

# Friday Morning, November 13, 2009

## Surface Science

Room: M - Session SS1-FrM

## Nanoclusters, Organics and Beam Induced Chemistry

Moderator: J. Zhou, University of Wyoming

8:20am **SS1-FrM1 Site-specific Adsorption of C60 on Au(111)**, X. Zhang, L. Tang, Q. Guo, University of Birmingham, UK

The well-known herringbone reconstruction of the Au (111) surface consists of a regular array of line dislocations, which may act as nucleation sites for metals or organic materials [1, 2]. In this study, we reveal for the first time the selective adsorption of C60 molecules at the elbow sites on Au(111). Deposition of submonolayer of C60 molecules onto a Au(111) surface at room temperature usually leads to the co-existence of three structures [3]. In recent experiments we observed site-selective adsorption of individual C60 molecules, which show an obvious preference for nucleating at the elbows of the x type dislocation lines. As coverage increases, compact C60 islands are observed to form on the FCC regions between two neighboring C60 molecules. Interestingly, only about 50% of the elbow sites are active in mediating the formation of these nanometre sized C60 islands. The observed site-specific adsorption and nucleation is interpreted based on findings from high resolution STM imaging which reveals the atomic scale structure of the surface defects around the elbow sites.

Another site-selective adsorption phenomenon was observed after depositing C60 molecules onto parallel gold stripes (gold-fingers) [4], which were fabricated from monoatomic gold steps by high tunnelling current STM scanning. These gold-fingers have different kinds of microfacet ( $\{111\}$  and  $\{100\}$ ) on their two parallel steps. The C60 molecules prefer to adsorb on the less stable  $\{100\}$  steps and form close packed islands, while the  $\{111\}$  steps only have their FCC regions been occupied by the molecules. Besides the energy difference, the different underlying herringbone patterns of the two steps may also be a key factor leading to site-selective adsorption to the gold fingers.

### References:

1. I. Chado et al., Appl. Phys. Lett. 226 (2004) 178.
2. T. Yokoyama et al., Nature 413 (2001) 619.
3. X. Zhang, R.E. Palmer and Q. Guo, Surf. Sci. 602 (2008) 885.
4. Q. Guo, F. Yin and R.E. Palmer, Small 1 (2005) 76-79.

8:40am **SS1-FrM2 Epitaxial Growth of Organic Nanocrystals with Antiferroelectric Stacking**, M. Trelka, A. Medina, C. Urban, C. Claessens, Universidad Autonoma de Madrid, Spain, R. Otero, UAM & IMDEA-Nano, Spain, J.M. Gallego, ICMM-CSIC, Spain, T. Torres, Universidad Autonoma de Madrid, Spain, R. Miranda, UAM & IMDEA-Nano, Spain

Organic nanoparticles display size-dependent absorption and fluorescence bands and single photon emission. The detailed understanding of these effects is hindered by the difficulty in the synthesis of organic nanocrystals, i.e. organic nanoparticles with an ordered molecular arrangement. A possibility that remains mostly unexplored is the synthesis of such nanocrystals on solid surfaces. In the same way in which crystalline inorganic nanodots can be epitaxially grown on suitable substrates under conditions in which 3D Volmer-Weber growth takes place, an organic system could in principle be devised such that the growth of crystalline 3D islands sets in before the completion of the first monolayer. In practice, however, for organic adsorbates deposited on inorganic substrates intermolecular interactions are much weaker than molecule-substrate interactions, thus promoting a layer-by-layer growth mode, and preventing the fabrication of isolated 3D nanocrystal.

Here we show that, upon deposition of cone-shaped subphthalocyanine (SubPc) molecules on Cu(111), isolated triangular nanocrystallites up to 3 ML high appear on the surface before the completion of the first monolayer. The different molecular layers show an alternating or antiferroelectric (AF) stacking of the molecular dipole moments. The structure of such nanocrystals can be explained by the joint effect of electrostatic (dipole-dipole) and dispersive ( $\pi$ - $\pi$ ) interactions. Although 1 ML-thick islands can also be found on the surface, the molecular arrangement in these areas is different from the geometry of the 1<sup>st</sup>-layer molecules in the crystallites. We

suggest that the formation mechanism of the organic nanocrystals is related to the existence of two different adsorption geometries, cone-up and cone-down, each of which sits on different molecular layers placed at different distances from the surface upon crystallite formation.

