Friday Morning, November 17, 2006

Surface Science
Room 2002 - Session SS-FrM

Oxide Surfaces and Interfaces

Moderator: S.A. Chambers, Pacific Northwest National Laboratory

8:00am SS-FrM1 Reduction of Sn-Oxide Phases on PtSn Alloys, *J. Kim,* Lehigh University*; S. Thomas,* University of Southern California*; **B.E. Koel**,* Lehigh University
The chemistry that occurs at oxide-metal interfaces found for metal nanoparticles on oxide supports or formed by oxidation of the metal nanoparticles themselves is important for understanding and controlling processes in heterogeneous catalysts, electrocatalysts, and sensors. For example, the origin of improved selectivity of Pt-Sn bimetallic catalysts for selective hydrogenation of unsaturated aldehydes has been attributed to the presence of cationic Sn sites. We have investigated the thermal stability, and reducibility in H_2 at pressures ranging from UHV to one atm., of several distinct ordered and disordered structures, monolayer and multilayer phases, of tin oxide films formed at the surface of Sn/Pt(111) and Sn/Pt(100) surface alloys. The oxide phases and the progress of their reduction were characterized using TPD, LEED, STM, AES, and high-resolution XPS. We find enormous sensitivity of the reduction of these tin oxide films on the detailed chemical nature and structure of the films. Such sensitivity can alter the thermal reduction temperature by 300 K and the reducibility in H_2 by many orders of magnitude.

8:20am SS-FrM2 First Principles Studies of CO Adsorption and Oxidation on Cu2O(100)*, *S. Stolbov, D. Le, T. Rahman,* Kansas State University
Recent experimental findings[1] indicate that the rate of CO oxidation on Cu2O surface is much higher than that on Cu and CuO surfaces. This result is also in qualitative agreement with results on copper oxide nanoparticles. To gain insight into the factors controlling the reactivity of oxide surfaces, we have examined from first principles the energetics of adsorption and oxidation of CO on Cu2O(100). Calculations are based on density functional theory using the generalized gradient approximation for the electron exchange-correlation term. Furthermore, we obtain the pressure/temperature (p,T) surface phase diagram by applying the ab initio thermodynamics approach[2] to the surface in contact with gaseous O2. We find that the O-termination of Cu2O(100) is preferred for all reasonable range of temperature and O2 pressure. We also find that CO molecules which chemisorb on the surface O, directly associate with it to form CO2 without any activation barrier. On the other hand, CO molecules which adsorb on a surface Cu atom are found to slide first towards the neighboring O atom to form CO2. We analyze the local densities of electronic states and valence charge densities of the systems to rationalize the results. @FootnoteText@ @footnote 1@T.-J. Huang and D.-H. Tsai, Catal. Lett. 87, 173 (2003). @footnote 2@K. Reuter and M. Scheffler, Phys. Rev. B 65, 035406 (2002). * Work supported in part by DOE under grant No. DE-FG02-03ER15465 and computational resources provided by NSF Cyberinfrastructure and TeraGrid grant No; DMR050039N.

8:40am SS-FrM3 Structure, Energetics and Reactivity of Step Edges on Anatase TiO2(101)*, *A. Selloni,* Princeton University   **INVITED**
Defects strongly affect the physical and chemical properties of metal oxide surfaces, and step edges are the most common type of defects. On nanoparticles the high concentration of step edge atoms may even dominate surface chemistry. Atomic-scale descriptions of metal oxide step edges are scarce. We report first-principles calculations of the structure, energetics, and chemistry of step edges on the (101) surface of TiO2 anatase, an important photocatalytic material. A procedure based on systematic calculations of related vicinal anatase TiO2 surfaces has been used, which yields step edge energies with remarkable accuracy. The electronic structures of the stepped surfaces and adsorption of prototype molecules have been also investigated. The present results allow us to obtain a detailed and complete understanding of available experimental observations. In particular, predictions of step edge configurations are in excellent agreement with Scanning Tunneling Microscopy measurements. @FootnoteText@ *Work in collaboration with Xue-Qing Gong, Department of Chemistry, Princeton University; Matthias Batzill and Ulrike Diebold, Department of Physics, Tulane University.

