In-Situ Spectroscopy and Microscopy Focus Topic
Room: 313 - Session IS+AS+MC+SS-TuA

Environmental Electron Microscopies
Moderator: Jorge Boscoboinik, Brookhaven National Laboratory

2:20pm **IS+AS+MC+SS-TuA1 Nanocrystal Shape Evolution during Growth**, ***Haimei Zheng***, Lawrence Berkeley Lab, University of California, Berkeley **INVITED**

An understanding of nanocrystal shape control mechanisms during growth is critical for the design of novel functional materials with surface-enhanced properties. However, the atomic level shape evolution of nanocrystals during growth is mostly unknown due to the lack of direct observation. We use liquid cells under transmission electron microscope (TEM) to study the growth of Pt or Pt-alloy nanoparticles in situ, where growth either by nanoparticle attachment or by monomer attachment has been observed. First, I will present Pt-Fe nanorods formation by shape-directed nanoparticle attachment under the electron beam. Winding polycrystalline nanoparticle chains are achieved at the early stage then they are straightened to yield single-crystal nanorods. Tracking their growth trajectories allows us to distinguish the force fields exerted by single nanoparticles and nanoparticle chains. Second, I will show the observation of platinum nanocube growth and the facet development. By in situ imaging with high spatial and temporal resolution, we have identified unique growth mechanisms that cannot be predicted by Wulff construction or other existing growth theorems. We found layer-by-layer growth of the {100} and {111} facets while the {110} facets show steps. We also found that the growth rates of these facets are similar until the {100} facets stop growth. Hence, the distance from {100} facets to the crystal center is fixed throughout the subsequent growth. The {110} facets are eliminated when two adjacent {100} facets meet. Lastly, the growth of {111} facets fills the corners to complete a nanocube. Our calculation suggests oleylamine ligand mobility on the facet is responsible for the arresting of {100} growing facets. References:

1. Liao et al. ¬“Facet Development during Platinum Nanocube Gro¬¬wth” Science in review.

2 . H. G. Liao, L. Cui, S. Whitelam, H. Zheng, "Real time imaging Pt3Fe nanorod growth in solution." Science 336, 1011 (2012).

3. We used TEM facility at National Center for Electron Microscopy of Lawrence Berkeley National Laboratory (LBNL), which is supported by the Office of Basic Energy Sciences, Division of Materials Sciences and Engineering of the U.S. Department of Energy under Contract #DE-AC02-05CH11231. H.Z. thanks the support of DOE Office of Science Early Career Research Program.

3:00pm **IS+AS+MC+SS-TuA3 Microfluidic Cell for *In Situ* Scanning Electron Microscopy of Hydrated Dynamic Systems**, ***Christopher Brown***, *A. Yulaev*, *A. Kolmakov*, National Institute of Standards and Technology (NIST)

The ability to conduct nanoscale imaging of fluid hydrated dynamic systems is a long sought goal within the scientific community. While improvement of commercial instrumentation and environmental cells has enabled in situ imaging of fluid hydrated systems using transmission electron microscopy (TEM) at the nanoscale, additional opportunities exist in implementing in situ techniques within scanning electron microscopy (SEM) instruments equipped with fluidic cells. Factors that motivate this work include: ubiquity and reduced cost of SEM instrumentation compared to TEM, drastically reduced restrictions on the sample size, and greater flexibility of systems and detectors designed for the SEM compared to TEM.

In this communication we report on development of the microfluidic environmental cell designed for in situ studies of fully hydrated dynamic objects. We describe strategies and experimental results that enable improved in situ imaging using the SEM, including development of electron transparent graphene windowed devices that increase signal-to-noise ratio of images of fluid hydrated objects. Limiting factors of in situ imaging of hydrated samples within the SEM are discussed including radiolysis and decreased electron beam penetration into liquid cells compared to higher acceleration voltage electron microscopy modalities.

3:20pm **IS+AS+MC+SS-TuA4 Liquid Jet –X-ray Photoelectron Spectroscopy and MD Simulations indicate that Li Cations in Aqueous Solutions Exhibit High Surface Propensity**, ***Kathryn Perrine***, *M.H.C. Van Spyk, M.J. Makowski, A.C. Stern, K. Parry, D.J. Tobias,* University of California Irvine, *A. Shavorskiy*, *H. Bluhm*, Lawrence Berkeley National Laboratory, *B. Winter*, Helmholtz-Zentrum Berlin für Materialien und Energie/Elektronenspeicherring BESSY II, Germany, *J.C. Hemminger*, University of California Irvine

Ions impact chemistry at the aqueous liquid/vapor interface in environmental chemistry, electrochemistry and biomolecular chemistry. Ions are characterized as structure makers or breakers for protein mixtures, and the trend is known as the Hofmeister series.[1] The Born electrostatic model of ions at interfaces has shown that ions should be repelled from the liquid/vapor interface due to a decrease in free energy when solvation by water occurs.[2] Molecular dynamic (MD) simulations and recent experimental studies have shown that anions tend to adsorb to the liquid interface in an inverse Hofmeister trend.[3, 4] Our synchrotron based XPS studies carried out over the last five years have provided experimental evidence that most cations follow classical ionic solution behavior and are repelled from the liquid/vapor interface, whereas some anions exhibit significant propensity for the surface. In this talk we present our recent experiments on Li salt solutions. Our experiments indicate that unlike larger cations, Li^+ is not repelled from the interface and has a significant surface propensity.

