Nanometer-scale Science and Technology Division
Room: 19 - Session NS+HC+SS-MoA

Oxides in Nanotechnology
Moderator: Nancy Burnham, Worcester Polytechnic Institute

2:00pm **NS+HC+SS-MoA2 Epitaxial Growth and Characterization of WO3 and $WO_{3-\delta}$ Thin Films**, ***Yingge Du***, *Z. Yang, Z.H. Zhu, C. Wang*, Pacific Northwest National Laboratory

Tungsten trioxide (WO_3) based thin-film materials are of significant importance because of their diverse structures and wide range of properties. These materials have found widespread applications in display devices, electrochromic "smart" windows, gas sensors, catalysis, and photocatalysis. Investigations of WO_3 films in epitaxial form offer definite advantages over porous or polycrystalline forms for fundamental science studies. For example, the ability to detect and eliminate secondary phases and surfaces simplifies the material system and makes it easier to establish defensible cause-and-effect relationships. While amorphous, polycrystalline, and epitaxial WO_3 films have been prepared by several methods such as evaporation of WO_3, sputtering, and pulsed laser deposition, the growth of epitaxial WO_3 films by molecular beam epitaxy (MBE) is much less explored.

We examined three different ways to grow epitaxial WO_3 films by MBE – by evaporating WO3 powders from an effusion cell, by evaporating WO_x surface layers formed on W metal surface, and by evaporating tungsten metal in an oxidizing environment. Epitaxial films are formed in all three cases but the growth characteristics vary significantly. The films from the first two methods are found to grow as stoichiometric islands first, while the third method leads to layer by layer growth, with significant amount of ordered oxygen vacancies. The films are characterized *in-situ* by RHEED and XPS, and *ex-situ* by XRD, SIMS, and STEM.

2:20pm **NS+HC+SS-MoA3 Oxide Surfaces: Structure, Adsorption, Growth**, ***Ulrike Diebold***, TU Wien, Austria **INVITED**

Fundamental investigations into the surface properties of oxides have experienced a continued growth. The reasons for this increasing interest are quite clear: after all, most metals are oxidized under ambient conditions, so in many instances it is the oxidized surface that deserves our attention. In addition, metal oxides exhibit an extremely wide variability in their physical and chemical properties. These are exploited in established and emerging technologies such as catalysis, gas sensing, and energy conversion schemes, where surfaces and interfaces play a central role in device functioning. Hence a more complete understanding of metal oxide surfaces is desirable from both fundamental and applied points of view.

By using Scanning Probe Microscopy measurements, in combination with Density Functional Theory calculations and area-averaging spectroscopic techniques, great strides have been made in understanding the atomic-scale properties of the surfaces of these complex materials.

In the talk I will give examples drawn from recent studies on several metal oxide systems, including TiO_2, Fe_3O_4, In_2O_3, ZrO_2, and perovskites. I will point out the advantages of directly viewing, and manipulating, point defects and single molecules with atomic precision, and how inspecting central processes such as charge transfer to adsorbates can further a deep mechanistic understanding. I will also discuss new opportunities based on recent technique development such as Scanning Force Microscopy, and the challenges and possible rewards in exploring more complex materials.

3:00pm **NS+HC+SS-MoA5 Imaging and Sensor Applications of infiltrated Zinc Oxide**, ***Leonidas Ocola***, Argonne National Laboratory, *V. Sampathkumar*, University of Chicago, *N. Kasthuri, R.P. Winarski*, Argonne National Laboratory, *Y. Wang, J.H. Chen*, University of Wisconsin - Milwaukee

With the increased portfolio of materials that can be deposited using atomic layer deposition (ALD) there has been an increased interest in infiltrated metal oxides such as zinc oxide for novel applications. We find that ZnO metal oxide ALD infiltration can be useful for nanoscale resolution imaging of biological samples in electron and X-ray microscopy and to fabricate novel UV and gas nanosensors with high sensitivity. The ALD infiltration utilizes similar concepts of the ALD coating process with the significant difference in process exposure times, pressure, and purpose. The purpose is to allow the precursor gases infiltrate a porous media (such as a dry biological sample or a photoresist polymer) and allow the reaction to occur inside the material matrix.

