). Orellana et al. have performed first-principles density functional calculations for a metallic (6,6) SWNT adsorbed onto a clean Si(100) surface [6]. They propose the formation of C-Si chemical bonds for stable geometries where the SWNT is aligned between two consecutive dimer rows, with a corresponding enhancement in the SWNT DOS near the Fermi level.

Our UHV-STM investigation is motivated by the technological relevance of the Si(100) substrate and the nanofabrication of hybrid SWNT-Si devices and interconnects. A recent report by Tseng and coworkers on the monolithic integration of SWNT three-terminal devices with Si metal-oxide-semiconductor (MOS) circuitry [7] emphasizes the feasibility of this approach, and atomic-scale UHV-STM characterization will serve to further promote this hybrid nanotechnology. Moreover, UHV DCT has been extended to the in situ transfer of SWNTs to cleaved GaAs(110), a surface that is incompatible with ambient exposure [8].

POSTER SESSION
Venue: FS-MRL 2nd floor interpass
12 Noon – 2:00 PM

1. Graphite Oxidation by Hyperthermal O(3P) Atoms: Morphologically Enhanced Surface Kinetics in Deep Cylindrical Pits -- Kenneth Nicholson, U of C


3. Si Epitaxial Growth on Br-Si(100): How Steric Repulsive Interactions Dictate Overlayer Development -- Guangjun Xu, UIUC


5. Surface Stress on Solid-Liquid Interfaces -- Xijing Zhang, UIUC

6. Electrical Characterization of Silicon and Diamond Surfaces Functionalized with Organic Monolayers -- Kiu-Yuen Tse, Wisconsin


8. Kinetic Monte Carlo Simulations of the Growth of Nanoscale Metal Clusters by Electrodeposition -- Tim Drews, UIUC

9. Multiscale Systems Engineering with Applications to Chemical Reaction Processes -- Effendi Rusli, UIUC

10. Characterization of Medium Range Order in a-Si thin films using Fluctuation Electron Microscopy -- Lakshminarayana Nittal, UIUC

11. Fabrication of Isolated Arrays of Single-Walled Carbon Nanotubes using Dry Contact Transfer -- Kyle Ritter, UIUC

12. Fabrication of high-aspect-ratio microchannels by using fast-etching metal sacrificial layer -- Zhiliang Wan, UIC

13. Fabrication and Testing of Metal-Insulator-Metal Devices -- Annette Raigoza, Notre Dame

14. Fabrication and Electrochemical Response of Nanoscale Gold Electrodes -- Kevin Metz, Wisconsin

15. Focus Ion Beam Patterning of Transparent Oxide Substrates for Epitaxial Assembly of Colloidal Crystal -- Ryan Kershner, UIUC

16. Directed Self-Assembly of Ge Nanostructures on Very High Index, Highly Anisotropic Si(hkl) Surfaces -- Kenji Ohmori, UIUC

17. Strained SiGe alloy instabilities on laser textured Si(001): Effects of growth rates and vicinality -- Fumiya Watanabe, UIUC

