

# Thursday Morning, November 6, 2003

## Surface Science

### Room 328 - Session SS3-ThM

#### Oxide Structure, Growth, and Defects

**Moderator:** M.A. Henderson, Pacific Northwest National Laboratory

8:20am **SS3-ThM1 Effect of Atomic Polarization on Adsorption on Ferroelectric Surfaces: BaTiO@sub 3@ (100), J. Garra, D.A. Bonnell, University of Pennsylvania**

Ferroelectric surfaces have become the focus of recent interest as templates for directed assembly and as thin film devices, yet the surface properties are largely unknown. It has been shown, however, that the local chemical reactivity on ferroelectric surfaces depends on the orientation with which the polarization vector intersects the surface. For example photo reduction (electron donation) occurs over domains with positive surface termination, while photo oxidation (hole donation) occurs over domains with negative surface termination. In order to determine how atomic polarization affects reaction mechanisms, we compare LEED and TPD measurements of desorption from BaTiO@sub 3@ (100) single crystals. Samples are poled in UHV above the Curie temperature and cooled in the electric field in order to achieve homogeneous and predefined polarization orientation before adsorption. Domain structure is confirmed with Piezo Force Microscopy. Water, methanol, and ammonium are used as probe molecules. Adsorbate bond energies above and below the ferroelectric-to-paraelectric phase transition will be discussed in the context of the magnitude of local electric fields.

8:40am **SS3-ThM2 Sodium Segregation and Morphology on Co@sub 3@O@sub 4@ Single Crystal Surfaces, S.C. Petitto, M.A. Langell, University of Nebraska-Lincoln**

The Co@sub 3@O@sub 4@(110) single crystal surface was characterized in its clean and sodium covered states using Low Energy Electron Diffraction, (LEED), X-Ray Photoelectron Spectroscopy, (XPS), and Auger Electron Spectroscopy, (AES). Annealing Co@sub 3@O@sub 4@(110) at T = 650K results in sodium segregation from the bulk material, quantified here by the AES I@sub Na@/I@sub Co@ intensity ratio. LEED analysis of the clean Co@sub 3@O@sub 4@(110) surface shows a well-ordered pattern with sharp diffraction features, whereas the Co@sub 3@O@sub 4@(110)-Na surface presents a more poorly ordered structure with a hexagonal superimposed pattern due to the sodium oxide overlayer. Concurrent with sodium segregation, the Co@sub 3@O@sub 4@(110) surface is reduced and the surface cannot be fully reoxidized as long as sodium remains present even upon extended oxygen annealing. XPS of the clean Co@sub 3@O@sub 4@(110) is characteristic of the spinel structure with Co@super 3+@ occupying the octahedral sites within the lattice and Co@super 2+@ in tetrahedral sites. Co@sub 3@O@sub 4@(110)-Na cobalt XPS, however, shows the cobalt chemical environment is closer to that in CoO with Co@super 2+@ in octahedral sites. Upon flashing to T@>= 800K, sodium desorbs from the surface, primarily as NaOH. Pre-dosing with H@sub 2@O does not appear to catalyze NaOH desorption but rather suppresses it, and the hydrogen is assumed to come from the ambient background in the UHV chamber.

9:00am **SS3-ThM3 Resonant Photoemission of Cobaltite Perovskites and Double Perovskites, W.R. Flavell, A.G. Thomas, D.T. Tsoutsou, A.K. Mallick, M. North, UMIST, UK; E.A. Seddon, C. Cacho, A.E.R. Malins, CLRC Daresbury Lab, UK; R. Stockbauer, R.L. Kurtz, P.T. Sprunger, Louisiana State U.; S.N. Barilo, S.V. Shiryayev, G.L. Bychkov, Belarus Academy of Sciences** **INVITED**

