

Tuesday Afternoon, October 30, 2012

Applied Surface Science

Room: 20 - Session AS+BI-TuA

Surface Analysis of Materials Using Vibrational Techniques (2:00-3:20 pm)/ Multi-Technique Analysis (4:00-6:00 pm)

Moderator: D. Roy, National Physical Laboratory, UK, C. Szakal, National Institute of Standards and Technology

2:00pm AS+BI-TuA1 Vibrational Spectrum and Stability of the Long-Debated Models for the $(\sqrt{7}\times\sqrt{7})R19^\circ$ Phase of S/Cu(111), *M. Alcantara Ortigoza, M. Aminpour, T.S. Rahman*, University of Central Florida

Recently, the structure of the copper sulfide overlayer formed on Cu(111) upon sulfur exposure has attracted attention because it serves as a substrate to form MoS₂ monolayers and MoS_x nanostructures in a controlled manner, which may have numerous technological applications. In the past, at least eight experimental techniques have been used to characterize the $(\sqrt{7}\times\sqrt{7})R19^\circ$ Cu-S overlayer on Cu(111) and to support or refute a large number of possible models but, as yet, at least three models are still in dispute. In this study, we provide firmer arguments to resolve the structure of CuS/Cu(111) at the atomic scale. Specifically, we perform density-functional-theory calculations of the total energy and the vibrational spectrum of the proposed structures to (1) attest their dynamical stability; (2) compare their thermodynamic stability as obtained from the total free energy; and (3) provide the vibrational frequencies that uniquely fingerprint these structures and which may serve for further experimental confirmation or refutation.

This work was supported in part by DOE grant DE-FG02-07ER15842

[1] Kim et al., Langmuir 27, 11650 (2011)

[2] Alfonso J. Phys. Chem. C 115, 17077 (2011)

2:40pm AS+BI-TuA3 First-principle Investigation of the Stability and Vibrational Spectrum of MoS_x Nanostructures Grown on Cu(111), *M. Aminpour, M. Alcantara Ortigoza, T.S. Rahman*, University of Central Florida

Recent experiments have successfully synthesized MoS_x nanostructures in a controlled manner by evaporating Mo adatoms on the copper sulfide monolayer that forms on Cu(111) upon sulfur preloading[1,2]. Based on STM observations and total-energy calculations based on density functional theory, including *ab initio* van-der-Waals interactions, several structures for MoS_x/Cu(111) have been proposed. In this study, we investigate the plausibility of those structures and provide elements for further experimental substantiation or refutation. Namely, we perform density-functional-theory calculations (also including *ab initio* van-der-Waals interactions) of the total energy and the vibrational spectrum of the proposed structure to (1) attest their dynamical stability; (2) compare their thermodynamic stability as obtained from the total free energy; and (3) provide the vibrational frequencies that uniquely fingerprint the proposed structures.

[1] Kim et al., Langmuir 27, 11650 (2011)

[2] Le et al., PRB 85, 075429 (2012)

This work was supported in part by DOE grant DE-FG02-07ER15842

4:40pm AS+BI-TuA9 New Desorption Mass Spectrometry Approaches for Inorganic Particle Analysis, *C. Szakal, A.R. Konicek, M. Ugelow, D.S. Simons, A. Herzog, R.D. Holbrook*, National Institute of Standards and Technology

Chemical characterization of inorganic particles becomes more difficult as the particle sizes decrease. For application areas ranging from semiconductor failure analysis to nanotoxicology, the distinct chemical signatures of both the surface and bulk of particles can provide insight into system mechanisms and behavior. New methods that aim to explore the surface chemistry of inorganic nanoparticles for both their elemental and organic overlayer signatures will be presented. Specifically, the “static” nature of time-of-flight-secondary ion mass spectrometry is used to provide mass spectral characterization at the very surfaces and sub-surfaces of well-prepared (via drop-on-demand inkjet printing) and well-characterized (via scanning transmission electron microscopy and ultraviolet-visible spectroscopy) nanoparticle aggregates. This information can potentially be combined with full aggregate analysis using more elementally sensitive dynamic SIMS instrumentation once target species are identified with ToF-SIMS. Both sets of SIMS data can be used to obtain a chemical distribution

of signals throughout the particle depths. Additionally, the question of whether the centers of inorganic nanoparticle aggregates are chemically similar to the overall aggregate surfaces will be explored.