18. Biomagnetic sensor based on Brownian relaxation of magnetic nanoparticles -- Seok-Hwan Chung, Argonne

19. Chromium Diboride Thin Films by CVD -- Emily Klein, UIUC

20. Macrotecture and growth chemistry in ultrananocrystalline diamond thin films -- Jennifer Gerbi, Argonne

21. Au Nanowire bio-modification and nanowire bridge formation -- Lu Shang, Wisconsin
The surface morphology derived from the anisotropic surface reaction kinetics of highly-ordered pyrolytic graphite (HOPG) with ground-state hyperthermal atomic oxygen is described. The reaction rate and surface morphology exhibit a profound dependence on sample temperature. Upon oxidation at modest temperatures (298-423 K), numerous nanoscale to microscale cylindrical pits embedded in the eroded areas of HOPG have been observed using atomic force microscopy (AFM) and scanning tunneling microscopy (STM). The most striking characteristic of these cylinders is the deepest point is at the peripheral edge of the base. Since lateral erosion ($k_{pim}$) is fast, the base curvature quickens the overall deepening of these cylinders by exposing additional prism carbon atoms for chemical reaction. In other words, the cylinders are further deepened, with respect to the rest of the reacted HOPG surface, from the periphery inward after the initial nucleation event. The reaction rates for horizontal etching, $k_{pim}$, and for reactivity at the peripheral edge of the base, $k_{periphery}$, have been determined and have also been found to follow the Arrhenius formalism for sample temperature dependence. At higher sample temperatures, these cylindrical pits are no longer observed in the surface morphology. Instead, a rough matted surface is imaged that contains towers or “hillocks” on the order of hundreds of nanometers in height. This morphological shift is commensurate with a tripling of the overall reaction rate upon raising the sample temperature from 298 to 493 K.

The local patterning of the Si chains reveals the influence of the strong steric repulsive interactions of Br as out-of-phase structures were favored over in-phase structures around any given chain. Eventually, those interactions favor adlayer (3x2) patches rather than (2x1) islands. Second layer chains appear after the deposition of ~0.3 ML, with layer-2 nucleation at antiphase domain boundaries of layer-1. Bromine loss was observed, even at 650 K, and it is probably tied to the dynamics of atom exchange involved with Si diffusion on a saturated surface.
P4: Low-Energy Electron Microscopy Studies of Interlayer Mass Transport Kinetics on TiN(111)

J. Bareño, S. Kodambaka, Navot Israeli, W. Święch, Kenji Ohmori, I. Petrov, and J.E. Greene
Dept. of Materials Science and the Frederick Seitz Materials Research Laboratory, University of Illinois, Urbana, IL
Department of Physics, University of Illinois, 1110 West Green St., Urbana, IL

In situ low-energy electron microscopy was used to study interlayer mass transport kinetics during annealing of three-dimensional (3D) TiN(111) mounds, consisting of stacked 2D islands, at temperatures T between 1550 and 1700 K. At each T, the islands decay at a constant rate, irrespective of their initial position in the mounds, indicating that mass is not conserved locally. From temperature-dependent island decay rates, we obtain an activation energy of 2.8±0.3 eV. This is consistent with the detachment-limited decay of 2D TiN islands on atomically-flat TiN(111) terraces [Phys. Rev. Lett. 89, 176102 (2002)], but significantly smaller than the value, 4.5±0.2 eV, obtained for bulk-diffusion-limited spiral step growth [Nature 429, 49 (2004)]. We model the process based upon step flow, while accounting for step-step interactions, step permeability, and bulk mass transport. The results show that TiN(111) steps are highly permeable and exhibit strong repulsive temperature-dependent step-step interactions that vary between 0.03 and 0.76 eV-A. The rate-limiting process controlling TiN(111) mound decay is surface, rather than bulk, diffusion in the detachment-limited regime.

P5: Electrical Characterization of Silicon and Diamond Surfaces Functionalized with Organic Monolayers

Kiu-Yuen Tse, Wenshao Yang, and Robert J. Hamers
University of Wisconsin-Madison

Recent studies have shown that semiconductor surfaces such as silicon and diamond can be functionalized with organic monolayers, and these monolayer films can be used to tether biomolecules such as DNA to the diamond surfaces. Electrical measurements of these interfaces show a change in response to DNA hybridization and other biological binding processes, but the fundamental nature of the electrical signal transduction has remained unclear. We have explored the electrical impedance of silicon and diamond surfaces modified with simple organic molecules such as dodecene. Our results show that by measuring the impedance as a function of frequency and potential, it is possible to dissect the complex interfacial structure into simpler equivalent circuits. The results have implications for understanding the ability to use molecularly-modified semiconductor surfaces for bio-electronic sensing.