Most biological materials have problems with charging when imaging with electrons and low contrast when imaging with hard X-rays. In this presentation we describe the use of infiltrated ZnO as a means to address both charge dissipation in electron microscopy and contrast enhancement for X-ray microscopy. With ZnO infiltration it is feasible to coat a 2 – 3 nm conductive metal oxide film throughout a porous biological sample, and image both the surface and the interior of a sample without any further sample recoating. We demonstrate this technique can be applied on tooth and brain tissue samples. We show that high resolution X-ray tomography can be performed on biological systems using Zn K edge (1s) absorption to enhance internal structures, and obtained the first nanoscale 10 KeV X-ray absorption images of the interior regions of a tooth.

In terms of device fabrication we use SU8 as a negative resist that allows for localization of the infiltration process. We have used this property to make a device that is UV sensitive, and that is sensitive to ppm concentrations of gases by using infiltrated zinc oxide. The large bandgap and semiconductor properties of ZnO allow for a visible-blind ultra violet light sensor. We used a standard UV flashlight that emits at 408 nm as the UV source. We also tested the same device for sensing gases like nitrous oxide and formaldehyde. We show that the device can detect these gases with concentrations of 5 ppm. The change in current for such low concentrations was measured to be between 25% and 35 %.

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3:20pm **NS+HC+SS-MoA6 Plasma Modified Gas Sensors: Bridging the Gap Between Tin Oxide Nanomaterials and Paper-Based Devices**, ***Kimberly Hiyoto***, *E.R. Fisher*, Colorado State University

Metal oxide nanomaterials are desirable for solid-state gas sensors because of their low manufacturing cost and ability to detect a wide variety of gases through changes in resistance resulting from gas-surface interactions. The substrates that support these materials, however, are often brittle and their smooth surface limits the amount of nanomaterial that can be exposed to target gases. Recent attempts to address these issues utilize paper substrates, that are not only low cost, but flexible to allow for a more robust device. Moreover, the porous, fibrous morphology of paper substrates provides significantly increased surface area for attaching more nanomaterials when compared to a traditional substrate of the same size. Despite recent improvements to paper-based metal oxide gas sensors, tin(IV) oxide (SnO_2) nanomaterials require high operating temperatures, thus have not yet been successfully translated to paper-based sensors. Here, we describe how low power (30 – 60 W) Ar/O_2 plasma modification, can be used to enhance gas-surface interactions of SnO_2 paper-based sensors while maintaining desirable bulk nanomaterial and substrate architecture. X-ray photoelectron spectroscopy revealed plasma treatment increased adsorbed oxygen, which is thought to improve sensor response by promoting gas-surface interactions. Indeed, plasma modified SnO_2 nanomaterials on a paper substrate exhibit improved response to ethanol, carbon monoxide, and benzene at ambient temperature. Furthermore, scanning electron microscopy demonstrates that plasma treatment does not damage the morphology of SnO_2 or the paper substrate. Response and recovery studies on these devices will be discussed along with SnO_2 nanomaterial gas sensors created on more traditional substrates (e.g. ZrO_2) as another measure of sensor performance. A better understanding of how plasma modification and the resulting changes in surface chemistry affect sensor performance is an important step towards achieving improved paper-based gas sensors using SnO_2 nanomaterials.

4:00pm **NS+HC+SS-MoA8 Understanding the Initial Stages of Oxidation in Nickel-Chromium Alloys**, *P. Reinke*, ***William H. Blades***, *G. Ramalingam*, University of Virginia

