# Thursday Morning, October 5, 2000

### Surface Science Room 208 - Session SS1+MC-ThM

## **Oxide Applications and Oxidation**

Moderator: E.I. Altman, Yale University

#### 8:20am SS1+MC-ThM1 Synthesis and Characterization of Self-assembled Cu@sub2@O Quantum Dots on SrTiO@sub3@(001) Surface, Y. Liang, D.E. McCready, A.S. Lea, S.A. Chambers, S. Gan, Pacific Northwest National Laboratory

Self-assembled quantum dots have received much attention recently because their atom-like electronic and optical behavior can be tailored. One common problem with many quantum dots has been the poor chemical and thermal stability as most of them are made of conventional semiconductors. An alternative to this problem is to use oxide based quantum dots due to their superior stability. We have successfully synthesized self-assembled Cu@sub2@O guantum dots on SrTiO@sub3@ substrates using a molecular beam epitaxial method. The structure and chemical states of Cu@sub2@O quantum dots have been confirmed by xray diffraction and x-ray photoelectron spectroscopy (XPS). Reflection high energy electron diffraction (RHEED), atomic force mic roscopy (AFM), and high-resolution scanning Auger microscopy (SAM) show that formation of Cu@sub2@O quantum dots occurs after deposition of a few monolayers of Cu@sub2@O due to the large compressive lattice mismatches between Cu@sub2@O and SrTiO@sub3@. SAM reveals that the interdiffusion between Cu@sub2@O guantum dots and SrTiO@sub3@ is significantly less than many other quantum-dot systems. XPS further shows that the interfacial electronic structure of Cu@sub2@O/SrTiO@sub3@ exhibits the so-called the type-II heterojunction, i.e., the valance and conduction bands of Cu@sub2@O are both higher than that of SrTiO@sub3@. Consequently the photo-excited electrons and holes are spatially separated with holes being confined to Cu@sub2@O quantum dots and electrons confined to SrTiO@sub3@, a property important for photocatalysis and solar cell applications. We are currently using AFM-based surface potential measurements to elucidate the spatial charge separation behavior of this system upon photo-excitation at different wavelengths. @FootnoteText@ # Pacific Northwest Laboratory is a multiprogram national laboratory operated by Battelle Memorial Institute for the U.S. Department of Energy under Contract DE-AC06-76RLO 1830.

#### 8:40am SS1+MC-ThM2 Correlation of Electronic Structure with Photoluminescence Properties in Oxidized Silicon Nanoclusters, J.A. Carlisle, I. Germanenko, Y. Pithawalla, M.S. El-Shall, Virginia Commonwealth University

The relationship between morphology, band-gap size, and photoluminescence data in surface-oxidized silicon nanoclusters is established using photon-yield measurements at the Advanced Light Source. After removal from the growth chamber, photoluminescence (PL) results indicate that as the clusters oxidize, the main PL peak moves from 1.83 eV to 1.94 eV in energy. The central focus of this work is to establish the origin of the PL peak, whether it arises due to quantum size effects or due to the formation of suboxides as the clusters oxidize. The changes in the morphology and bonding structure of the clusters were established using soft-x-ray fluorescence spectroscopy (SXF) and photon-yield nearedge x-ray absorption fine structure (NEXAFS) spectroscopy, which probe the element-specific density of occupied (SXF) and unoccupied (NEXAFS) electronic structure. Our finding is that the as-synthesized nanoclusters consist of a pure, crystalline Si core within a nearly pure SiO2 shell. Very few suboxides are present, and the oxidation process does not lead to an increase in the amount of suboxides present within the particles. As the nanoclusters oxidize, the radius of the crystalline core decreases in size, which gives rise to the change in the position of the PL signal.

#### 9:00am SS1+MC-ThM3 The Behavior of Ultrathin Al@sub 2@O@sub 3@ Films in Very High Electric Fields: STM-induced Pitting and Dielectric Breakdown, N.P. Magtoto, C. Niu, J.A. Kelber, University of North Texas

