

## Surface Science

Room: 112 - Session SS+AS+EN+NS-TuM

### Nanostructures, Nanoplasmonics and Surface Reactions

Moderator: Bruce Koel, Princeton University

8:20am **SS+AS+EN+NS-TuM2** **ENDOM: A Simple Method to Deposit Nanostructures from Nanowires to Nanopores**, *Ashley Ellsworth, A.V. Walker*, University of Texas at Dallas

A key challenge in the practical application of nanostructures is their effective integration through assembly, patterning and alignment on technologically relevant substrates. We have recently demonstrated a new technique, electroless nanowire deposition on micropatterned substrates (ENDOM), by which to simultaneously synthesize and place nanowires on chemically patterned substrates. The nanowires can be precisely oriented on the surface in arbitrary shapes, such as an arch and around a right angle bend. In ENDOM, the shape of the deposit is controlled by the substrate pattern while its width is controlled by the reaction conditions. By employing longer deposition times and the appropriate substrate patterns, nanopores and nanochannels can be produced. However for sensing and nanoelectronic applications, free standing nanopores and nanochannels are generally employed. We have observed that the nanostructure adhesion to the surface is dependent upon the reagent concentrations. For example in Cu ENDOM, upon reduction of triethanolamine (complexing agent and buffer) concentration, nanowires no longer adhere strongly to the substrate and can be transferred to another substrate. In this presentation, we shall discuss the mechanisms of adhesion, transfer of these nanostructures to other substrates and proof-of-concept studies to synthesize free-standing nanostructures.

8:40am **SS+AS+EN+NS-TuM3** **Chemical Reaction on Photo-excited Plasmonic Nanostructures**, *Sulio Linic*, University of Michigan

INVITED  
We will also show that plasmonic silver nanoparticles, optically excited with low intensity visible light, exhibit direct photo-catalytic activity in a number of oxidation reactions. We will discuss underlying mechanisms associated with these phenomena and predictive models that can capture the outcome of chemical transformations on these materials.<sup>2,3,4</sup> We propose that this new family of plasmonic metal photo-catalysts could prove useful for many heterogeneous catalytic processes that cannot be activated using conventional thermal processes on metals or photo-catalytic processes on semiconductors. I will show an example of such a process.<sup>5</sup>

1. D. B. Ingram, S. Linic, JACS, 133, 5202, 2011
2. Suljo Linic, Phillip Christopher and David B., Nature Materials, 10, 911, 2011.
3. Ingram P. Christopher, H. Xin, S. Linic, Nature Chemistry, 3, 467, 2011.
4. P. Christopher, H. Xin, M. Andiappan, S. Linic, Nature Materials, 11, 1044, 2012.
5. M. Andiappan, J. Zhang, S. Linic, Science, 339, 1590, 2013

9:20am **SS+AS+EN+NS-TuM5** **Structured Noble Metal Nanosurfaces for Biosensing and Bioanalysis (4): TLC-SERS and In Situ Monitoring of Surface-Adsorbed Target Molecules**, *Hiroyuki Takei, J. Saito, K. Watanabe*, Toyo University, Japan, *T. Okamoto*, Riken, Japan, *H. Vieker, A. Beyer, A. Götzhäuser*, Bielefeld University, Germany

Surface-enhanced Raman spectroscopy, SERS, is a powerful technique for in-situ characterization of chemical species. Requisite noble metal nanosurfaces can be prepared with a variety of techniques, ranging from simple vacuum deposition of a metal followed by annealing to intricate processing by electron beam lithography. Some commercial SERS plates are now available, and it is sometimes possible to detect signals from even single molecules if pure. However, in real-world applications, target molecules are often found in mixtures, either containing other Raman-active chemical species or a background material that can overwhelm the target molecule. It can also happen that one might be interested in directly obtaining SERS spectra of chemical species adsorbed on a solid surface.