Liquid jet-X-ray photoelectron spectroscopy (LJ-XPS) is used to explore the relative ion concentrations at different depths in aqueous salt solutions. Low photoelectron kinetic energies are used to probe the surface of solutions yielding relative ionic concentrations that are present at the liquid/vapor interface. Higher photoelectron kinetic energies probe deeper into the bulk of aqueous solutions. The relative ionic concentrations of solutions prepared from lithium halide salts are compared to potassium halide solutions at different depths. MD simulations support our studies and suggest that Li^+ cations have interfacial propensity due to factors such as the tight water solvation shell on the Li^+ ions. Density profiles reveal anion and Li^+ ion adsorption to the liquid/vapor interface. In addition, we also compare various concentrations of KI and LiI aqueous solutions to determine ion adsorption at the aqueous interface.

1. K. D. Collins and M. W. Washabaugh, *Quarterly Reviews of Biophysics*, 1985, **18**, 323-422.

2. M. Born, *Zeitschrift Fur Physik*, 1920, **1**, 45-48.

3. P. Jungwirth and D. J. Tobias, *Journal of Physical Chemistry B*, 2002, **106**, 6361-6373.

4. D. J. Tobias, A. C. Stern, M. D. Baer, Y. Levin and C. J. Mundy, *Annual Review of Physical Chemistry, Vol 64*, 2013, **64**, 339-359.

4:20pm **IS+AS+MC+SS-TuA7 Complementary Microscopy and Spectroscopy Investigations of the Initial Oxidation Stages of Binary Alloy Thin Films**, ***Judith Yang***, University of Pittsburgh **INVITED**

The transient stages of oxidation − from the nucleation of the metal oxide to the formation of the thermodynamically stable oxide − represent a scientifically challenging and technologically important terra incognito. These issues can only be understood through detailed study of the relevant microscopic processes at the appropriate length scale in situ. We are studying the dynamics of the initial and transient oxidation stages of a metal and alloys with complementary in situ methods - ultra-high vacuum (UHV) transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS). We have previously demonstrated that the formation of epitaxial Cu2O islands during the transient oxidation of Cu and Cu-Au thin films bear a striking resemblance to heteroepitaxy, where the initial stages of growth are dominated by oxygen surface diffusion and strain impacts the evolution of the oxide morphologies. We are presently investigating the early stages of oxidation of binary alloys where both elements compete to oxidize. Specifically, we are studying Cu-Ni and Ni-Cr single crystal thin films as a function of relative concentration, oxygen partial pressures and temperatures. For Cu-Ni oxidation, the addition of Ni causes the formation Cu2O and/or NiO where the oxide type(s) and the relative orientation with the film depend on the Ni concentration, oxygen partial pressure and temperature. For Ni-Cr model alloys containing 4, 8 and 16 at.% Cr and isothermally oxidized at 600°C and 10-7 to 10-3 torr O2 pressure, our XPS experiments reveal that after 2 min of oxidation only Cr2O3 forms on the surface of all three alloys. However, with further exposure (i.e., 30 min or 2 h), a competitive growth between Cr2O3 and NiO under all the tested conditions is clear. These XPS data are remarkable results, since prior studies reported in the literature suggest that NiO + internal Cr2O3 or NiO/NiCr2O4/Cr2O3+ internal Cr2O3 should form at least for the lower Cr content (4 and 8%) alloys. These experiments will be complemented with electron microscopy of scale cross sections to better understand the competitive nucleation and growth processes as a function of the oxygen partial pressure.

5:00pm **IS+AS+MC+SS-TuA9 Direct Observation of Structure Controlled Carbon Growth by Environmental TEM**, *J. Kling, T.W. Hansen*, ***Jakob Wagner***, Technical University of Denmark **INVITED**

In order to meet the increasing demand of faster and more flexible electronics and optical devices and at the same time decrease the use of the critical metals, carbon based devices are in fast development. Furthermore, the rich resource of carbon element limits the need for recycling and the material supports the friendly environment approach.

Layered carbon structures spanning from graphene to few layered graphite are used for extremely compact devices with outstanding performance [1,2]. A relative cheap and easy way to produce layered carbon structures on the large scale is via chemical vapor deposition (CVD) growth on catalysts like copper and nickel. However, the exact growth mechanism is still under debate and is most likely dependent on precursor pressure and growth temperature.