The behavior of ultrathin oxides under high electric fields is of critical importance to areas as diverse as microelectronics (gate oxides, magnetoresistance devices) and corrosion. We report the use of high electric fields applied via the STM to induce pits and dielectric breakdown in ultrathin @gamma@'-Al@sub 2@O@sub 3@ films (7 Å thick) grown on Ni@sub 3@Al(111) substrates in UHV. Voltage pulses (bias voltages of 1-6 V, either polarity) are applied to a specific location on the oxide surface with the feedback current loop operative to prevent tip/sample physical

interaction. Subsequent imaging at 0.1 V bias voltage and 1 nA feedback current reveal the effects of high field on surface composition and topography. Results show that dielectric breakdown occurs at a field of 12.3 $\pm$ 0.7 MV/cm. Breakdown is marked by the creation of an area ~20 nm high and 100 nm wide and the loss of the insulating nature of the oxide as deduced from I/V spectroscopy. Once the threshold breakdown voltage is reached, the STM tip retracts precipitously (~20-25nm) from the sample surface due to the onset of the leakage current. At fields ~ 60 % of breakdown, small pits in the oxide that are 0.4-0.8 nm deep can be created. Repeated application of this field within the pit will cause dielectric breakdown, even though the same field will not induce breakdown in regions away from the pit. The results provide direct evidence of the ability of localized defects to decrease the barrier to dielectric breakdown in an ordered oxide film.

#### 9:20am SS1+MC-ThM4 Oxidation of Sn/Pt (111) Surface Alloys under UHV Conditions- Formation of Ultrathin SnOx Films on Pt(111), *M. Batzill, D. Beck, B.E. Koel,* University of Southern California

Platinum-tin systems are important as hydrocarbon reforming catalysts when supported on alumina. The tin may however exist in oxidic form and thus SnOx may be responsible for the altered catalytic properties of the Sn-Pt system compared to pure Pt, rather than alloying of Sn and Pt. In order to study ultrathin SnOx overlayers on Platinum we have oxidized both ordered Sn/Pt(111) surface alloys (the p(2x2) and the (sqr3 x sqr3)R30 alloy structure) using NO2 as an oxidant. The structure, chemical state and thermal stability of the oxide films have been examined by LEED, STM, XPS, AES and TPD. Oxidation of p(2x2) alloy results in a discontinuous mono-layer thick SnOx film that decomposes at 760 K. Oxidation of the (sqr3 x sqr3)R30 in contrast forms a thermally more stable continuous overlayer that shows two ordered surface phases depending on the annealing temperature. These structures have been analyzed using LEED and STM. The chemical activity of these surfaces was probed by small hydrocarbon molecules and CO.

#### 9:40am **SS1+MC-ThM5 Monte Carlo Simulation of Initial Al(111) Oxidation**, *D.E. Oner*, *R. Chakarova*, *I. Zori@aa c@*, *B. Kasemo*, Chalmers University of Technology, Sweden

In this work a Monte Carlo simulation technique is applied, exploring the influence of several models for O@sub 2@ dissociation on the initial Al(111) oxidation. The primary experimental data motivating this are the STM studies by Brune et al. (J. Chem. Phys. 99 (1993) 2128). The simulations are performed to gain more insight into the kinetics of the oxidation process. The Monte Carlo simulation is based on the lattice-gas approach using the Metropolis algorithm. The simulations assume alternatively "normal" dissociation (deposition of O atoms at adjacent surface sites), hot dimer dissociation (widely separated O atoms due to hot dissociation fragments) or abstraction (one of the separating O atoms performs a ballistic motion away from the surface). Further elements of the model are surface mobility, attractive forces between adsorbed O-atoms (i.e. adsorbate-adsorbate interaction), and in-diffusion of O atoms into the 2nd and deeper layers to form 2D and 3D oxide. Input data are, when available, taken from experiments or first-principles calculations. The results of this computational work are compared to the experimental results by Brune et al. The calculated surface configurations of chemisorbed O-atoms at 300 K in the low coverage regime, based on the hot dimer dissociation model, are in good agreement with the observed experimental STM data. The simulations of thermal annealing of chemisorbed oxygen islands are in fair agreement with the observed island kinetics by Trost et al. (J. Chem. Phys. 108 (1998) 1740). In the latter case, the O-O interaction strength is a crucial parameter. The present simulation model provides a useful platform for further simulations of Al oxidation. @FootnoteText@ Keywords: Monte Carlo simulation, surface oxidation, oxide nucleation and growth, hot chemisorption, metal oxidation, kinetics, aluminium.