When faced with a mixture sample, we can carry out separation before SERS measurement. To do so, we incorporated a SERS layer into a thin layer chromatographic plate. While a number of workers have reported applying noble metal nanoparticles after separation with a conventional TLC plate, we feel that such an additional step is cumbersome and does not guarantee uniformity in SERS signals. Our TLC-SERS is prepared with the following procedure; (1) adsorption of 100 nm diameter SiO<sub>2</sub> nanospheres as a dense monolayer on a glass slide, (2) evaporation of gold or silver with

thicknesses up to 100 nm, and (3) spreading of chromatography silica gels. Steps (1) and (2) give rise to surface-adsorbed cap-shaped noble metal nanoparticles. We demonstrate that the TLC-SERS can actually separate mixture samples and provide in-situ SERS spectra. Two examples will be used to demonstrate the utility of our TLC-SERS plates. One deals with a mixture of roughly equal portions of Raman-active chemical species, rhodamine 6 G, crystal violet and BPE. The other is skim milk to which a trace amount of melamine has been added. We show that the three-component mixture could be separated and SERS spectra of all three components could be obtained separately and that melamine added to skim milk could be detected after separation but not before.

For detection of surface-adsorbed chemical species, we prepared silver nanoparticles on a PDMS sheet, using the same protocol as above. The PDMS sheet can be made less than 1 mm thick so that with an appropriate pressurization system, pressure can be applied to the PDMS sheet in order to press the silver nanoparticles against a near-by solid surface to which target molecules are adsorbed. Such a system can be utilized to detect, for example, residual pesticides on agricultural produces. We will demonstrate direct detection of ferbam on a grapefruit.

9:40am **SS+AS+EN+NS-TuM6** **Growth and Intercalation of Cu and Dy on the Basal Plane of Graphite**, *Patricia A. Thiel, D. Appy, E.J. Kwolek, D. Shao, M. Wallingford, M.C. Tringides, J.W. Evans, Y. Han*, Iowa State University, *H. Lei*, Institute of Solid State Physics, CAS, China, *C.-Z. Wang*, Iowa State University

Graphite, and surface processes on graphite, serves as a valuable benchmark for carbon-based materials such as graphene. We have studied copper and dysprosium on graphite, deposited by an e-beam evaporator in UHV and imaged with STM, to determine the characteristic features of nucleation and growth of metal islands. One of the fundamental questions that arises naturally is whether metal nucleates homogeneously on the terraces or whether it nucleates heterogeneously at defect sites. To answer this question we employ several tools, especially a comparison between high-level van der Waals theory for single atom diffusion, and measured island density. We also present evidence for unexpected metal intercalation at the surface of graphite, after treatment at elevated temperature.

11:00am **SS+AS+EN+NS-TuM10** **Surface-Mediated Self-assembly of a Flexible Nucleoside Analogue into Micron-sized Hydrogen-bonded Polymers**, *Jun Wang, P. Bonnesen*, Oak Ridge National Laboratory, *E. Rangel, E. Vallejo, A. Sanchez-Castillo*, Universidad Autónoma del Estado de Hidalgo, Mexico, *H.J. Cleaves*, Tokyo Institute of Technology, Japan, *A.P. Baddorf, B. Sumpter, M. Pan, P. Maksymovych, M. Fuentes-Cabrera*, Oak Ridge National Laboratory

We report on an extraordinary large-scale surface-mediated molecular self-assembly of a flexible nucleoside analogue into a well-organized hydrogen-bonded polymer on Au(111). The nucleoside analogue is (RS)-N<sup>2</sup>-(2,3-Dihydroxypropyl)Adenine (R,S-DHPA), and it consists of the Adenine nucleobase and a tethered glycol group. Employing scanning tunneling microscopy and density functional theory calculations we show that the polymer primarily self-assembles along the Au(111) herringbone reconstruction pattern and extends to the micrometer scale and beyond. The profound propensity toward self-assembly in this case arises from the properties of the glycol moiety of the R,S-DHPA molecule: it is linear and flexible, and these features, together with the specific ways in which the glycol and the Adenine moieties can hydrogen bond, confer R,S-DHPA with a superior self-assembly ability. Our results suggest that nucleoside analogues with flexible acyclic groups could provide the means for synthesizing substrate-supported mesoscale hydrogen-bonded polymers.

#### ACKNOWLEDGEMENTS

This research was conducted at the Center for Nanophase Materials Sciences (CNMS), which is a DOE Office of Science User Facility .

11:20am **SS+AS+EN+NS-TuM11** **Nanowire Kinking during Vapor-liquid-solid Growth: Experiments and Simulations**, *Yanning Wang, Y. Li*, Stanford University, *S. Ryu*, Korea Advanced Institute of Science and Technology, *P.C. McIntyre, W. Cai*, Stanford University

Nanowires (NWs) are promising components for next-generation electronic and optical devices, and the vapor-liquid-solid (VLS) growth is a widely studied method for NW fabrication. However, many fundamental questions regarding the VLS mechanism are still not understood, such as NW kinking during growth. Kinking, a sudden change in axial orientation of nanowires during growth, is a common defect that complicates the directed synthesis of these nanocrystals. Understanding such defects is important for better control of the NW orientation, yield and quality required for applications.