P6: Kinetic Monte Carlo Simulations of the Growth of Nanoscale Metal Clusters by Electrodeposition

Timothy O. Drews, Richard D. Braatz, and Richard C. Alkire
Dept. of Chemical and Biomolecular Engineering, University of Illinois at Urbana-Champaign

Kinetic Monte Carlo (KMC) simulations have the potential to predict the operating conditions that result in nanometer-sized zero-dimensional metal clusters with a controlled size distribution. Here simulations are performed with a 2+1 dimensional KMC simulation code that has a FCC lattice as the underlying substrate. Ten-atom metal clusters are templated onto the substrate and KMC simulations are used to predict the evolution of the surface morphology under various electrodeposition conditions. The number of templated clusters, the applied potential, and the metal-substrate surface diffusion energy barrier were varied in the simulations. When 16 or fewer nuclei are templated evenly across a 300×300 lattice, the cluster distribution is dominated by secondary nuclei formed during deposition. For substrates with a metal-substrate surface diffusion energy barrier greater than 3.5×10⁻²⁰ J, it is more difficult to control the cluster size distribution. It is shown that at low applied potentials it is possible to grow larger nuclei with a more controlled size distribution. Moreover, it is shown that larger clusters with a more controlled size distribution can be grown when more clusters are templated evenly onto the surface.

P7: Multiscale Systems Engineering with Applications to Chemical Reaction Processes

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New applications in materials, medicine, and computers are being discovered where the control of events at the molecular and nanoscopic scales is critical to product quality, although the primary manipulation of these events during processing occurs at macroscopic length scales. This motivates the creation of tools for the engineering of multiscale reacting systems that have length scales ranging from the atomistic to the macroscopic. This paper describes a systematic approach that consists of stochastic parameter sensitivity analysis, Bayesian parameter estimation applied to ab initio calculations and experimental data, model-based experimental design, hypothesis mechanism selection, and multistep optimization.
Creating ordered arrays of single-walled carbon nanotubes (SWNTs) is critical for the realization of integrated carbon nanotube-based electronics. Utilizing a novel dry deposition technique developed for imaging SWNTs with scanning tunneling microscopy (STM), aligned SWNTs have been observed on the Si(100) surface by using atomic-force microscopy (AFM) in ambient conditions. Dry contact transfer (DCT) is first performed in the STM chamber under ultrahigh-vacuum (UHV), where solid phase HiPco SWNTs are deposited onto pristine UHV-prepared Si(100)-2x1:H surfaces [1]. A fiberglass applicator uniformly coated with SWNTs is brought into gentle mechanical contact with the Si sample, delivering predominantly individual SWNTs to the surface with minimal contaminants (catalysts and carbon residue).

After removal from UHV, large area AFM scans show that the SWNTs exist almost entirely in the form of aligned arrays. The AFM tip has been used to manipulate the SWNTs to verify that the aligned features are not applicator induced defects. DCT can be generalized to printing SWNTs in ambient conditions, using different applicator materials, and substrates. In addition to observing aligned arrays with AFM from UHV prepared samples using fiberglass applicators, ambient depositions on Si(100) using a piece of a cotton sock yield identical aligned arrays. In addition, the DCT technique can be extended to transferring isolated SWNTs to the cleaved GaAs(110) surface[2]. The mechanisms underlying these observations will be discussed by using scanning electron microscopy to image the DCT process. Current experiments include using AFM and STM to characterize SWNTs on different surfaces, as well as to studying the effect of changing different variables in the dry transfer process.


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**P10: Fabrication and Electrochemical Response of Nanoscale Gold Electrodes**

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As a step along the development of nano-bioelectronic sensing systems, we have explored the fabrication of nanoscale gold electrodes and their electrical response. Gold-nanoelectrodes were fabricated using electron-beam lithography to define small pores in photore sist, followed by electrochemical reduction of gold into the pore. By controlling the deposition conditions, it is possible to fabricate gold nanoelectrodes that protrude from the photoresist to form small nano-stubs. Measurements of the electrochemical oxidation-reduction current when bare gold nanoelectrodes are immersed in solutions containing Ru+2/Ru+3 as a redox couple show diffusion-limited behavior. This poster will present our recent work on fabricating and characterizing the electrical response of gold nanoelectrodes.