9:00am **SS1-FrM3 Trapping Dynamics on Complex Surfaces: Organic Thin Film Growth on Surfaces Terminated with Self-Assembled Monolayers**, T.V. Desai, A.R. Woll, S. Hong, K.J. Hughes, J.R. Engstrom, Cornell University

A significant challenge in fabricating organic thin film transistors is that of controlling and understanding the properties of the interface between the organic semiconducting layer and the dielectric. It has been observed that charge transport can be affected significantly by chemically altering the dielectric surface with self-assembled monolayers (SAMs). However, the effects of the molecular scale interactions between the organic molecule and the substrate remain unclear. Diindenoperylene (DIP) is a promising candidate for applications in organic thin film electronics owing to the ability to form highly ordered films with excellent electrical properties. Here, using supersonic molecular beam techniques and *in situ* real time synchrotron X-ray scattering, we have examined the adsorption dynamics of DIP on silicon dioxide (SiO<sub>2</sub>) and SiO<sub>2</sub> modified with a number of SAMs. These SAMs included octadecyltrichlorosilane (ODTS), octyltrichlorosilane (OTS), fluorooctyltrichlorosilane (FOTS), and hexamethyldisilazane (HMDS), representing a range of molecular sizes and chemical terminations (-CH<sub>3</sub> vs. -CF<sub>3</sub>). In this work, we make use of x-ray intensity oscillations at the so-called anti-Bragg position to extract the occupation (coverage) of the individual layers as a function of time. These coverage-exposure relationships give us a direct measure of the (relative) probabilities of adsorption as a function of coverage. For the conditions examined (E<sub>i</sub> = 5.1-12.3 eV, T<sub>s</sub> = 40 °C) on all the starting surfaces (SiO<sub>2</sub> and SAM/SiO<sub>2</sub>) we observe a decrease in the probability of adsorption with increasing incident energy indicative of trapping-mediated adsorption. The probability of adsorption on these starting surfaces is dependent on both the chain length and the chemical composition of the SAM, where the probability of adsorption is greatest on the thickest organic layer, ODTS, followed by OTS, SiO<sub>2</sub>, FOTS, and HMDS. Once all surfaces are covered by DIP, however, the effects of incident kinetic energy are greatly reduced, and trapping is very efficient over the range of kinetic energies examined. For organic layers of comparable chemical composition and density, the initial probability of adsorption depends strongly on the layer thickness, where trapping on ODTS is most efficient, and on HMDS, least efficient. In a selected set of cases we will compare our experimental results with recent results from molecular dynamics simulations to obtain insight into the possible molecular-scale mechanisms/events that may occur in these systems. One such event appears to be the undeniable role of direct molecular insertion into the thicker organic layers such as ODTS.

9:20am **SS1-FrM4 Real-time Microscopic Investigations of the Growth of Thin Organic Films**, J.T. Sadowski, Brookhaven National Laboratory, A. Al-Mahboob, Y. Fujikawa, T. Sakurai, Tohoku University, Japan

The growth mode, morphology, crystallinity and electronic structure of thin rubrene (5,6,11,12-tetraphenylnaphthacene: C<sub>42</sub>H<sub>28</sub>) films grown in ultra-high vacuum (UHV) conditions have been studied *in situ* in the low-energy electron microscope (LEEM).

Rubrene is attracting a considerable attention since it has shown promise in OTFT's, with field-effect mobilities of the single-crystal FET devices surpassing that of amorphous silicon and even pentacene. However, still little is known how the electronic and chemical properties of the substrate affect the crystallinity of rubrene thin films.

When rubrene is deposited on clean semiconductor surfaces, such as Si(111)-7x7, it reacts with the dangling bonds, partially dissociating and forming a disordered wetting layer. The nucleation of the crystalline islands follows, but high nucleation density and slow surface diffusion, due to a rough and disordered interface, result in a poor crystallinity of the films.