Double perovskites based on Co(III), e.g. GdBaCo@sub 2@O@sub 5.5@, show GMR behaviour and a range of poorly understood spin-state transitions. Whereas the Co(III) ion occupies only octahedral sites in perovskites such as LaCoO@sub 3@, in double perovskites, Co is present in two environments, octahedral and pyramidal. In order to investigate the electronic structure of these oxides, resonant photoemission of single crystals of the double perovskites GdBaCo@sub 2@O@sub 5.5@ and DyBaCo@sub 2@O@sub 5.5@ and of the perovskite HoCoO@sub 3@ has been carried out at the UK Synchrotron Radiation Source. Co 3p->3d resonance photoemission has been shown to be a powerful diagnostic of the LS (low spin) state of d@super 6@ Co(III) in cobaltites. The resonance onset position of features associated with the LS state lies typically around 2.5 eV higher than those associated with Co (III) in HS (high spin) or IS (intermediate spin) states. This is thought to be because the t@sub 2g@ states are full in the LS state so the Co 3p -> 3d transitions are delayed until the e@sub g@ states, which lie ~2-3 eV higher, can be occupied. This

diagnostic test is used to explore the Co spin fluctuations in double perovskites with temperature. In contrast with previous data for LaCoO@sub 3@, we see no delayed resonance for GdBaCo@sub 2@O@sub 5.5@ or DyBaCo@sub 2@O@sub 5.5@ at temperatures as low as 50 K, consistent with the idea that the Co spin in the pyramidal sites does not fluctuate with temperature. However, a delayed resonance is observed at temperatures up to 400 K in HoCoO@sub 3@. This resonance delay disappears as the temperature is raised, as does a low binding energy feature of the valence band associated with LS Co(III). These observations are consistent with a LS to IS transition in octahedral Co(III) in HoCoO@sub 3@. The giant RE 4d->4f resonances are also probed, and used to identify the 4f DOS. We show that the DOS closest to the Fermi energy for all materials is of TM 3d/O2p character, with no RE 4f contribution. Comparison is made with recent LDA+U calculations.

9:40am **SS3-ThM5 Growth Modes in a System Requiring Bulk Mass Transport: Step Motion and Island Nucleation on TiO@sub 2@ (110) Exposed to Oxygen, K.F. McCarty, J.A. Nobel, N.C. Bartelt, Sandia National Laboratories**

We use low-energy electron microscopy (LEEM) to systematically investigate how the (110) surfaces of oxygen-deficient rutile crystals grow when exposed to oxygen. This growth is interesting because it requires a combination of bulk and surface diffusion -- as established by Onishi and Iwasawa (1996) using scanning tunneling microscopy, growth occurs as titanium interstitials from the bulk react with ambient and adsorbed oxygen. If the reaction only occurred at step edges, then one might expect to observe only step-flow growth. Instead, we find that distinct growth processes occur, depending primarily on temperature and oxygen pressure. The temperature/pressure dependence of these growth regimes has been systematically determined for a slightly reduced crystal. At high temperature, TiO@sub 2@ growth occurs by pure step flow without the nucleation of new islands. At low temperatures, however, crystal growth proceeds by two-dimensional islands nucleating and spreading laterally. In this layer-by-layer growth regime, the surface periodically oscillates between structures with 1x1 and 1x2 periodicity. The threshold temperature above which island nucleation does not occur depends upon the local terrace width and pressure. For a range of temperatures around the threshold, nucleation occurs on wide terraces but not on narrow terraces. In the regime of pure step flow, we analyze the rate at which isolated islands and interacting island arrays grow. Comparison of the experimental data to numerical simulations of island growth allows us to discuss the relative importance of Ti transport through the bulk and oxygen-containing species on the surface.

10:00am **SS3-ThM6 The Effect of Nitrogen Doping on Rutile Single Crystals - A Photochemical Surface Science Study, O.E. Diwald, T.L. Thompson, J.T. Yates Jr., University of Pittsburgh**