5:00pm AS+BI-TuA10 TOF SIMS Analyses of Ga Concentration as a Function of Distance from FIB Milled Features, *C. Santeufemio*, University of Massachusetts, *B.P. Gorman*, Colorado School of Mines, *C. Zhou, F.A. Stevie*, North Carolina State University, *L.A. Giannuzzi*, L.A. Giannuzzi & Associates LLC

Focused ion beams are routinely used for site-specific specimen preparation, nanopatterning, and analysis. It is important to know whether the primary ion beam is present outside the region targeted for ion beam modification. A previous report showed that $> 1E12$ atoms/cm² of Ga was detected up to several millimeters away from a focused ion beam (FIB) milled feature [1]. In this work, we reproduce this earlier report using a blind study of 2 different state-of-the-art Ga-FIB columns. Each column was used to FIB mill a 100 μm x 100 μm square into a (100) Si wafer at 30 keV with a nominal beam current of 20 nA at constant dose. Time of flight secondary ion mass spectrometry (TOF SIMS) was used to measure Ga depth profiles and Ga surface concentration at a distance up to 6.5 mm from the FIB milled square. In column “A,” $> 1E12$ atoms/cm² of Ga was detected up to ~ 5 mm from the FIB milled square. Column “B” showed considerably less Ga with $> 1E12$ atoms/cm² detected within ~ 250 μm from the FIB milled square. The depth profiles show that the Ga concentration was fairly uniform to a depth of ~ 2 nm from the surface for column “A” and ~ 1 nm into the surface for column “B”. Using SRIM [2] simulations we determine that these implantation depths correspond to an ion energy < 500 eV. The consequences of the presence of Ga at long distances from desired FIB milled features will be discussed.

[1] U. Muehle, R. Gaertner, J. Steinhoff, W. Zahn, “Characterisation of Ga-distribution on a silicon wafer

after inline FIB-preparation using inline ToFSIMS,” M. Luysberg, K. Tillmann, T. Weirich (Eds.): EMC 2008, Vol. 1: Instrumentation and Methods, pp. 749–750, DOI: 10.1007/978-3-540-85156-1_375, © Springer-Verlag Berlin Heidelberg 2008

[2] www.srim.org

5:20pm AS+BI-TuA11 The Surface Characterization of Oligo(Ethylene Glycol) Functionalized Gold Nanoparticles, *A. Rafati, D.G. Castner*, University of Washington

Extensive surface analysis of available gold nanoparticles (AuNPs) is crucial to understand how their production and functionalization affects their final properties. This information is needed to improve the performance of engineered nanoparticles in research and commercial applications. Ethylene glycol functionality is desirable owing to the benefits such as the reduction of protein adhesion which if not properly controlled can lead to activation of an immune response and/or clearance.

In this work AuNPs ~14nm and ~40nm in diameter are synthesized and functionalized with 1-undecanethiol (HS-CH₂)₁₁ terminated with either (OEG)₄OH or (OEG)₄CH₃. The AuNPs were characterized with transmission electron microscopy (TEM), time of flight secondary ion mass spectrometry (ToF-SIMS), X-ray photoelectron spectroscopy (XPS), attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) and low energy ion scattering (LEIS). These studies provided both qualitative and quantitative information about the functionalization of the AuNPs with an OEG containing monolayer.