Experimental studies of coherent kinking of germanium nanowires detect two different kinking structures. One structure, which is most pronounced for Ge NW's of diameter close to 20 nm, involves kinking from a vertical  $\langle 111 \rangle$  to  $\langle 110 \rangle$  growth axis on Ge (111) single crystal substrates. The other involves kinking from the vertical  $[111]$  axis to an inclined  $\langle 111 \rangle$  growth direction for NWs of  $> 30$  nm diameter.

The balance of capillary forces driving these two modes of kinking are analyzed quantitatively. We developed a 3D multi-phase field model for VLS NW growth. The model captures the NW tapering and sidewall facets in good agreement with experimental observations. The model predicts the steady-state NW growth velocity is a linear function of the vapor chemical potential and the inverse of catalyst diameter, providing a confirmation of the Gibbs-Thomson effect in nanowire growth. With anisotropic interfacial energies, the model shows the NW growth orientation dependence on catalyst diameter and hence it provides an explanation of the NW kinking in the steady-state growth regime. In this model, we introduce a perturbation force to induce the NW structural transition and the free energies are evaluated at different stages during the droplet movement. It enables us to discuss the instability of the catalyst droplet for different pedestal structures, which is important for understanding the onset of the kinking at the NW base.

11:40am **SS+AS+EN+NS-TuM12 Adsorption of Water and Bromine on Gold Nanoclusters Investigated by Neutralization in Low Energy Alkali Ion Scattering**, *Christopher Salvo, J. Keagy, J.A. Yarmoff*, UC Riverside

Small gold (Au) nanoclusters have been heavily studied because of their intriguingly high catalytic activity, especially when compared to bulk gold. We employ a specialized method of Low Energy Ion Scattering (LEIS) to probe the electronic properties of nanoclusters prepared with a variety of methods. The experiments measure the neutralization probability of singly scattered alkali ions, which is acutely sensitive to the local electrostatic potential a few Å's above the surface. Because the Au atoms are much more massive than the substrate atoms, this method allows the signal from the nanoclusters to be separated from that of the substrate so that the neutralization reflects the local properties of the cluster surfaces. Earlier work had demonstrated that the neutralization is a function of cluster size, and that it is enhanced for the smallest clusters presumably because they are negatively charged [1]. The work presented here investigates the adsorption of water and Br on Au nanoclusters grown on TiO<sub>2</sub> or SiO<sub>2</sub>. There are multiple factors that can contribute to a change in the neutralization of the scattered ions, such as the cluster size, shape, or charge state. When Br attaches to a nanocluster, the neutralization decreases presumably due to charge transfer from the cluster to the electronegative Br atom. Surprisingly, it is found that the neutralization of scattered K<sup>+</sup> ions increases in the presence of adsorbed water at liquid nitrogen temperatures. Furthermore, the increase of neutralization for adsorbed water is independent of whether the water or the Au is deposited first. Possible explanations for these observations will be discussed.

[1] G.F. Liu, Z. Sroubek and J.A. Yarmoff, Phys. Rev. Lett., **92**, 216801 (2004).

12:00pm **SS+AS+EN+NS-TuM13 Optical Constants Measured for Fe, Ni and Pd by Reflection Electron Energy-Loss Spectroscopy Spectra**, *H. Xu, B. Da, S.F. Mao*, University of Science and Technology of China, *J. Toth, K. Tokesi*, Institute for Nuclear Research, Hungarian Academy of Sciences (ATOMKI), *Zejun Ding*, University of Science and Technology of China

The energy loss function (ELF), which is directly related to optical constants of a solid, dominates the energy loss process of an electron moving inside or flying nearby a solid. It is therefore able to obtain optical constants by surface electron spectroscopy technique. Accurate measurement of optical data by optical methods in a photon energy range up to 10<sup>2</sup> eV is still insufficient; delicate experimental conditions are required when measuring data in vacuum ultraviolet region (20-50 eV). Fortunately, such information is essentially contained in and, therefore, can be extracted from a reflection electron energy loss spectroscopy (REELS) spectrum due to the shorter information depth of signal electrons compared with that of photons.

