

Tuesday Afternoon, November 11, 2014

Surface Science

Room: 309 - Session SS+NS-TuA

Nanostructures: Growth, Reactivity and Catalysis

Moderator: Judith Harrison, United States Naval Academy,
Greg Kimmel, Pacific Northwest National Laboratory

2:20pm SS+NS-TuA1 **Building Nanostructured Nanowires via Sequential Catalyst Reactions**, *Frances Ross*, IBM T.J. Watson Research Center **INVITED**

By exposing catalytic nanoparticles to reactive source gases, nanowires can be grown with excellent control over length, diameter, crystal structure and composition. Here we discuss the degree to which this vapour-liquid-solid growth mechanism can be augmented by “programming” a sequence of reactions in the catalyst. Our aim is to produce complex structures in which quantum dots and quantum wells of precise dimensions are incorporated into single nanowires. We supply different species to nanowire catalysts, either as reactive gases or by evaporation, triggering the formation of new phases that become incorporated into the nanowires as they grow. *In situ* transmission electron microscopy allows us to view this process, identify phases and measure kinetics. As an example, we discuss the formation of silicide quantum dots within Si nanowires. Supplying metals such as Co and Ni to catalysts composed of liquid AuSi results in the formation of faceted silicide nanocrystals. These floating nanocrystals subsequently attach at the AuSi/Si interface. Further growth of Si incorporates these quantum dots into the nanowire. We discuss the generality of this phenomenon and the control of silicide structure and dimensions. The formation of narrow quantum wells, such as Ge layers within Si nanowires, can also benefit from understanding the sequential changes in the catalyst. We describe the relationship between catalyst properties and quantum well compositional abruptness, strain and stability. We finally consider the possibilities of combining quantum dots and quantum wells in single nanowires. We suggest that control of reaction pathways within the catalyst provides exciting opportunities for the growth of complex nanostructures.

3:00pm SS+NS-TuA3 **Ar/O₂ and H₂O Plasma Modified SnO₂ Nanomaterials for Gas Sensing Applications**, *Erin Stuckert, E.R. Fisher*, Colorado State University

Tin oxide (SnO₂) is an excellent material for gas sensing applications. The sensing mechanism of SnO₂ is controlled through gas interactions with adsorbed oxygen, which alters the charge flow through the sensing material. By measuring changes in charge flow, sensitivity and selectivity of a gas sensor can be determined. Sensitivity is improved by increasing surface-gas interactions of high surface area materials, SnO₂ nanoparticles and nanowires, combined with surface modification. One surface modification method that can achieve greater oxygen adsorption is plasma treatment; with an expansive parameter space, plasmas allow for greater control of the modification process. In this work, commercial SnO₂ nanoparticles and chemical vapor deposition (CVD)-grown SnO₂ nanowires were plasma modified to create oxygen vacancies with the aim of increasing oxygen adsorption during sensing. Specifically, we employed Ar/O₂ and H₂O plasmas because they can etch materials like SnO₂ to increase oxygen adsorption by creating surface oxygen vacancies. Ar/O₂ plasma treatment of SnO₂ nanoparticles and nanowires showed increasing oxygen adsorption with increasing plasma power and treatment time without changing Sn oxidation state or morphology, as measured by X-ray photoelectron spectroscopy (XPS) and powder X-ray diffraction (PXRD). With low power H₂O plasma treatments, however, greater oxygen adsorption was observed with nearly complete Sn reduction as well as significant morphological changes evidenced in XPS, PXRD, and scanning electron microscopy (SEM). Plasma treated materials were evaluated for their sensitivity and selectivity for a variety of gases including ethanol, formaldehyde, and benzene. Results for both Ar/O₂ and H₂O plasma treated SnO₂ nanoparticles and nanowires will be presented and discussed with respect to their sensing capabilities, including changes in selectivity and sensitivity.