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**P11: Focused Ion Beam Patternning of Transparent Oxide Substrates for Epitaxial Assembly of Colloidal Crystals**

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Direct writing with a focused ion beam (FIB) was used to generate 2-D square arrays of dimpled features in transparent oxide substrates. These periodic patterns were created with well controlled hole diameter and depth at a pitch of 500 nm (~colloid diameter) to guide the epitaxial assembly of colloidal crystals. In the absence of precise FIB calibration, large variations between the targeted and actual pitch (500 ± 100 nm) were observed for the patterns generated. This degree of control is not suitable for colloidal templating, since size variations of less than 5% of the colloid diameter are required for
crystallization. Through an iterative FIB calibration involving the use of an internal standard, the pattern reproducibility was improved by an order of magnitude, such that a substrate pitch of 500 ± 10 nm was achieved. The effects of ion beam current, beam dwell time, and total milling time on the resulting patterned features were systematically studied. Atomic force microscopy (AFM) was carried out on as-patterned and etched substrates to quantify their uniformity and characteristic feature sizes. By etching, we can generate smooth, enlarged dimpled features free of remnant debris produced during the milling process. Experiments are now underway to explore the epitaxial assembly of colloidal microspheres during gravity-driven sedimentation on these patterned substrates.

P12: Directed Self-Assembly of Ge Nanostructures on Very High Index, Highly Anisotropic Si(hkl) Surfaces

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Families of very high-index planes, such as those composed of (1 1 3) and (1 5 7) facets in a Si(hkl) hill-and-valley structure, provide natural templates for the directed growth of uniformly spaced position-controlled self-organized nanostructures with shapes, under the same deposition conditions, ranging from anisotropic domes to triangles to teardrops to one-dimensional wires. The ridgeline formed by the intersection of (1 1 3) and (1 5 7) facets corresponds to the [2 1 1] direction and all (1 k 2k) planes, in which -5 < k < 1, obtained by rotating (1 5 7) toward (1 1 3) about the [2 1 1] axis will form a hill-and-valley structure with varying ratios R of (1 1 3) to (1 5 7) facet widths. As an example, we show that with R = 1.7 corresponding to Si(100 173 384), a field of Ge nanowires, 40-nm-wide with a uniform period of 61 nm, grows in a directed fashion along [1 8 7 72 81].

P13: Strained SiGe alloy instabilities on laser textured Si(001): Effects of growth rates and vicinality

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A combinatorial study of strained layer growth morphology as a function of substrate miscut has been enabled by the usage of laser textured substrates. Texturing with nanosecond laser pulses produce Si substrates with miscuts varying from q = 0 to 15 degrees off (001). Besides the vicinality, we have focused on the effects of growth rates on film morphology by fixing the alloying content (20% Si, 80% Ge) and the growth temperature (600 °C). Ge0.8Si0.2 growth rates are varied over a wide range, 1.7 to 90 monolayers per minute. Film morphologies at all growth rates show strong dependence on the local miscut q within the dimpled regions of the substrate: the results demonstrate the importance of anisotropy in surface stiffness for the formation of epitaxial nanostructures. The length scales of all structures, either quantum dots or elongated instabilities, display a similar trend of decreasing size with increasing growth rate because coarsening is suppressed at high growth rates.

P14: Biological Sensors based on Brownian Relaxation of Magnetic Nanoparticles

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We present a biological sensing platform that is based on a modification of the dynamic magnetic properties of ferromagnetic nanoparticles suspended in a liquid. For a narrow size range the ac magnetic susceptibility of the ferromagnetic nanoparticles is dominated by Brownian relaxation. By coating the nanoparticles with a suitable ligand the Brownian relaxation and thus the ac magnetic susceptibility can be modified through the binding to the corresponding bio-receptor. The size of the particles has to be large enough to avoid superparamagnetism and at the same time small enough to have a homogeneous single domain magnetization. We demonstrate a proof-of-principle of this concept by using avidin-coated Fe3O4 particles that are ~10 nm in diameter, which were investigated before and after binding to biotinylated S-protein and bacteriophage particles. The ac susceptibility measurements show that the magnetic relaxation occurs via a Brownian mechanism; the frequency shift for the peak in the imaginary part of the susceptibility after binding to the target indicates the increase of the hydrodynamic radius. We are currently developing magnetic phage viruses in order to further improve this bio-sensing platform.

