

Surface Science Division

Room 102A - Session SS+EM+PS+TF-ThA

Deposition, Etching and Growth at Surfaces

Moderator: Bruce E. Koel, Princeton University

2:20pm SS+EM+PS+TF-ThA-1 Controlled Deposition and High-Resolution Analysis of Functional Macromolecules in Ultrahigh Vacuum, *Giovanni Costantini*, University of Warwick, UK

INVITED

The ultimate spatial resolution of scanning tunnelling microscopy (STM) has allowed to gain an exceptional insight into the structure and the intra- and inter-molecular bonding of a huge number of adsorbed molecular system. Unfortunately, these remarkable analytical capabilities are achieved only under ultrahigh vacuum (UHV) conditions and therefore cannot be directly applied to more interesting systems composed of functional (bio)molecules or complex synthetic compounds. In fact, thermal sublimation is the strategy of choice for preparing ultrathin films of small and heat-resistant molecules in UHV but larger, complex (bio)molecules are not compatible with this process.

This challenge has been overcome in recent years by adapting soft-ionisation techniques developed in mass spectrometry (mainly electrospray ionisation, ESI) to transfer intact fragile molecules into the gas phase and to soft-land them onto atomically flat and clean substrates. When combined with advanced scanning probe microscopes operating under UHV conditions, these novel set-ups allow the surface deposition and high-resolution characterisation of a wide range of functional organic molecules and inorganic nanoparticles.

This talk will present recent advances in the development of ESI-deposition techniques and their combination with UHV-STM to analyse complex (bio)molecule-surface systems. It will start by reviewing the limits that standard molecular deposition imposes on the size of (bio)molecules that can be studied in surface science. It will continue by presenting a recently developed ESI-deposition setup based on a simple, efficient and modular design with a high intensity and mass selectivity. The discussion will then proceed to the application of ESI-STM to the characterisation of adsorbed polypeptides and polymers. In particular, it will be shown that this technique allows the imaging of individual macromolecules with unprecedented detail, thereby unravelling structural and self-assembly characteristics that have so far been impossible to determine.

3:00pm SS+EM+PS+TF-ThA-3 Unconventional Nucleation and Growth Kinetics: *in situ* Variable-temperature Scanning Tunneling Microscopy Studies of Chemical Vapor Deposition of Inorganic Monolayers on Metallic Substrates, *Pedro Arias*, University of California, Los Angeles; *A Abdulslam*, Colorado School of Mines; *A Ebnonnasir*, University of California at Los Angeles; *C Ciobanu*, Colorado School of Mines; *S Kodambaka*, University of California, Los Angeles

The growth of thin films from atoms and/or molecules deposited from the gas phase onto solid substrates is a non-equilibrium phenomenon where the structure, composition, and crystallinity of the films are determined by kinetic and thermodynamic processes. Over the past few decades, vast and fruitful efforts have been devoted to understanding the kinetics of thin film growth. As a result, conventions of the kinetic factors have been developed to predict the growth mechanism and, hence, microstructure of the as-grown films: for example, nucleation at terraces (steps) is expected to occur when surface diffusion of adsorbed species is significantly lower (higher) compared to the deposition flux and is observed at higher (lower) fluxes and lower (higher) substrate temperatures. Here, we report an unconventional growth mode of inorganic monolayers on metallic substrates.

Using *in situ* ultra-high vacuum scanning tunneling microscopy (UHV STM), we investigated the chemical vapor deposition (CVD) kinetics of hexagonal boron nitride (hBN) monolayers on Pd(111). In each experiment, STM images are acquired while exposing Pd(111) to borazine (10^{-7} – 10^{-6} Torr) at temperatures 573 K and 673 K and for times up to 2500 s. The STM images reveal the nucleation and growth of two-dimensional islands on the Pd surfaces. From the images, we measure the areal coverage, island sizes, and island density as a function of time, temperature, and borazine flux. We find that the rates of areal coverage and island density increase ten-fold with increasing borazine pressure from 10^{-7} to 10^{-6} Torr at 573 K and three-fold with increasing temperature from 573 K to 673 K and borazine pressure of 10^{-7} Torr. Our STM images reveal an unusual nucleation and growth mode: at lower deposition flux and higher temperature, islands

form on terraces; increasing the flux and/or lowering the temperature result in preferential nucleation and growth at the step edges.

Interestingly, the step-edge growth of borazine islands is observed on both up and down steps. We attribute this phenomenon to the structure and the highly anisotropic bonding of borazine on Pd(111). Our results provide new insights into the growth dynamics of two-dimensional layered materials.