Here, we have used environmental transmission electron microscopy (ETEM) to follow the growth of layered structures directly at the atomic level and thereby coupling growth rate and quality of the material on the local scale to the growth parameters. Acetylene and methane are exposed to the catalyst (Ni or Cu) in situ in the microscope at pressures ranging from 0.1Pa 100Pa at temperatures ranging from 500-700C. Following the subsequent appearance of carbon layers allows for determination of instant growth rates under controlled conditions.

Single walled carbon nanotube (SWCNT) based electronics is another way of addressing the environment friendly approach of faster and better electronics. In order to exploit the potential of SWCNTs in the electronic industry fully, selective growth of either conducting or semiconducting tubes is of high importance. Growing the tubes in situ in the ETEM under relevant growth conditions gives fundamental insight in the parameters controlling the chirality and thereby the electronic properties of the SWCNTs.

References:

[1] K. S. Novoselov, S. V. Morozov, T. M. G. Mohinddin, L. a. Ponomarenko, D. C. Elias, R. Yang, I. I. Barbolina, P. Blake, T. J. Booth, D. Jiang, J. Giesbers, E. W. Hill, and a. K. Geim, Phys. Status Solidi **244**, 4106 (2007).

[2] F. Schwierz, Proc. IEEE **101**, 1567 (2013).

5:40pm **IS+AS+MC+SS-TuA11 *In Situ* Energy Loss Spectroscopy, A Novel Approach to the Characterization of Surfaces during MBE Growth**, ***Philippe Staib***, Staib Instruments, Inc.

A new energy analyzer for Auger Electron Spectroscopy (AES), the Auger Probe, is able to operate in growth vacuum chambers to measure *in-situ during growth* the composition of the surface [1,2,3]. The primary beam is provided by the RHEED electron gun at a very grazing incidence angle (2 to 3 degrees). The analyzer is also used in EELS mode to measure Characteristic Energy Losses (CEL). The use of a grazing incidence angle strongly enhances the strength of the energy losses peaks, which become more prominent than the elastic line

EELS data from the Auger Probe are presented showing the evolution of the CEL distributions during oxidation (ZnO), during thermal de-oxidation of GaSb, and during growth of binary and ternary materials (GaAsSb). Surprisingly, even during deposition of homoepitaxial layer, the CEL distribu tions show a marked dependence upon the flux of material to the sample which can reflect the formation of physi- rather than chemisorbed layers and the smoothness of the surface [4].

The CEL spectra cannot be interpreted simply, due to the strong overlapping of multiple excitations of single energy losses. A model is presented that takes into account the probability distribution for multiple losses, and allows extraction of the el ementary energy loss lines from the distribution. Using this model, ac curate energy loss values can be measured and an effective electron density can be calculated. The intensity of the extracted energy losses versus the intensity of the elastic peak is a measure of the ratio d/ l between the electron path length d and mean inelastic free path l of the specific loss. The inelastic mean free path for each loss line can be deducted using d values from monte-carlo simulation of the electron trajectories and the intensity ratio of the loss peak vs. elastic peak.

Special thanks to S. Svensson and W. Sarney of ARL for their collaboration during measurements used in this work.

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[1] P. Staib, J. Vac. Sci. Technol. B 29(3), (2011).

[2] W.L. Calley, et al. J. Vac. Sci. Technol. B, (2013).

[3] P. Staib in "*In situ* Characterization of Thin Film Growth", Edited by G. Koster and G. Rijnders, Woodhead Publishing In Materials, (2011)

[4] Strawbridge B., Shinh RK.,Beach C.,Mahajan S., Newman N., J. Vac. Sci. Technol. A 24 (5) 1776 (2006) .

6:00pm **IS+AS+MC+SS-TuA12 Selective Staining for Enhanced Spectroscopic Identification of Domains in Immiscible Polymer Blends by Micro-Raman Spectroscopy**, ***Nicholas Heller***, *C.R. Clayton*, SUNY Stony Brook, *S.L. Giles, J.H. Wynne*, Naval Research Laboratory, *M.J. Wytiaz, M.E. Walker*, Sherwin-Williams Company

Blends of incompatible polymers combined with fillers and pigments were used to produce unique low reflectance thermoset coatings. Understanding the origins of low reflectance from the coatings was approached through microscopy, thermal analysis and spectroscopic analysis of both pigmented and control clear coatings. Polymeric phase separation was confirmed by the presence of two distinct glass transition temperatures. Microscopy revealed random surface features for the pigmented coatings. Therefore, the pigments and fillers were removed to observe the polymer-polymer interactions within the blend under curing conditions. Identification of the polymeric domains was obtained using Raman spectroscopy mapping of cross-section samples embedded within a polyester resin. Cross-section samples of coatings were utilized to isolate encapsulated polymer domains from the continuous polymer network to minimize spectral averaging from both domains. Raman analysis of the blends was compared to cured films generated using the individual resins. The embedding process produced a marker peak in one phase and in one individual resin. The marker peak was found to be from styrene monomer and was found to selectively bind to one component of the polymer blend, based on polar and hydrogen bonding characteristics..

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