#### 10:00am SS1+MC-ThM6 Thin Epitaxial Oxide Films and Interfaces for Advanced Microlectronics and Magnetics, S.A. Chambers, Pacific Northwest National Laboratory INVITED

Metal oxides constitute an extremely diverse class of materials, with virtually all types of electronic and magnetic behavior represented. These materials thus possess many properties that make them unique and potentially important for future technologies. No other class of materials exhibits such a wide range of behavior: band gaps spanning the visible and UV; electronic properties ranging from superconducting to metallic to semiconducting to insulating; magnetic properties ranging from ferromagnetic to antiferroma gnetic; and dielectric properties ranging from

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low-k to ferroelectric and piezoelectric. In addition, metal oxides exhibit a wide range of crystal structures, including spinel, perovskite, and corundum. As a result, a variety of heteroepitaxial structures can be designed and synthesized. In this talk, I present recent results on three heteroepitaxial oxide systems that illustrate the fascinating interface physics and potential technological advantages of these materials: (1) SrTiO@sub 3@(001)/Si(001), (2) CoFe@sub 2@O@sub 4@(001)/MgO(001) and, (3) MgO(001)/Ag(001) and Pt(111)/@alpha@-Cr@sub 2@O@sub 3@(0001)/Pt(111)/@alpha@-Al@sub 2@O@sub 3@(0001). System 1 is of considerable interest as a high-k gate oxide in next-generation MOSFETs.@footnote 1@ System 2 is a model that permits us to investigate thin films of what appears to be a very promising high-magneticanisotropy, insulating ferrimagnet.@footnote 2@ System 3 allows us to examine the effects of polarizable metals on the optical, electronic and magnetic properties of ultrathin oxides that are within electronic screening lengths of the metal.@footnote 3@ Structural, electronic and magnetic properties of these systems, all grown by molecular beam epitaxy, will be presented. @FootnoteText@ @footnote 1@ R.A. KcKee et al., Phys. Rev. Lett. 72, 2741 (1994). @footnote 2@ Y. Suzuki et al., Appl. Phys. Lett. 68, 714 (1996). @footnote 3@ S. Altieri et al., Phys. Rev. B59, R2517 (1999).

# 10:40am SS1+MC-ThM8 The Oxidation of Pd(100), G. Zheng, E.I. Altman, Yale University

Motivated by interest in Pd as a catalyst for oxidation reactions and the catalytic combustion of CH@sub 4@, the interaction of Pd(100) with O@sub 2@ was studied using LEED, STM, and TPD. Initial exposure of Pd(100) to O@sub 2@ at room temperature resulted in a (2x2) structure that saturated at an oxygen coverage of 0.25 ML (1 ML = 1 O/Surface Pd ) following 30 L exposure. Further exposure to O@sub 2@ at room temperature resulted in a mixture of (2x2) and p(5x5) LEED patterns, which persisted until the oxygen coverage reached a saturation value of 0.68 ML. Increasing the exposure temperature to 475 K resulted in the p(5x5) structure in the oxygen coverage range of 0.60-0.80 ML, which transformed into a (@sr@5x@sr@5)R27° pattern beyond 0.80 ML. TPD experiments revealed four oxygen desorption features from Pd(100) following exposure to O@sub 2@, including peaks at 800 K, 700 K and 650 K, as well as a low temperature oxygen shoulder at 600 K. The highest temperature peak corresponds to the (2x2) chemisorption structure, and the other two peaks fall into the regime where p(5x5) and (@sr@5x@sr@5)R27° patterns appear. The three peaks saturated in sequence, and the low temperature shoulder showed up before saturation of the 650 K peak. These results indicate at least four distinct oxygen states on Pd(100). Upon annealing, the (@sr@5x@sr@5)R27° LEED pattern transformed into the (2x2) pattern without stepping through the p(5x5), and the p(5x5) structure converted into the (2x2) pattern. The temperature dependence of oxygen up-take was also studied. Oxygen was found to have the highest sticking coefficient on Pd(100) at 550 K. STM studies revealed the atomic structures of various oxygen phases on Pd(100), as well as their relative reactivity towards reduction by in-situ monitoring of the surface during exposure to CO and propylene.