3:20pm SS+EM+PS+TF-ThA-4 Redox-Active Ligands for Single-Site Metal-Organic Complexes on Surfaces as Heterogeneous Catalysts, *Tobias Morris*, Indiana University; *D Wisman*, Indiana University, NAVSEA Crane; *I Huerfano*, *N Maciullis*, *K Caulton*, *S Tait*, Indiana University

The utilization of single-site transition metal centers at surfaces is of growing interest in the heterogeneous catalysis community. One advantage of single-site metal centers is the high dispersion so that a much higher fraction of atoms contribute to chemical activity compared to nanoparticle catalysts. Our approach to forming single-site metal centers is on-surface complexation with a redox-active ligand, which allows a high degree of ordering on the surface as well as intimate chemical contact of the metal center with the support surface. The ligand design enables us to tailor the coordination geometry and oxidation state of the metal and thus affect the cooperation between metal and ligand and the chemical reactivity. Several ligands, differing in backbone, binding pocket, design, and peripheral units were examined in this study. Tetrazine-based ligands are known for their redox activity. The on-surface two-electron redox process utilizes vapor deposition of 3,6-di-2-pyridyl-1,2,4,5-tetrazine (DPTZ) with vanadium cations onto an Au(100) surface. The metal-organic complexation leads to the growth of 1D chains consistent of one metal per ligand due to the divergent binding pockets created by the tetrazine core and pyridine rings. Exposing the V-DPTZ chains to oxygen results in a dissociative reaction of molecular oxygen to form a terminal oxo species on the vanadium, while allowing the metal-organic complex to remain intact. Interestingly, the dioxygen activation contributes adsorbed oxygen to the support surface by a spillover mechanism. The stable V-oxo species is the only oxidation product, unlike the unselective oxidation of V nanoparticles. A newly synthesized ligand, tetraethyltetra-aza-anthraquinone (ETAAQ), utilizes a quinone backbone with adjacent pyrazine rings to generate four symmetric binding pockets. Quinones are one of the oldest studied redox-active ligands. ETAAQ has the capacity for up to a four-electron reduction, enabling the possibility for multiple metal sites per ligand. Continued work on redesigning ligands is showing promise in increasing the cooperativity of the ligand and the metal which could lead to heightened reactivity.

4:00pm SS+EM+PS+TF-ThA-6 Oxidation and Ablation of HOPG Using Supersonic Beams of Molecular Oxygen Combined with STM Visualization, *Ross Edel*, *T Grabnic*, *B Wiggins*, *S Sibener*, University of Chicago

Graphite is widely studied due to its importance in high-performance materials applications such as high velocity flight systems as well as its key role as a model system for other carbonic materials such as graphene and carbon nanotubes. Our research focuses on the reaction of highly oriented pyrolytic graphite (HOPG) with molecular oxygen, the mechanism of which is not yet fully understood. Utilizing a one-of-a-kind instrument that combines a supersonic molecular beam and scanning tunneling microscope (STM) in ultra-high vacuum, we are able to tightly control the energy and angle of impinging oxygen and examine the nanoscopic and mesoscopic evolution of the surface. We have found that different oxygen energies, incident angles, and surface temperatures produce morphologically distinct etching features: anisotropic channels, circular pits, and hexagonal pits faceted along crystallographic directions. The faceted and circular etch pits were formed at low O_2 energy, with faceting only apparent below a critical surface temperature, while anisotropic etching was observed with exposure to higher energy oxygen. Comparison of low- and high-grade reacted samples show that anisotropic channels likely result from the presence of grain boundaries. Reaction probability increased with beam energy and demonstrated non-Arrhenius behavior with respect to surface temperature, peaking at around 1375 K. Beam impingement angle had only minor effects on the reaction probability and etch pit morphology. Reactivity was enhanced by natural grain boundaries and artificially created point defects, showing the critical influence of small structural imperfections. Our combination of STM imaging with well-defined and controlled oxidation conditions connects interfacial reaction kinetics with time-evolving nanoscopic surface morphology, providing new insight into the oxidation of graphitic materials under high-temperature conditions. Spatio-temporal correlations obtained in this manner shed new light on interfacial erosion mechanisms, and provide an incisive complement to the

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information obtained using spatially-averaged gas-surface reactive scattering measurements.