A completely different growth mechanism is observed upon rubrene deposition on semi-metallic Bi(0001) surface. In this case rubrene islands nucleate immediately, without formation of any wetting layer. Keeping the substrate temperature at 400K results in nucleation of large, single-crystalline rubrene islands preferentially oriented along the surface terraces. Low-energy electron diffraction (LEED) patterns indicate formation of a new rubrene phase. Most interestingly, this phase is characterized by chiral ordering of the molecules within single crystalline domains having sizes in the range of tenths of micrometers. Such chiral ordering has a great potential for improvement of the crystallinity of rubrene films, and thus performance of rubrene-based devices.

9:40am **SS1-FrM5 In Situ Characterization of Surfaces Following Soft and Reactive Landing of Complex Ions.** *Q. Hu, P. Wang, P.L. Gassman, J. Laskin*, Pacific Northwest National Laboratory

Soft- and reactive landing (SL/RL) of mass-selected ions enables highly selective preparation of uniform thin films of a variety of complex molecules on surfaces. We have recently demonstrated covalent immobilization of several model peptides on the self-assembled monolayer (SAM) of N-hydroxysuccinimidyl ester terminated alkythiol on gold (NHS-SAM) using RL. Another remarkable finding is that SL and RL can be utilized for purification of peptide conformations that may not be stable in solution on SAM surfaces. For example, while Ac-Ala<sub>15</sub>-Lys peptide mainly exist in its  $\beta$ -sheet conformation in solution, SL and RL of this peptide on the surface results in immobilization of a very stable  $\alpha$ -helical conformation. This study presents a pathway for preparation of conformationally-selected peptide arrays that cannot be prepared using traditional solution-phase approaches. Here we present SL of singly and doubly protonated peptides (Gramicidin S, Substance P, Ac-Ala<sub>15</sub>-LysH<sup>+</sup> and Ac-LysH<sup>+</sup>-Ala<sub>15</sub>) onto inert SAMs of alkythiol (HSAM) and fluorinated alkythiol (FSAM) on gold, and RL of singly protonated diamines and multiply protonated dendrimers onto reactive NHS-SAM and COF-terminated SAM surfaces. The modified SAM surfaces were characterized using *in situ* real time infrared reflection absorption spectroscopy (IRRAS) and secondary ion mass spectrometry (SIMS). *In situ* analysis of substrates during and after the SL/RL processes is essential for understanding charge transfer phenomena, reactivity of soft-landed molecules, and modification of the secondary structure of the molecule as a result of interaction with the surface.

10:00am **SS1-FrM6 Surface Deposition and Characterization of Cu Clusters Utilizing Soft-Landing Drift Tube Spectrometry.** *G.F. Verbeck, S. Davila*, University of North Texas

Intro

The soft-landing of ion cluster onto a surface is a novel approach for the deposition of specifically selected cluster. Our approach differs from current deposition/ soft landing techniques in that it allows specific molecule to be landed with a KE of around 1-5 eV where current soft-landing techniques are in the range around 30 - 50 eV. Large KE may not be ideal for the landing of metal clusters as the energy is translated into motion along the surface resulting in aggregation along defects in the surface. We have recently developed soft-landing system using a drift tube, high pressure (1 - 100 torr), and a modified substrate to create a soft-landing around 1 - 5 eV. Surface modifications can isolate clusters and protect them from aggregation. This soft-landing method allows for the characterization of a specific soft landed metal cluster on the surface via AFM, Raman Spectroscopy, and Electrochemistry.

Method

Our soft-landing instrument allows for the direct ablation of metal samples via laser or atmospheric plasma. Laser ablation of a metal sample by a pulsed Nd:YAG laser for duration of 1-3 hrs acts as our source for ion clusters. The instrument is operated at a pressure between 1-13 torr, with a voltage between 10-500  $\pm$ V that is applied uniformly across the drift tube. Helium is used as a buffer gas and acts as a means to control cluster formation. The high pressure narrows the clusters KE from 40 eV to about 1 eV through collisions via the buffer gas. Clusters travelling within the drift tube are separated based on collisional cross-section. A pulsed split ring assembly at the end of the drift tube isolates specifically selected clusters directly on an unprepared or modified surface. The sample surface is then removed for characterization.