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P15: Chromium Diboride Thin Films by CVD

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Chromium diboride is a metallic ceramic, a class of materials that possess a unique combination of high melting temperature (T_{mp} = 2200 °C), good thermal conductivity (31 Wm^{-1}K^{-1}), low electrical resistivity (56 Ω-cm) and high hardness (22.5 GPa). We present the first results of metallic CrB_{2} films deposited by CVD using a novel single source precursor – bis(octahydrotriborate)chromium(II), Cr(B_{2}H_{5})_{2}. The films can be grown at a temperature as low as 200 °C with a resistivity of 105 Ω-cm. The films deposited at low temperature are X-ray amorphous and highly stoichiometric (B/Cr ratio ~ 2). The process is able to conformally coat trench features with a depth to width ratio of 8:1. We will report our initial studies on growth kinetics and film characterization and outline the prospects for applications like hard coatings and microelectronics.

P16: Macrotecture and growth chemistry in ultrananocrystalline diamond thin films

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Ultrananocrystalline diamond (UNCD) is a fine-grained (3-5 nm) diamond material. Synthesized by MPECVD using Ar-rich Ar/CH_{4} plasmas, the electronic, structural, and tribological film properties of UNCD can be tailored by doping with a controlled amount of nitrogen or hydrogen. These changes correspond with clear transformations in the film structure. Here, we have determined the average preferred crystalline orientation of thin ultrananocrystalline diamond films using x-ray diffraction. The grain size and lattice parameters of the films were also calculated. We show how these characteristics change markedly with the gas chemistry used during growth, adding either 0-20% nitrogen or 0-15% hydrogen to the argon-rich, argon and methane microwave plasma used. We discuss how these changes give evidence that there is a competing growth mechanism between C_{2} dimer mediated growth and the more widely used methyl radical growth process. Finally, we identify an additional x-ray diffraction peak, dependent on both the substrate used and growth conditions, as silicon carbide. We discuss these results in the context of the growth mechanisms and device applications of ultrananocrystalline diamond.

P17: Surface Stress on Solid-Liquid Interfaces

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Surface energy of solid-liquid interface remains to be an interesting problem but it is impossible to be measured directly. We are trying to measure interface stress because surface energy can be calculated from it. We make different films on two opposite faces of AFM cantilever and set it into mixture of liquids and use an optical system to measure the bending angle of the cantilever to get the interface stress. Now we are doing some experiments in mixture of alcohols (methanol + 2-propanol) using a cantilever with one side of SiO_{2} and the other of Au. The results turn out to be the most interface stress changing happens in low methanol concentration in 2-propanol.

P18: Electrochemical Modification of Carbon Nanotube-modified Electrodes

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The development of high-density biosensor arrays requires developing new methods for producing individually-addressable nanoscale sensing elements. We have developed an electrochemical method for selectively modifying individual nanotube-based electrodes in such a way as to place specific chemical functional groups on the nanotubes. We show that these functional groups can be used to link biomolecules such as DNA and antibodies to the nanotubes. Measurements using fluorescently-labeled complementary DNA and complementary antigens show that the biologically-modified carbon nanotubes retain the biomolecular recognition properties. On small length scales, we have investigated the functionalization and subsequent biomolecular interactions using DNA and antigens labeled with gold nanoparticles, and using scanning electron microscopy to image the spatial distribution of the particles. Our results suggest that electrochemical transformations on nanotube electrodes can be used as a pathway for fabricating arrays of individually-modified nanoscale sensing elements.
Hot electrons (i.e., conduction band electrons with energies above the Fermi level) have the potential to transiently populate electronic excited states of adsorbates bound to a surface. However, it remains a challenge to develop a source of monoenergetic electrons that can be continuously tuned to energies ranging from the Fermi level to well above the vacuum level. Metal-Insulator-Metal (MIM) devices provide a promising means to generate and deliver hot electrons to the metal-vacuum interface.