9:20am SS-FrM5 Nitrogen Doping of TiO@sub 2@ Single Crystals, *M. Batzill, E.H. Morales, U. Diebold,* Tulane University
TiO@sub 2@ is one of the most widely used photocatalytic materials for photo degradation of organic pollutants, self cleaning surfaces, and photolysis of water for hydrogen production. The wide band gap of TiO@sub 2@ limits its photoactivity to UV radiation, however. For utilizing a wider spectrum of the solar light a narrower band gap would be advantageous. In a recent paper by Asahi et al.@footnote 1@ it was proposed that such a band gap narrowing can be achieved by doping TiO@sub 2@ with nitrogen. Here we present detailed photoemission and scanning tunneling microscopy studies of single crystal rutile and anatase TiO@sub 2@ samples, which were nitrogen-doped by ion implantation.@footnote 2@ Only one oxynitride species was identified in XPS for nitrogen. Valence band spectra showed additional states at the top of the valence band for N-doped samples. These were identified as N-2p states, which appear to be not strongly hybridized with the O-2p valence band of pure TiO@sub 2@. Changes in Ti-3d induced defect states within the band gap are discussed in terms of N@super 3-@ induced charge compensation processes. We conclude that N-doping lowers the O-vacancy formation energy, which also triggers a 2x1 surface reconstruction of the rutile-TiO@sub 2@(110) surface upon N-doping. @FootnoteText@ @footnote 1@ R. Asahi, T. Morikawa, T. Ohwaki, K. Aoki, Y. Taga, Science 293, 269 (2001).@footnote 2@ M. Batzill, E.H. Morales, U. Diebold, Phys. Rev. Lett. 96, 026103 (2006).

9:40am SS-FrM6 Growth and Properties of High-Quality Epitaxial N-doped TiO@sub 2@(110) Grown by Molecular Beam Epitaxy, *S.H. Cheung, D.E. McCready, A.G. Joly, S.A. Chambers,* Pacific Northwest National Laboratory
N-doped TiO@sub 2@ is of potential interest for bandgap reduction and enhanced visible light absorption for water splitting. Despite a plethora of papers, typically lacking adequate materials characterization, very little is known about the fundamental properties of N:TiO@sub 2@. To this end, we have undertaken a study of TiO@sub 2-x@N@sub x@ films grown on rutile TiO@sub 2@(110) by molecular beam epitaxy. A mixed beam of atomic N and O was prepared in an electron cyclotron resonance plasma source while Ti was supplied using an effusion cell. Due to the interplay between substitutional N (an acceptor) and interstitial Ti (a donor), the conductivity and majority carrier type depend sensitively on the three atomic fluxes during growth. N incorporation at O sites appears to be thermodynamically limited to less than 2 at. % unless heavily defective material is deliberately made, in which case higher concentrations can be achieved. Optical absorption shows that substitutional N results in a new broad feature at the top of the valence band which functionally reduces the rutile bandgap by ~0.5 eV. The high degree of structural quality was evidenced by observations of finite thickness fringes in the vicinity of the (330) Bragg peak in high-resolution X-ray diffraction. Lattice expansions of 0.5% along the a axis and 0.8% along the c axis accompanies N substitution for O. A preliminary investigation of N-doped anatase grown on LaAlO@sub 3@(001) reveals that the same limited extent of N incorporation occurs for anatase as for rutile.

10:00am SS-FrM7 N and C Doping in TiO2 Using Ion Implantation for Photocatalysis Applications, *P. Nachimuthu,* UNLV*; S. Thevuthasan,* PNNL*; E.K. Vestergaard,* University of Washington*; M.H. Engelhard, I. Lyubinetsky, V. Shutthanandan,* PNNL*; T. Tyliszczak, D.K. Shuh,* LBNL*; Z. Dohnalek, M.A. Henderson,* PNNL
In semiconductor photochemistry, the redox potential of a photocatalyst is strongly influenced by its bandgap, which dictates the energy separation of the electron-hole (e@super -@/h@super +@) pairs by its band edge positions relative to electron donor/acceptor orbitals in the reactants. This in turn influences the degree of overlap between adsorbate molecular orbitals (in this case water) and the electronic states associated with the e@super -@/h@super +@ pairs. TiO@sub 2@ is one of the few candidates with promising photocatalytic properties although the optical absorption spectra of TiO@sub 2@ have poor overlap with the solar spectrum and high e@super -@/h@super +@ pair recombination rates. Solid state doping of anions causes a red-shift of the TiO@sub 2@ absorption spectrum into the visible region and visible light phtotoactivity has been observed from N-doped TiO@sub 2@. Recently, we have investigated the N and C doped in rutile TiO@sub 2@ by ion implantation. C 1s near-edge x-ray absorption fine structure (NEXAFS) shows features characteristic of Ti@sub 4@C and the intensity of these features are significantly improved following annealing at high temperatures. On the other hand, N 1s NEXAFS indicates that the features characteristic of N@sub 2@ increase with increasing annealing temperatures. XPS measurements clearly show peaks