A major goal in the development of new materials for photocatalysis and photo electrochemistry is to shift the solid's photoresponse into the visible light region, in order to utilize solar light more efficiently. Recently, doping of polycrystalline TiO@sub 2@ with non metal ions such as nitrogen@footnote 1@ has attracted much attention, as these materials have shown activity under visible light irradiation (@lambda@ @<= 550 nm). In order to investigate the effect of nitrogen doping on the photoactivity of TiO@sub 2@(110) single crystals, nitrogen incorporation into the rutile lattice was achieved either by sputtering with mixtures of N@sub 2@@super +@ and Ar@super +@ ions or by thermal treatment in ammonia (NH@sub 3@). Secondary Ion Mass spectroscopy and X-ray photoelectron spectroscopy were employed to measure depth distribution and chemical state of the implanted nitrogen. For rutile single crystals, these two doping methods result in different chemical states of the incorporated nitrogen. Ion implantation by sputtering produces substitutionally bound nitride species N@super -@, whereas NH@sub 3@ treatment leads to the formation of a N-H bonded dopant in the rutile lattice. For investigation of the photoactivity, the photodesorption of O@sub 2@ was measured as a function of excitation energy and photon flux.@footnote 2@ Compared to the undoped TiO@sub 2@ (110) rutile crystal, the action curve of the crystal that was doped with substitutionally bound nitride exhibits an unexpected blueshift. These findings will be related to changes in the electronic structure of rutile TiO@sub 2@ due to the different dopant species. This work was supported by the DoD Multidisciplinary University Research Initiative (MURI) program administered by the Army Research Office under Grant DAAD-19-01-0-0619. @FootnoteText@ @footnote 1@ R. Asahi, T. Morikawa, T. Ohwaki, K. Aoki, Y. Taga, Science, 293, 269 (2001), @footnote 2@ G. Lu, A. Linsebigler, J. T. Yates Jr., J. Chem. Phys., 102, 4657, (1995).

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10:20am **SS3-ThM7 STM Study of Defect Production on the TiO@sub 2@(110)-(1x1) and TiO@sub 2@(110)-(1x2) Surfaces Induced by UV-light, P. Maksymovych, S. Mezheny, D.C. Sorescu, J.T. Yates, Jr., University of Pittsburgh**

The photoinduced hydrophilicity of the TiO@sub 2@ surface has been the subject of extensive research due to its technological importance in the development of antifogging and self-cleaning coatings. The phenomenon has been postulated to be due to structural changes of TiO@sub 2@; however, the exact mechanism of the process is unknown. The effect of broadband UV radiation on the stoichiometric TiO@sub 2@(110)-(1x1) and the reduced TiO@sub 2@(110)-(1x2) surfaces was observed using the scanning tunneling microscope (STM) in ultra-high vacuum. It was found that the TiO@sub 2@(110)-(1x1) surface is not affected by UV radiation within the statistical error of the experiment. The majority of defect sites on the surface are the bridging oxygen vacancies, and their surface density remains unchanged after UV irradiation. In contrast, production of line defects in the direction was observed on the TiO@sub 2@(110)-(1x2) surface. The overall defective area of the surface was found to increase linearly with UV-exposure, the estimated cross section of the defect formation being  $10^{-23.5 \pm 0.2} \text{ cm}^2/\text{photon}$  ( $h\nu \geq 3.0 \text{ eV}$ ). The origin of the defects is attributed to collective removal of oxygen from the surface. In order to determine whether the UV-induced defects can cause hydrophilicity of TiO@sub 2@, adsorption of H@sub 2@O on the TiO@sub 2@(110)-(1x2) surface was studied by STM. At 300K adsorption of H@sub 2@O occurred preferentially on the crosslinks of the TiO@sub 2@(110)-(1x2) surface. However, cooling the surface to 110K during H@sub 2@O exposure led to more efficient adsorption, which took place on the added rows of the TiO@sub 2@(110)-(1x2) surface in addition to the crosslinking sites. No changes in the topology of the UV-induced defects were observed after H@sub 2@O exposures.

10:40am **SS3-ThM8 The Oxygen Chemistry of Rutile TiO@sub 2@(110) - A Comprehensive STM Study, R. Schaub, E. Wahlström, A. Ronnau, E.K. Vestergaard, F. Besenbacher, Interdisciplinary Nanoscience Center, Denmark**

The detailed understanding of the oxygen chemistry on titanium oxide is an important issue for chemical and photo-chemical processes on this material. We present a thorough high resolution variable temperature STM investigation of the interaction of oxygen molecules with the (110) surface of TiO@sub 2@. Single oxygen molecules interact with oxygen vacancies, mediating their diffusion through a simple oxygen atom exchange mechanism. Surprisingly, this mechanism does not account for healing of the vacancies as speculated in the literature until now. The adsorption of molecular oxygen leads also to the creation of different oxygen-related species, which are readily distinguishable by their contrast in STM images and their dynamics in time-resolved STM experiments. The subtle interaction of these different species present on the surface accounts for the healing of the vacancies through an unanticipated and complex mechanism discussed in detail.