In the present work, reflection electron energy loss spectra of transition metals, Fe, Ni and Pd, were measured at several primary energies ranging from 0.5 keV up to 5 keV and in a wide energy-loss range. Prior to the measurements in situ cleaning of the sample surface was performed using Ar<sup>+</sup> ion sputtering with proper current density and time. Vacuum was kept as 1.5×10<sup>-9</sup> mbar in the measurement chamber during the REELS measurements. Surface cleanness was checked by XPS in several cases after the REELS measurements. An improved reverse Monte Carlo simulation for determination of optical constants via accurate description of electron inelastic transport process was performed. ELF of those metals were

extracted from experimental REELS spectra. The accuracy of the obtained optical data has been confirmed by f-sum and ps-sum rules. Comparisons of our data with other sources from either experimental measurements or density functional theory calculation are given.

# Authors Index

**Bold page numbers indicate the presenter**

## — A —

Appy, D.: SS+AS+EN+NS-TuM6, 1

## — B —

Baddorf, A.P.: SS+AS+EN+NS-TuM10, 1

Beyer, A.: SS+AS+EN+NS-TuM5, 1

Bonnesen, P.: SS+AS+EN+NS-TuM10, 1

## — C —

Cai, W.: SS+AS+EN+NS-TuM11, 1

Cleaves, H.J.: SS+AS+EN+NS-TuM10, 1

## — D —

Da, B.: SS+AS+EN+NS-TuM13, 2

Ding, Z.J.: SS+AS+EN+NS-TuM13, 2

## — E —

Ellsworth, A.A.: SS+AS+EN+NS-TuM2, **1**

Evans, J.W.: SS+AS+EN+NS-TuM6, 1

## — F —

Fuentes-Cabrera, M.: SS+AS+EN+NS-TuM10, 1

## — G —

Göhlhäuser, A.: SS+AS+EN+NS-TuM5, 1

## — H —

Han, Y.: SS+AS+EN+NS-TuM6, 1

## — K —

Keagy, J.: SS+AS+EN+NS-TuM12, 2

Kwolek, E.J.: SS+AS+EN+NS-TuM6, 1

## — L —

Lei, H.: SS+AS+EN+NS-TuM6, 1

Li, Y.: SS+AS+EN+NS-TuM11, 1

Linic, S.: SS+AS+EN+NS-TuM3, **1**

## — M —

Maksymovych, P.: SS+AS+EN+NS-TuM10, 1

Mao, S.F.: SS+AS+EN+NS-TuM13, 2

McIntyre, P.C.: SS+AS+EN+NS-TuM11, 1

## — O —

Okamoto, T.: SS+AS+EN+NS-TuM5, 1

## — P —

Pan, M.: SS+AS+EN+NS-TuM10, 1

## — R —

Rangel, E.: SS+AS+EN+NS-TuM10, 1

Ryu, S.: SS+AS+EN+NS-TuM11, 1

## — S —

Saito, J.: SS+AS+EN+NS-TuM5, 1

Salvo, C.R.: SS+AS+EN+NS-TuM12, 2

Sanchez-Castillo, A.: SS+AS+EN+NS-TuM10, 1

Shao, D.: SS+AS+EN+NS-TuM6, 1

Sumpter, B.: SS+AS+EN+NS-TuM10, 1

## — T —

Takei, H.: SS+AS+EN+NS-TuM5, **1**

Thiel, P.A.: SS+AS+EN+NS-TuM6, **1**

Tokesi, K.: SS+AS+EN+NS-TuM13, 2

Toth, J.: SS+AS+EN+NS-TuM13, 2

Tringides, M.C.: SS+AS+EN+NS-TuM6, 1

## — V —

Vallejo, E.: SS+AS+EN+NS-TuM10, 1

Vieker, H.: SS+AS+EN+NS-TuM5, 1

## — W —

Walker, A.V.: SS+AS+EN+NS-TuM2, 1

Wallingford, M.: SS+AS+EN+NS-TuM6, 1

Wang, C.-Z.: SS+AS+EN+NS-TuM6, 1

Wang, J.: SS+AS+EN+NS-TuM10, **1**

Wang, Y.: SS+AS+EN+NS-TuM11, **1**

Watanabe, K.: SS+AS+EN+NS-TuM5, 1

## — X —

Xu, H.: SS+AS+EN+NS-TuM13, 2

## — Y —

Yarmoff, J.A.: SS+AS+EN+NS-TuM12, 2