Keywords:

Plasma treatment

Gas sensor

Tin oxide

Nanowire

Nanoparticle

3:20pm SS+NS-TuA4 **Interaction of D₂O on the Surface Grown ZnO(0001) Nanostructures**, *Xingyi Deng, D.C. Sorescu, J. Lee, C. Matranga*, National Energy Technology Laboratory

D₂O on the ZnO nanostructures grown on Au(111) has been investigated using a combination of experimental and theoretical methods as to probe the reactivity of model ZnO catalysts at the atomic level. We performed a series of D₂O temperature programmed desorption (TPD) experiments on two distinctive surfaces, one consisting of single layer Zn(0001) nanostructures, and the others consisting of mixtures of single and bilayer ZnO(0001) nanostructures. On the basis of our TPD data and in comparison with the ZnO structural characteristics, we are able to assign each D₂O TPD peak to a specific site existing on the ZnO nanostructures. Specifically, desorption peaks at 150 and 200 K are assigned to sublimation of D₂O multilayers and desorption of D₂O adsorbed directly on the ZnO surfaces, respectively; and D₂O adsorbed on the edges of either single or bilayer ZnO desorbs at a slightly higher temperature ~260 K. More importantly, we identify that D₂O binds to the steps between the single and bilayer ZnO much stronger than any other sites, desorbing around 400 K. Computational modeling based on density functional theory (DFT) calculations provides detailed adsorption geometry and energetics of the D₂O-ZnO(0001)/Au(111) system, further supporting our TPD assignments. Implications of our fundamental results for ZnO based catalysts will be discussed.

4:20pm SS+NS-TuA7 **2014 AVS Medard Welch Award Lecture: Quasicrystals to Nanoclusters: It's All on the Surface**, *Patricia Thiel**, Iowa State University **INVITED**

Surface science continues as an exciting frontier—perhaps more so now than in the past—for at least two reasons. First, powerful new tools are emerging, and second, a broad and robust body of knowledge has been established which is serving as a springboard for new breakthroughs, and is critically guiding other fields. In this talk I will present some of the contributions that I and my coworkers have been privileged to make in this field, particularly in the area of quasicrystal surfaces, and in the area of growth and stability of nanoclusters and thin films at surfaces. Metallic quasicrystals have a remarkable atomic structure that engenders unusual properties, including surface properties, and our goal has been to establish the structure-property relationship at the surface. One of our achievements was to show that quasicrystal surfaces are generally bulk-terminated. This laid the groundwork for showing that one of the characteristics of quasicrystals—low friction—derives (at least in part) from the quasiperiodic atomic structure. It also allowed us to understand unusual features of thin film nucleation and growth on these surfaces, and facilitated efforts of other groups to exploit quasicrystals and complex metallic alloys as catalysts. Nucleation and growth of nanoclusters and thin films also shows surprising features on more conventional (crystalline metal) surfaces, and has been a topic of investigation in my group for some time. We discovered that unusual smooth growth at low temperature, and associated non-monotonic temperature dependence of roughness, reflects a process now called “downward funneling”. In addition to non-equilibrium growth morphologies, we have also explored the relaxation of these morphologies towards equilibrium. We found that two-dimensional homoepitaxial metal nanoclusters can diffuse significant distances, leading to coarsening (a reduction in the cluster density) via agglomeration. Nanocluster destabilization and coarsening can also occur via Oswald ripening, but the identity of the mass carriers may not be obvious. The presence of even trace amounts of adsorbates can lead to formation of additive-metal complexes which more efficiently transport mass than metal atoms. We have searched for these complexes under conditions which have rarely been investigated in the past, i.e. very low temperature and very low coverage, with some surprising results.

5:00pm SS+NS-TuA9 **Photodeposited Pt Nanoparticles on Iron Oxide Nanoparticles Supported on Highly Oriented Pyrolytic Graphite**, *Jayde Kwon, J.C. Hemminger*, University of California Irvine

Metal-semiconductor hybrid systems have been of great interest due to their unique photocatalytic properties. In metal-semiconductor hybrid systems, semiconductors are used as light absorbing components. They absorb photons and create electron holes localized at the semiconductor, which are formed by excited electrons that move through the heterointerface. Fe₂O₃ is a promising semiconductor photocatalyst due to its visible light absorption ($E_g = 2.2$ eV), abundance, non-toxicity, and stability against photo corrosion. However, Fe₂O₃ suffers from short hole diffusion length, low electrical conductivity and high rate of electron hole recombination. To