at 403 eV characteristic of N-N interaction and at 396 eV from N atom present in the substitutional/interstitial site. Nuclear reaction analysis (NRA) and XPS depth profile measurements show that N remains in the lattice following high temperature annealing. These results will be discussed along with the of ion implantation for applications in photocatalysis.

10:20am SS-FrM8 STM Characterization of TiO$_2$(011)-2x1 Surface Morphology, *O. Dulub, M. Batzill, U. Diebold,* Tulane University*; A. Selloni,* Princeton University*; C. Di Valentin,* Università degli Studi di Milano-Bicocca, Italy

Titanium dioxide has a wide range of applications where its surface properties play an important role. Therefore, their study on the atomic scale is essential. The TiO$_2$(011) surface prepared by sputtering and annealing exhibits a stable (2x1) reconstruction in agreement with a previously proposed model by Beck et al. [Phys. Rev. Lett. 93 (3) (2004) 036104]. Atomically resolved STM images of the surface reveal flat terraces separated by monatomic steps. Unlike other TiO$_2$ surfaces, the (011) surface contains one-fold coordinated Ti=O (titanyl) groups, which are expected to have a diverse effect on surface chemistry. The Ti=O species form zig-zag chains along the [01bar1] direction, with O atoms imaged bright in empty-state STM. The most frequently occurring defects observed on the surface after argon ion sputtering and high-temperature UHV annealing are point defects (oxygen vacancies) and monolayer deep holes with several atoms missing. Oxygen vacancies appear as dark spots in STM images, in good agreement with DFT calculations. The density of such defects on the surface is reduced substantially upon re-annealing in molecular oxygen. Oxygen vacancies, as well as anti-phase domain boundaries in the (2x1) structure, are reactive sites for adsorption of gas molecules. Hydrogen atoms of hydroxyls groups, formed from dissociation of either H$_2$ or H$_2$O in the residual gas, are imaged as bright spots in STM. Argon ion bombardment and subsequent annealing in oxygen results in a rough surface with some (3x1) reconstructed areas. Segregation of calcium impurities from the bulk leads to a well-ordered overlayer structure with a centered (2x1) unit cell.

10:40am SS-FrM9 Structure and Properties of MBE-grown Epitaxial Anatase Films with Rutile Nanocrystalline Inclusions, *R. Shao, D.E. McCready, C.M. Wang, S.A. Chambers,* Pacific Northwest National Laboratory

TiO$_2$ is a wide band-gap oxide which is of interest for photocatalytic oxidation of organic pollutants. It is known that TiO$_2$ nanoparticles, which are suspected to consist of an anatase core and a rutile shell, enhance photocatalytic reactions compared to the pure phases. It has been suggested that this phenomenon is due to enhanced electron-hole pair lifetimes associated with the spatial separation of carriers across the anatase/rutile interface due to a staggered band alignment. Fundamental insight calls for the preparation and characterization of a model system with a well-defined anatase/rutile interface. To this end, we have used a region of the molecular beam epitaxy growth phase space for TiO2 on LaAlO$_3$ (001) and SrTiO$_3$ (001) in which rutile inclusions nucleate within a continuous epitaxial anatase layer. We start by growing a pure anatase (001) layer and then change the growth conditions to drive the nucleation of rutile particles. Control of the density and size of the rutile nanocrystals is highly sensitive to the growth conditions. X-ray diffraction shows that the rutile [100] axis is normal to the film plane. The anatase/rutile interface is atomically sharp and the preferential orientations of rutile nanocrystals in the film are determined from high-resolution transmission electron microscopy. X-ray photoemission measurements for anatase, rutile and anatase/rutile composite films indicate that the interface forms a nested rather than staggered heterojunction. In this talk, we will present details of the growth and properties of this system along with a study of electron transport across the interface as measured by scanning tunneling microscopy.