4:20pm SS+EM+PS+TF-ThA-7 Kinetically Trapped Molecular Growth during the Self-assembly of ZnTPP on Ag(100), Sylvie Rangan, P Kim, C Ruggieri, R Bartynski, Rutgers, the State University of New Jersey; S Whitlam, Lawrence Berkeley National Laboratory

The result of the self-assembly of organic molecules on a noble metal surface is often analyzed in terms of equilibrium configurations, implicitly assuming that molecular adsorbates are mobile enough to reach global thermodynamic equilibrium. For example, tetraphenylporphyrins (TTPs), which have a 4-fold symmetry and a high surface mobility, generally assemble on surfaces in highly-ordered nearly-square arrays, locked in place by phenyl T-stacking. Here, using scanning tunnel microscopy, a highly ordered metastable phase is observed for a monolayer of ZnTPP molecules self-assembled at 300 K on Ag(100). This phase is composed of two rows of the expected nearly-square phase, alternated with a row of rotated molecules. The usually reported square phase is found only after higher temperature anneal. Using a Kinetic Monte Carlo model, molecular self-assembly is simulated and reveals that this system is an unusual example of 2D molecular growth, where kinetic factors could be the limiting process directing self-assembly.

4:40pm SS+EM+PS+TF-ThA-8 Early Stage Oxidation and Evolution of Surface Oxides in Ni(100) and Ni-Cr(100) Thin Films, William H. Blades, P Reinke, University of Virginia

The interaction of molecular oxygen with Ni(100) and Ni-Cr(100) thin films has been studied through a synergetic experimental and computational effort. The physical and chemical processes behind the initial stages of oxidation prior to the formation of a full oxide layer are not well understood. By oxidizing Ni(100) and Ni-Cr(100) thin films and studying the growth of the surface oxides with Scanning Tunneling Microscopy and Scanning Tunneling Spectroscopy, the evolution of oxides grown within the pre-Cabrera-Mott regime can be captured. The data collected are combined with Bandgap and Density of States maps and statistical distributions of the surface's electronic structure are generated. Pure Ni(100) and Ni-(8-12)wt.%Cr(100) thin films were prepared on MgO(100) in UHV and exposed to oxygen up to 400 L. Under these oxidation conditions the Ni(100) prefers the Ni(100)-c(2x2)O reconstruction, which drives step faceting into {100} segments subsequently limiting the growth of NiO at elevated temperatures. Our experiments demonstrate that once a nominal amount of Cr is added to Ni(100), the Ni-Cr(100) surface will undergo a different oxidation reaction pathway. After just 14 L of O₂ exposure we observe NiO growth across the surface, the presence of large oxide nodules and three distinct chemisorbed phases. Initial NiO nucleation and growth occurs along the step edges of the Ni-Cr surface. The superlattice and modulation of tip bias has revealed a NiO-Ni(6x7) cube-on-cube interfacial relationship. NiO wedge-like features are also observed and have characteristically different superlattice spacing, which offers insight into the manner in which metal-oxides mitigate strain within the pre-Cabrera-Mott regime. One of the chemisorbed phases we observe has been identified as Cr(100)-c(2x4)O, suggesting surface segregation and subsequent phase separation of BCC Cr. Two other chemisorbed domains are present and possess distinct electronic signatures that have been captured by STS. Density Functional Theory is used to develop an understanding of the effect of Ni and Cr on the local bonding environment of the prevalent chemisorbed phases of Ni-Cr(100). This combined experimental and theoretical approach has offered greater insight into alloy-oxide interface structure, and the role of transition metal dopants in the oxidation process in the pre-Cabrera-Mott regime. This work is supported by the Office of Naval Research MURI "Understanding Corrosion in Four Dimensions," Grant N00014-14-1-0675.

5:00pm SS+EM+PS+TF-ThA-9 DLC Films by Modified HiPIMS with Effect from Pulse Parameters on Plasma Parameters and Film Quality, David Ruzic, I Haehnlein, University of Illinois at Urbana-Champaign; B Wu, Southwest Jiaotong University; D Barlaz, University of Illinois at Urbana-Champaign; B Jurczyk, Starfire Industries

Diamond like carbon (DLC) films have made waves as of late in many industries. DLC provides a high strength low friction surface with the potential for high chemical resistivity. High Power Impulse Magnetron Sputtering (HiPIMS) is a promising physical vapor deposition (PVD) that creates high ionization fractions at the substrate using high power pulses over low duty factors. The resulting high plasma densities (as high as 10¹⁹ m⁻³) creates ionization fractions of sputtered material at the target surface.