TEM showed the 14nm AuNPs had a narrower size distribution and more spherical shape than the 40nm AuNPs. ToF-SIMS clearly differentiates the two SAMs based on the C₃H₇O⁺ peak attributed to the CH₃ terminated SAM. Angle-resolved XPS high-resolution C1s spectra from flat gold samples at photoelectron take-off angles of 0°, 55° and 75° from the surface normal shows an increase in the ether component and reduction in CH with an increase in take-off angle. The changes in these values are comparable for both SAMs. This illustrates the increased presence of ethylene glycol monomers in the outer surface region and shows little difference between the two types of terminal functional groups. The 40 nm AuNPs show a slightly greater surface OEG concentration than 14 nm AuNPs, possibly indicating a more vertically oriented SAM on the 40 nm AuNPs. FTIR indicates similar crystalline CH₂ backbones for all samples, however it appears the structure of OEG head groups are less crystalline on the 14nm AuNPs. This likely results in thicker and/or higher density SAMs on the 40 nm AuNPs compared to the 14nm AuNPs. This is consistent with the nearly identical XPS determined surface elemental compositions determined for OEG SAMs on the two different sized AuNPs. This is contrary to previously XPS results observed for AuNPs functionalized with COOH SAMs [1].

1. Techane, S.D., L.J. Gamble, and D.G. Castner, *Multi-technique Characterization of Self-assembled Carboxylic Acid Terminated Alkanethiol Monolayers on Nanoparticle and Flat Gold Surfaces*. J Phys Chem C Nanomater Interfaces, 2011. **115**(19): p. 9432-9441.

5:40pm **AS+BI-TuA12 Characterization Challenges of Ceria Nanoparticles: When is a Nanoparticle Not a Nanoparticle?**, **D.R. Baer**, P. Munusamy, A.S. Karakoti, EMSL, Pacific Northwest National Laboratory, S.V.N.T. Kuchibhatla, Battelle Science and Technology India, S.S. Seal, University of Central Florida, S. Thevuthasan, C.F. Windisch, Jr., EMSL, Pacific Northwest National Laboratory

Cerium oxide (ceria) nanoparticles are widely studied for their current and potential use in catalytic, energy, environmental protection and bio-medical applications. The performance of ceria in many of these applications depends on the ability of cerium to switch between +3 and +4 oxidation states. Unfortunately the physical and chemical properties of ceria nanoparticles reported in the literature are often inconsistent and at times contradictory. Our research involves examination of the properties of ceria nanoparticles as they apply to materials science research and impact biological systems. We have found that it is possible to obtain what appears to be a self-consistent understanding of these particles by integrating dynamic light scattering, surface potential and UV-Vis adsorption measurements made in solution with *ex situ* x-ray photoelectron spectroscopy (XPS), x-ray diffraction (XRD) and transmission electron microscopy (TEM) observations. These measurements have demonstrated that a simple understanding of the chemical state of ceria nanoparticles as dependent on size is not adequate and has led to some of the inconsistent results in the literature. However, Raman and microXRD of wet ceria nanoparticles (pseudo *in situ*) show that the nature of the particles in solution is even more complex than indicated by the above measurements. Raman and microXRD measurements indicate that both the chemical state and structure of the smallest nanoparticles can change depending on the nature of the solution. In solutions with low oxygen activity these particles have a ceria structure with cerium in +3 oxidation state while in highly oxidizing conditions the chemical state switches to +4 but the structure can be highly defected (XRD) and appears to be some type of cerium oxyhydroxide (Raman). The extent of the transformation depends on the size of the particles and appears complete for the smallest particles and partial or possibly not present for larger particles. These measurements demonstrate that the environment, size and time can impact the nature of these particles and that a variety of analysis methods – *in situ* as well as *ex situ* – are required for comprehensive understanding of ceria nanoparticle behaviors. Acknowledgement - Aspects of the work have been supported by the National Institute of Environmental Health Sciences under grant NIH U19 ES019544. Portions of this work were conducted in the Environmental Molecular Sciences Laboratory, a DOE user facility operated by Pacific Northwest National Laboratory for the Office of Biological and Environmental Research of the DOE.

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