11:00am SS1+MC-ThM9 Surface Characterization of Oxidative Corrosion of U-Nb Alloys, D. Kelly, Los Alamos National Laboratory; W.L. Manner, Union Carbide Corporation; J.A. Lillard, R.J. Hanrahan, Jr., M.T. Paffett, Los Alamos National Laboratory

We have studied the relative rates of oxidative corrosion of U-Nb alloys containing 2 to 8 wt. % Nb, using X-ray photoelectron spectroscopy (XPS) and depth profiling by sputtered neutrals mass spectroscopy (SNMS), The alloys have been characterized after exposure to dry and humidified air (up to 50% relative humidity) at temperatures from 25 to 125 @super o@C, and exposure to electrochemical solutions. XPS studies of U-6 wt. % Nb following oxidation at 300 K with oxygen indicate formation of a thin overlayer of stoichiometric UO@sub 2@ intermixed with Nb@sub 2@O@sub 5@. This same stoichiometry is exhibited upon oxygen treatment at 500 K, however, niobium is much less oxidized, forming a mixture of NbO and Nb. SNMS depth profiling indicates that oxides formed using oxygen are thicker than those obtained using water. The formation of a critical density of Nb@sub 2@O@sub 5@ is suggested to enhance corrosion resistance by preventing diffusion of oxygen and/or hydroxyl species into the oxide/metal interface region. Tube furnace oxidation of the U-Nb alloys produces oxide layers comprised of UO@sub 2@ and Nb@sub 2@O@sub 5@ under all experimental conditions used. The thickness of the oxides increased with treatment time and temperature, but decreased with increasing Nb alloy content. For example, a 48 hour treatment at 75 @super o@C and 50% relative humidity results in oxide thickness on U-2%Nb that are three times that on U-8%Nb. Electrochemical

oxidation of U-Nb alloys facilely generated UO@sub 3@ and Nb@sub 2@O@sub 5@ oxide layers with thicknesses qualitatively similar to thermal oxidation results. U-Nb alloys electrochemically oxidized at low pH exhibit oxide layers with near-surface regions (50 ???) enhanced in Nb content, as compared to the bulk material. Surface UO@sub 3@ was not readily reduced upon exposure to molecular D@sub 2@; however, D atoms facilely reduced UO@sub 3@ to UO@sub 2@.

#### 11:20am SS1+MC-ThM10 AFM Non-contact Imaging of Titaniumdioxid at Variable Temperatures, A. Bettac, P. Güthner, S. Molitor, A. Feltz, T. Berghaus, Omicron Vakuumphysik GmbH, Germany; A.W. Grant, S. Fain, University of Washington

True atomic resolution in AFM non-contact mode has been achieved on several samples. Here we present first images on a TiO@sub 2@ (110) single crystal at sample temperatures from as low as 50 K up to 400° C. A new instrument design allows to perform true atomic resolution AFM images in a temperature range from 25 K to 1000 K. The sample was prepared by several cycles of ion sputtering and annealing in UHV. After this treatment it is conducting enough to perform STM measurements for controlling the quality of surface preparation. Non-contact AFM images on the TiO@sub 2@ (110) crystal show atomic resolution across mono-atomic steps. The surface is mostly showing a 1x1 reconstruction. At the step edges, lines with 1x2 reconstruction are starting. These lines may be associated with the formation of Ti@sub 2@O@sub 3@ strings along the surface. The density of areas with 1x2 reconstruction is increased with the annealing temperature which can be explained by the desorbtion of oxygen during the annealing process. Atomic resolution images on the TiO@sub 2@ (110) crystal were achieved at low temperatures down to 50 K sample temperature and at high temperatures up to 400° C.

11:40am SS1+MC-ThM11 Plasma Oxidation as a Tool to Design Oxide Films at Low Temperatures, *R. Schennach*, Lamar University; *D.G. Naugle*, Texas A&M University; *H. McWhinney*, Prairie View A&M University; *D.L. Cocke*, Lamar University

Interfacial oxidation is an established approach to produce surface thin films for catalysts, corrosion, ware protective coatings and electronic structures. The three main oxidation methods: thermal, anodic and plasma, still lack adequate fundamental physical-chemical models that can allow film design, particularly on alloys. Plasma oxidation of a CuZr alloy is studied using XPS (X-ray Photoelectron Spectroscopy). The dependence of the resulting oxide film on alloy composition and sample temperature during plasma oxidation is investigated. In contrast to thermal and electrochemical oxidation leads to the formation of a zirconium oxide film, plasma oxidation leads to the formation of a copper oxide or metallic copper over layer depending on temperature and copper concentration in the bulk. It is shown that plasma oxidation can be used to design oxide films at room temperature, which require high temperatures using thermal oxidation.

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