The increase in energy of atoms due to high ionization rates at the

substrate yields higher density and smoother films. In combination with a positive polarity pulse to drive ions to the substrate surface, the DLC film hardness can be increased while producing a smoother film surface.

By introducing a larger ion flux, determined through a gridded energy analyzer, the ratio of sp³ bonded carbon to sp² is presented for a multitude of parameters. This work explores not only the use of positive polarity pulses, but the effect of pulse parameters, has on film hardness and morphology. By controlling the deposition rate through pulse width and repetition rate while controlling deposition energy increases by approximately 5% in sp³ fraction were observed while surface roughness decreased by a factor of 4 for a non-hydrogenated amorphous carbon film by just the introduction of a positive polarity pulse. Further increases are reported through fine tuning the discharge parameters while looking at plasma densities, ion fraction, surface roughness, sp³ fraction, and hardness for DLC on silicon substrates.

5:20pm SS+EM+PS+TF-ThA-10 Adsorption and Reactions on Topological Insulators Surfaces Probed by Low Energy Ion Scattering, Haoshan Zhu¹, W Zhou, J Yarmoff, University of California - Riverside

Bi₂Se₃ and Bi₂Te₃ are two-dimensional topological insulators (TIs) that have attracted intense interest in recent years. TIs are promising candidates for superconductor, spintronics and quantum computing applications due to topological surface states (TSS) that connect the conduction and valence bands. The clean Bi₂(Se,Te)₃ surfaces prepared under ultra-high vacuum (UHV) are terminated with Se or Te, but the termination can change if exposed to air or prepared under non-ideal conditions. The adsorption and reactions of various atoms and molecules with Bi₂(Se,Te)₃ have thus been studied extensively, as they can result in changes to the TSS, doping and surface reconstruction. Here, TI surfaces are exposed to Cs, Bi, and halogens (Cl₂ and Br₂) in UHV and investigated by low energy electron diffraction (LEED), work function measurements and low energy ion scattering (LEIS). It is found that Cs lowers the work function and remains stable at small coverages but becomes mobile at larger coverages. Bi grows in a quasi bilayer-by-bilayer mode with the first Bi bilayer being strongly bonded to the TI surface. Both clean TI surfaces and Bi-covered surfaces are exposed to halogens. The clean surfaces are relatively inert to halogens, but they readily adsorb onto Bi films. The Bi is etched away when the samples are lightly annealed, restoring the clean Se- or Te-terminated surfaces.

5:40pm SS+EM+PS+TF-ThA-11 Atomically Controlled Metallation of Porphyrinoid Species with Lanthanides on Surfaces, Borja Cierera, IMDEA Nanoscience, Spain; J Björk, Linköping University, Sweden; G Bottari, T Torres, Universidad Autonoma Madrid, Spain; R Miranda, D Ecija, IMDEA Nanoscience, Spain

Metallation of surface confined porphyrinoid architectures have emerged as an important research topic due to its importance for biological phenomena and potential applications including optoelectronics, nanomagnetism, sensing and catalysis.

Hereby, the in-situ design of mutant porphyrinoids, either by selection of unconventional metal centers like lanthanides or by choosing different backbones, is attracting great attention. In this talk we report our latest research regarding the metallation by dysprosium, an archetype lanthanide metal for magnetic applications, of porphyrinoid species of distinct cavity size.

On one hand, the deposition of Dy on top a submonolayer of fluorinated tetraphenyl porphyrin species on Au(111) affords the expression of three different Dy-derived compounds, which are identified as the: initial, intermediate and final metallated states. Importantly, the initial metallated complexes exhibit a narrow zero bias resonance at the Fermi level that is assigned to a molecular Kondo resonance with T_k ≈ 120 K, which can be switched off by means of vertical manipulation.

On the other hand, the adsorption on Au(111) of an expanded hemiporphyrazine with 27 atoms in its internal cavity is investigated, showing a long-range orientational self-assembly. Furthermore, a spatially controlled "writing" protocol on such self-assembled architecture is presented, based on the STM tip-induced deprotonation with molecular precision of the inner protons. Finally, the capability of these surface-confined macrocycles to host lanthanide elements is assessed, introducing a novel off-centered coordination motif.

The presented findings represent a milestone in the fields of porphyrinoid chemistry and surface science, revealing a great potential for novel surface

¹ Morton S. Traum Award Finalist

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patterning, opening new avenues for molecular level information storage,
and boosting the emerging field of surface-confined coordination chemistry
involving f-block elements.

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