Data

Drift Tube spectra collected at 8 torr shows a cluster range of  $n = 1-8$  along with corresponding Cu<sub>n</sub>O. Clusters that have been landed on the surface are characterized using AFM. Images show an aggregation of the clusters in a striation patterns along the surface. The bridging across a defect instead of deposition within has also been seen. This clustering, aggregation, and growth shows a soft-landing has been made on the surface keeping the Cu cations and clusters intact. Self assembly of specifically isolated cluster groups has also been shown to occur on the surface of mica. Other characterization methods and various clusters may be specifically selected and landed with time allowing further development.

Instrument operates at pressure/temperature closer to ambient conditions than currently available, allowing ions to be soft landed on various modified surfaces for isolation and characterization.

10:20am **SS1-FrM7 Plasma Induced Interfacial Reaction of Hafnium Nano Particle and SiO<sub>2</sub> Film for Direct HfSiON Growth.** *T. Kitajima, T. Nakano*, National Defense Academy, Japan, *T. Makabe*, Keio University, Japan

In the paper, we show the example of the non-thermal chemistry over the nano-metal/semiconductor interface caused by the non-equilibrium low pressure RF plasma exposure. The process is directed to the new fabrication scheme of high-k dielectric thin film for MOSFETs with fewer process steps, lower impurity, and minimized EOT (equivalent oxide thickness). In the process, high density hafnium metal nano particle with 4 nm diameter is formed on SiO<sub>2</sub>/Si surface and subsequent nitrogen plasma exposure (~10 min.) leads to the growth of HfSiON high-k dielectric film with SiN interfacial layer.

Current ULSI technology requires the use of hafnium related high-k dielectrics with ~3 nm thick for MOSFET to lower the power consumption. HfSiON is the most applicable chemistry for the high-k material with proper energy band alignment, large area uniformity, and thermal stability. The direct formation of HfSiO film from the Hf overlayer and underlying SiO<sub>2</sub> utilizing the thermal interfacial reaction was previously proposed [1]. The process demonstrates remarkably low impurity in the film due to the lack of carbon in contrast to the case of MOCVD processes. In our

case, 2.5 nm thick Hf metal layer is deposited with e-beam deposition source on SiO<sub>2</sub>/Si(100) surface uniformly. The morphology obtained with the in-situ non-contact AFM measurement revealed the surface consists of the high density array of Hf nano particles with the size of 4 nm in diameter. The exposure of atomic nitrogen and ions from the non-equilibrium plasma enables the introduction of N into the film and increases the interfacial reaction rate of Hf and SiO. Within the first 1 min., the Hf nano particles are oxynitrided with the N atoms from the plasma and the O atoms supplied from the lower interface judging from the XPS analysis. The following plasma exposure (~10min.) enables the diffusion of Si atoms into the high-k film from the underlying SiO layer. The Si content in the film increases with the exposure time and becomes comparable to the Hf content with 35 min. exposure. The XPS spectrum shows the Si incorporated is mostly nitrided in the film. The spectrum also indicates the interfacial SiO layer is nitrided and this leads to the minimized EOT of the high-k stack structure.

[1] H. Watanabe, Appl. Phys. Lett. 85, 449 (2004).

10:40am **SS1-FrM8 Modeling Thin Film Deposition Processes in an HDP-CVD Reactor.** *A. Bhoj, K. Shah*, ESI US R&D, Inc., *M. Megahed*, ESI Group, Inc., *P. Kothnur, R. Kinder*, Novellus Systems, Inc.

Modeling HDP-CVD processes for high quality dielectric film deposition in high aspect ratio device structures remains a challenging task. A number of details such as the reactor geometry, inductive and capacitive power deposition, gas-phase chemistry and surface kinetics need to be addressed in a coupled manner. In this multi-physics approach, a reactor scale model in conjunction with a feature scale model is used to investigate the process dependence of deposition rates across the wafer and within features. Plasma properties, gas flow and deposition at the walls are addressed in the reactor scale model. The resulting film growth inside microscopic trenches is captured in the feature scale model. The reactor geometry is similar to that described in an earlier publication [1]. Data for gas phase and surface reaction kinetics are obtained from published literature [2]. In an earlier work [3], trends in deposition rate at the wafer with inductive power were discussed. In this paper, the impact of reactor scale process parameters such as bias power deposition, gas flow rates and wafer temperature on deposition at the wafer are investigated, and modeling results are compared to experimental data [4].

[1] M. Tuszewski and J. A. Tobin, *J. Vac. Sci. Technol. A* **14**, 1096 (1996).