* Medard W. Welch Award Winner

overcome these barriers, different transition metals (e.g. Au, Si, Pt) have been deposited on Fe₂O₃. Particularly, Pt on Fe₂O₃ is an ideal heterogeneous catalyst that has a variety of uses such as photoelectrochemical water splitting and CO oxidation. Importantly, Pt on Fe₂O₃ provides an improvement in photocatalytic properties on the degradation of dyes, such as methylene blue. Although many studies deposit Pt on various forms of Fe₂O₃ (e.g. films, nanorods, and cores/shells), Pt nanoparticles on discrete Fe₂O₃ nanoparticles on highly oriented pyrolytic graphite (HOPG) has not been studied. The deposition of Pt on Fe₂O₃ has been studied using various methods such as electrodeposition and solution based synthesis. However, photodeposition of Pt on Fe₂O₃ has not yet been studied. In this work, we demonstrate photodeposition of Pt nanoparticles selectively on Fe₂O₃ nanoparticle arrays formed by physical vapor deposition on HOPG. We find that the Fe₂O₃ nanoparticles are in the range of 7-20 nm in diameter. Ongoing studies of the catalytic properties of these unique materials will be presented.

5:40pm **SS+NS-TuA11 Formation and Stability of and Surface Chemistry on Dense Arrays of Au Nanoclusters on Hexagonal Boron Nitride/Rh(111)**, *M.C. Patterson, Phillip Sprunger, J.R. Frick, Y. Xu*, Louisiana State University, *B.F. Habenicht*, University of California Merced, *R.L. Kurtz*, Louisiana State University, *L. Liu*, Texas A&M University

We have studied the nucleation and growth of Au clusters at sub-monolayer and greater coverages on the h-BN nanomesh grown on Rh(111) by means of scanning tunneling microscopy (STM), X-ray photoelectron spectroscopy (XPS), and density functional theory (DFT). STM reveals that sub-monolayer Au deposited at 115 K nucleates within the nanomesh pores and remains confined to the pores even after warming to room temperature. Whereas there is a propensity of mono-atomic high islands at low temperature, upon annealing, bi- and multilayer Au clusters emerge. Deposition of higher coverages of Au similarly results in Au confined to the nanomesh pores at both 115K and room temperature. XPS analysis of core-level electronic states in the deposited Au shows strong final-state effects induced by restricted particle size dominating for low Au coverage, with indications that larger Au clusters are negatively charged by interaction through the h-BN monolayer. DFT calculations suggest that the structure of the Au clusters transitions from monolayer to bilayer at a size between 30 and 37 atoms per cluster, in line with our experiment. Bader charge analysis supports the negative charge state of deposited Au. Using vibrational EELS, CO and O₂ are used to probe the activity of these gold model catalysts.

6:00pm **SS+NS-TuA12 Collective Multi-Atom Diffusion in Ag/Ge(110) 1D Nanoisland Growth**, *Shirley Chiang, C.H. Mullet*, University of California, Davis, *M.C. Tringides*, Iowa State University and Ames Lab-USDOE, *M.S. van Zijll, B.H. Stenger, E.S. Huffman, D.J. Lovinger, E.C. Poppenheimer*, University of California, Davis

The growth of Ag deposited on Ge(110) was studied with low energy electron microscopy (LEEM) and scanning tunneling microscopy (STM). The LEEM studies showed the formation of long, one-dimensional (1D) multi-height islands over the temperature range 430C-530C. During deposition, the length of the islands increases at a constant rate ($\sim 10^9$ atoms/sec reaching ~ 20 microns) and constant width (100-200nm) for 9ML total deposition. Stochastic diffusion cannot account for these very high island growth rates. When smaller islands decay, the rate is $\sim 2 \times 10^7$ atoms/sec, which is also exceedingly fast, based on the Ag diffusion and detachment barriers. These high rates are not consistent with independent adatom events and imply multi-atom correlated diffusion. Such collective mass transport must be related to the mobility of the wetting layer. STM images show the crystalline structure of the 1D Ag islands and also indicate that the reconstructed regions between the islands consist of bare Ge. These data are corroborated by LEEM IV curves. Together, they confirm that the wetting layer provides the material for the islands to grow at these high rates.

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