11:00am **SS3-ThM9 Measuring Defect Sites on TiO@sub 2@(110): The CO@sub 2@ Probe, T.L. Thompson, O.E. Diwald, J.T. Yates, Jr., University of Pittsburgh**

Defect sites govern the chemical and photochemical behavior of TiO@sub 2@ rutile surfaces. We have found that CO@sub 2@ binds more strongly (54.0 kJ/mol) to oxygen-vacancy Ti@super +3@ defect sites made by thermally reducing TiO@sub 2@(110) than to the fully-oxidized 5-fold coordinated Ti@super +4@ surface sites (48.5 kJ/mol). Enhanced surface reduction at temperatures up to 1000K causes an increase in the relative amount of the strongly-bound CO@sub 2@.

11:20am **SS3-ThM10 Surface Structure and Properties of Vanadia Supported on Anatase TiO@sub 2@(001), W. Gao, E.I. Altman, Yale University**

We have successfully grown epitaxial anatase TiO@sub 2@(001) thin films on LaAlO@sub 3@(001) substrates using oxygen plasma assisted molecular beam epitaxy (OPA-MBE). A two-domain (1x4)/(4x1) reconstruction was observed by reflection high energy electron diffraction (RHEED) and low energy electron diffraction (LEED). With OPA-MBE, monolayer to multi-layer vanadia was deposited on the reconstructed anatase (001) surface. Photoelectron spectroscopy (UPS and XPS) was used to characterize the chemical state of the vanadia. XPS results showed that the vanadia was predominantly in the 5+ oxidation state after deposition of a monolayer at 525 K, while UPS showed a small peak in the TiO@sub 2@ bandgap consistent with a small amount of V@super +4@. After 1 ML vanadia was deposited on anatase (001), the anatase (1x4)/(4x1) LEED and RHEED

patterns were replaced by (1x1) patterns indicating that the vanadia lifts the reconstruction and suggesting that the monolayer is pseudomorphic. The reducibility of the monolayer was studied by monitoring XPS peak shifts as a function of annealing temperature. At temperatures between 625 K to 875 K, the vanadia was reduced to the 3+ oxidation state; these results were very similar to vanadia on SiO@sub 2@. XPS results also showed a decrease in the intensity of the V peaks with increasing temperature. At ~875 K, nearly no vanadium was detected by XPS and the (1x4)/(4x1) pattern of the bare surface was restored suggesting that V migrated into the bulk. Vanadia growth beyond the first monolayer caused the RHEED pattern to fade and produced no discernible LEED patterns suggesting that pseudomorphic growth cannot be continued beyond 1 ML. The structural evolution of the surface as vanadia was deposited was also characterized by scanning tunneling microscopy (STM).

11:40am **SS3-ThM11 Initial Stages of Cu@sub 2@O Nano-Clusters Formation on SrTiO@sub 3@(100)@footnote 1@, I. Lyubinetzky, S. Thevuthasan, A.S. Lea, D.E. McCready, D.R. Baer, Pacific Northwest National Laboratory**

Self-assembled crystalline cuprous oxide (Cu@sub 2@O) nano-clusters have been grown on the SrTiO@sub 3@(100) substrate using oxygen plasma assisted molecular beam epitaxy. The growth mechanism, composition and structure were examined by x-ray photoelectron spectroscopy, x-ray induced Auger electron spectroscopy, scanning probe microscopy, scanning Auger microscopy, and x-ray diffraction. Growth parameters for the formation of pure Cu@sub 2@O nano-clusters have been optimized accordingly to the surface phase diagram of the Cu-O system, which has been determined for temperature versus oxygen pressure. Unlike typical semiconductor systems, e.g. Si-Ge, initial stages of the growth for studied here metal oxide system proceed without formation of the wetting layer, with formation of the 3D truncated square Cu@sub 2@O dots starting already at sub-monolayer coverages. At following stages of the growth, nano-dots underwent shape/structure transformation similar to the semiconductor systems. Under different surface conditions of the SrTiO@sub 3@(100) substrate (high temperature annealed, perfect TiO@sub 2@-terminated surface vs. original mixed-terminated surface) significant differences in the uniformity of the nano-clusters distribution have been observed. Complications due to the re-growth of the Sr-rich nanostructures in addition to the Cu@sub 2@O nano-dots formation at the certain substrate conditions will be also discussed. @FootnoteText@ @footnote 1@ This work has been conducted as part of the PNNL Nanoscience and Nanotechnology Initiative supported by the U. S. Department of Energy.

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