[2] E. Meeks, *et al*, *J. Vac. Sci. Technol. A* **16**, 544 (1998).

[3] A. Bhoj, *et al*, *EuroCVD and CVD XVII, 216th Meeting of the Electrochemical Society*, Vienna, Austria (2009).

[4] A. Bhoj, P. Kothnur, and R. Kinder, *61st Annual Gaseous Electronics Conference*, Dallas, TX (2008).

11:00am **SS1-FrM9 Ion Scattering Studies of Isolated Au Nanoclusters**, S. Balaz, J.A. Yarmoff, R.D. Gann, University of California, Riverside

Isolated Au nanoclusters are grown atop amorphous solid water (ASW) at low temperature. This process, which represents the first step in the growth of nanoclusters via the buffer layer assisted growth (BLAG) method, is a unique way in which to fabricate small deposited clusters that have minimal interactions with a substrate. Such clusters are able to serve as model systems for investigations of how nanocluster electronic structure depends on shape and size. Low energy alkali ion scattering was used to probe the atomic and electronic structures of the clusters *in situ*. ASW was first deposited as a separation layer onto SiO<sub>2</sub>/Si(111) at liquid nitrogen temperature, and then Au was evaporated onto the ASW to form nanoclusters. The mean size of the clusters is expected to increase with increased Au deposition. Time-of-flight (TOF) spectroscopy was used to collect charge-resolved spectra of scattered 2 keV <sup>7</sup>Li<sup>+</sup> and <sup>39</sup>K<sup>+</sup> ions. Spectra collected following small Au depositions display only a sharp single scattering peak, while multiple and plural scattering features are present following larger depositions. The change in spectral shape is indicative of the formation of multilayer nanoclusters. The experimental findings are interpreted with the aid of Monte-Carlo ion scattering simulations. The neutral fraction of scattered K<sup>+</sup>, 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. The lack of any angular dependence to the neutralization implies that the clusters behave as atomic-like structures. Further experiments will investigate how the clusters evolve when deposited onto the substrate by heating to desorb the ASW layer.

11:20am **SS1-FrM10 Initial Nucleation and Growth of Oxide Scale on Haynes® 214® Alloy**, V. Shutthanandan, S.V.N.T. Kuchibhatla, A.S. Lea, Z. Zhu, M.H. Engelhard, S. Thevuthasan, Pacific Northwest National Laboratory, P. Singh, University of Connecticut, V. Deodeshmukh, Haynes International, Inc., H. Ghezelayagh, Fuel Cell Energy, Inc.

A combination of ion beam and electron spectroscopy techniques have been used to precisely understand the initial oxidation of a multicomponent alloy system, Haynes®214®. Surface sensitive nature of these techniques has been rightly exploited to precisely identify different phases formed at different times of oxidation. Haynes® 214® is a high temperature, Ni-Cr-Al-Fe based alloy, widely used in a plethora of applications ranging from “clean firing” of ceramics to the gas turbine industry. Various reports exist in the literature, which describe the long term stability of this alloy under oxidizing environments at temperatures above 900°C. *Despite the number of applications and significant interest in this alloy, a clear mechanism of the early stage oxidation has not been documented.* An effort is underway to estimate the initial nucleation and growth of oxide scale on this alloy in various environments (such as dry and humid air). A combination of ion and electron based techniques such as Rutherford backscattering spectrometry (RBS), nuclear reaction analysis (NRA), particle induced x-ray emission (PIXE), secondary ion mass spectrometry (SIMS) and Auger electron spectroscopy (AES) and x-ray photoelectron spectroscopy (XPS) were used to measure the initial nucleation of the oxide scale on this alloy. NRA was used to track the oxygen depth profile while PIXE and RBS were used to track the changes in matrix components of the alloy for the formation of oxide scale for as-low-as 1 min of oxidation. Chemical analysis of this early stage of oxidation formation was studied by AES and XPS. Chemical surface mapping obtained from Auger analysis indicated that the initial oxide formed is chromia which is completely dominated by alumina after 7 min of oxidation treatment at 900°C in air. Various merits of this work will be discussed along with possible future scope for using Ion beam techniques for processes such as oxidation of metals, a most widely studied problem.

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