Through a combined experimental and computational effort, the interaction of oxygen with Nickel-Chromium alloys is studied. Prior to the formation of a full oxide layer, the physical and chemical processes behind the initial stages of oxidation are not well understood. This work fills a significant gap in our understanding of binary alloy oxidation. Scanning Tunneling Microscopy and Spectroscopy were used to observe the onset of oxide formation. These surface techniques are combined with Bandgap and Density of States maps, which lend themselves as powerful tools when studying surfaces with heterogeneity at the nanoscale. Ni-Cr(100) thin films with a range of compositions were prepared on MgO(100) in UHV and exposed to controlled amounts of oxygen up to 400L. Previous experiments have shown chromia to be the dominant oxide when Ni-Cr alloys are oxidized with a partial pressure of $p(O_2)<10^{-7}$mbar at 300ºC. Under these oxidation conditions the Ni prefers the kinetically favorable Ni(100)-c(2x2)-O reconstruction. Our experiments demonstrate that a combination of increased chromium concentration, which locally catalyzes the Ni, and an elevated oxidation temperature of 500ºC can overcome the activation barrier for NiO formation. The statistical analysis of island densities and sticking coefficient, in direct comparison of Ni and Ni-Cr surfaces, support the idea that NiO nucleation is facilitated by the presence of Cr. Early oxidation steps reveal that initial NiO nucleation and growth occurs along the step edges of the Ni-Cr alloy. This is in contrast to Ni(100)-c(2x2)-O where the step edges are passivated and devoid of reactive kink sites. We suggest that the presence of Cr at the step edges lowers the activation barrier and thus promotes rapid NiO formation. Anneal periods have shown that at low coverage, the NiO is readily desorbed from the surface leaving behind small oxides particles and regions with chemisorbed oxygen. Further oxidation steps create a high quality crystalline oxide layer, which is significantly more stable at elevated temperatures. Density Functional Theory is used to develop an understanding of the electronic and geometric structure of the oxidized Ni-Cr alloys and the effect of chromium on the local bonding environment. This collective 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 Navel Research MURI "Understanding Corrosion in Four Dimensions," Grant N00014-14-1-0675.

4:20pm **NS+HC+SS-MoA9 Evaluation of Titanium Doped β-Ga_2O_3 Thin Films in Extreme Environment for Application in Oxygen Sensors**, ***Sandeep Manandhar***, *A.K. Battu, C.V. Ramana*, University of Texas at El Paso

The reliable and efficient operation of power generation systems has become one of the grand challenges of today's research in order to meet the ever-increasing demand for energy and sustainability. The improvement in power/energy generation processes, in particular, for those depend on fossil fuels, the higher temperature and accurate measurement of the combustion environment and the emissions produced by the combustion via proper selection of sensing materials can enhance the efficiency and reliability. While several candidate metal oxides (SnO_2, ZnO, TiO_2, WO_3, and Ga_2O_3) exhibit high sensitivity chemical gases, β-Ga_2O_3 has shown to function as oxygen sensor at high temperatures (>700°C). However, the response time and sensitivity must be improved in order to utilize them in practical applications. While improved sensor characteristics are seen in various metal/ion doped β-Ga_2O_3, fundamental understanding of the long term effects of high temperature exposure on the structure and properties of doped β-Ga_2O_3 films is missing at this time. However, such studies are quite important to predict the thermodynamic stability and performance in extreme environments. In this work, we performed a detailed study to understand the effect of extreme environment on titanium (Ti) doped β-Ga_2O_3. The real environment condition for sensor (>700°C) application were simulated to understand the effect of temperature on the crystal structure, mechanical properties, electronic properties and oxidation states of Ti doped β-Ga_2O_3. The results will be presented and compared with as prepared Ti doped β-Ga_2O_3 films in the context of utilizing these materials in oxygen sensor applications.

4:40pm **NS+HC+SS-MoA10 Characterization of Infiltrated ZnO in PS-b-PMMA Nanostructures**, ***Paris Blaisdell-Pijuan***, University of Chicago, *L.E. Ocola*, Argonne National Laboratory

We have characterized the growth of ZnO using sequential infiltration synthesis (SiS) on PS-b-PMMA block copolymers (BCP) of spherical and cylindrical sub-20nm morphologies and studied how the photoluminescence of these nanostructures varies per its seed layer. Investigation of these structures was done using atomic force microscopy (AFM), spectrofluorometry, Raman spectroscopy, and scanning electron microscopy (SEM). We report blue-shifted photoemission at 335nm (3.70eV), suggesting quantum confinement effects. Samples of ZnO prepared with an alumina seed layer showed additional defect state photoemission at 470nm and 520nm for spherical and cylindrical BCP morphologies, respectively. Defect photoemission was not observed in samples prepared without a seed layer. No Raman peaks were observed for any samples with less than four cycles of ZnO, implying the absence of phonons and the functionality of these ZnO nanostructures as isolated emitters. Rapid thermal annealing of samples in air above 500 ºC began to coalesce and show photoemission characteristic of bulk ZnO at 370nm (3.35eV). Our work demonstrates that ZnO nanostructures grown on PS-b-PMMA via SiS are advantageous in uniformity and size, and exhibit unique fluorescence properties. These observations suggest that infiltrated ZnO in PS-b-PMMA nanostructures lends itself to a new regime of applications in photonics and quantum materials.

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