An array of Metal-Insulator-Metal (MIM) devices is fabricated on a glass substrate using electron beam evaporation. The devices are composed of a SiO$_2$ insulating layer sandwiched between an underlayer of Ti and an overlayer of Au. A Quartz Crystal Microbalance monitors the Au, SiO$_2$, and Ti layer thicknesses (10-50 nm) during deposition. When a bias of 6–12 V is applied across the device, electron emission is observed. The kinetic energy distribution of the emitted electrons reveals a high-energy peak corresponding to electrons that travel ballistically to the metal-vacuum interface with minimal energy loss. The most probable kinetic energy for the emitted electrons increases linearly with voltage bias across the two metal layers.

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**P20: Fabrication of high-aspect-ratio microchannels by using fast-etching metal sacrificial layer**

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We observed significant undercutting while etching Cr/Cu or Cr/Cu/Cr layer in copper etchant CE-100 and in Chrome etchant CEP-200 (*Transene Company Inc*). This phenomenon occurs only if the chrome and copper layers are both present. The existence of chrome layer also dramatically increases the etch rate of the copper. The chemical mechanism of this phenomenon is under investigation. By utilizing this phenomenon, we fabricated microchannels with height of 0.2µm, width of 5µm and 200µm, and length from 200µm to 4mm. Lift-off lithography is used to pattern a Cr/Cu (100Å/2000Å) layer or Cr/Cu/Cr layer (100Å/2000Å/100Å) on a silicon substrate as the fast-etching metal sacrificial layer; 1 µm silicon dioxide is then deposited by PECVD as the wall of the channel; last, opening is etched in buffered oxide etchant (BOE). The metal sacrificial layer is removed by immersing the sample in the CE-100 or CEP-200 solution. The average etch rate of the 200µm-wide channel is up to 17.8µm/min, which is 40 times the etch rate for the same size channel when the sacrificial layer is the copper layer only. The channel is observed to be completely cleared. The SEM micrograph is taken to show the channel cross section. This channel fabrication method is quite flexible: the height can be from 100Å to a few microns; the width can be reduced down to 0.5µm depending on the resolution of lithography; and the geometry of the channel is easy to be patterned. This method is also quite compatible with other microfabrication processes and can be used to build the microfluidic system or Lab-on-Chip system.

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**P21: Au Nanowire bio-modification and nanowire bridge formation**

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In recent years, there has been a merger of microelectronics and the biological sciences for the purpose of developing micro or nano scale biosensors. Nanowires are particularly interesting nanoscale materials because their shape anisotropy allows them to be manipulated in electric and/or magnetic fields. My research focuses on the synthesis, manipulation, recognition, and electrical properties of biomolecularly modified nanowires. By template synthesis, metallic nanowires can be grown and manipulated with electric or magnetic fields. These can be combined with biological recognition—as an aid in nano scale assembly and to develop novel types of nano-biosensors. As an example, gold nanowires are synthesized electrochemically in alumina membranes and then terminated by biotin groups through self-assembled monolayer (SAM) on nanowire surface. When an individual nanowire bridges a pair of biotin-avidin modified microelectrodes, a biotin-avidin-biotin sandwich molecular junction is formed at the interfaces, and a large change in the AC electrical conductivity across the electrodes is observed. Measurements of the amplitude and phase of the current across individual nanowire junctions as a function of frequency provide information on the electrical properties of the biomolecular interface. The final goal will be to establish methods for manipulating, integrating nanowires into biological detecting devices, and for understanding the electrical response of biological systems.