11:00am SS-FrM10 Sputtering Induced Vacancy Cluster Formation on TiO$_2$(110), *P. Karmakar, G.F. Liu, J.A. Yarmoff,* University of California, Riverside

Defects and oxygen vacancies markedly affect the electronic structure and adsorption properties of metal oxides, such as TiO$_2$. In addition, the catalytic behavior of supported metal particles, such as Au nanoclusters, can be enhanced by defects within the substrate. In this work, defects are introduced in a controllable manner via low energy ion bombardment, and the resultant material is probed with Scanning Tunneling Microscopy (STM) and X ray Photoelectron Spectroscopy (XPS). It is shown that 0.5 keV Ar$^+$ bombardment of TiO$_2$(110)

leads to a change of stoichiometry and the formation of mesoscopic features. XPS measurements reveal the loss of oxygen and the reduction of Ti^{4+} to Ti^{3+}. STM reveals the formation of nanometer scale vacancy clusters. The instabilities initiated by sputtering lead to the formation of these structures. The process can be explained within the framework proposed by B. Kahng et al.[1] Following significant Ar$^+$ bombardment, the cavities extend below the surface and diffuse out when the sample is annealed. Regular rectangular holes with single atomic layer steps form when sputtered TiO$_2$ is annealed at 880° C. @FootnoteText@ [1] B. Kahng, H. Jeong and A. L Barabasi, Appl. Phys. Lett. 78, 805 (2001).

11:20am SS-FrM11 Atomic Structure of the MgO(111)-($\sqrt{3}\times\sqrt{3}$)R30° Phase by Direct-Method Analysis of Surface X-Ray Diffraction Data, *S.S. Parihar, H.T. Johnson-Steigelman, P.F. Lyman, V.L. Shneerson, R. Fung, D.K. Saldin,* University of Wisconsin-Milwaukee*; F.U. Renner, T.-L. Lee, J. Zegenhagen,* ESRF, Grenoble, France

Polar-terminated oxides, where the bulk stacking produces a net dipole moment perpendicular to the surface, exhibit a rich set of energy-lowering mechanisms at the vacuum interface. For example, the polar oxide surface MgO(111) is known to undergo several air-stable reconstructions, including p(2x2) and ($\sqrt{3}\times\sqrt{3}$)R30° phases. The observed periodicity depends on O partial pressure and temperature. The ($\sqrt{3}\times\sqrt{3}$)R30° phase has been the subject of several structural investigations,[1,2] but agreement has not been reached on a unique structure. We report on a structural investigation of the MgO(111)-($\sqrt{3}\times\sqrt{3}$)R30° reconstruction by surface x-ray diffraction. Our direct-methods analysis[3] reveals maxima in the surface electron density. The atomic model suggested by the analysis can then be refined using the conventional χ^2 process. For the MgO(111)-($\sqrt{3}\times\sqrt{3}$)R30° surface, we observe 1/3 ML of adatoms, and 2/3 ML vacancies. Implications for structural models via conventional refinement will be discussed. @FootnoteText@ [1] R. Plass et al., Phys. Rev. Lett. 81, 4891 (1998).[2] A. Subramanian et al., Phys. Rev. Lett. 92, 026101 (2004).[3] P. F. Lyman et al., Surf. Sci. 600, 424 (2006).

11:40am SS-FrM12 Surface Structure of BaTiO$_3$ (001), *D.B. Li, R. Shao, D.A. Bonnell,* University of Pennsylvania

Although the structures of oxide surfaces have been the focus of much research for several decades, those on BaTiO$_3$ (001) have received relatively little attention. We have recently shown that this surface adopts several reconstructions depending on thermo-chemical history. The influence of ferroelectric domains on surface structure is not known. Here we use STM, nc-AFM, LEED and Auger electron spectroscopy to compare morphologies and reconstructions that form under different annealing conditions. In the evolution of a series of reconstructions a structural model, based on a comparison of STM and nc-AFM contrast of the (r5xr5)-R26.6^o and (3x1) superstructures, is proposed. Differences with analogous SrTiO$_3$ surfaces will be discussed.

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