

Surface Science

Room 203 - Session SS2-TuM

Defects on Oxide Surfaces

Moderator: D. Bonnell, University of Pennsylvania

8:20am **SS2-TuM1 Structure and Properties of SrTiO₃ (100) Surface**, *R. Shao, M. Nikiforov, D. Bonnell*, University of Pennsylvania

The surfaces of Strontium Titanate, one of the simplest perovskites, have been intensively studied because of its relevance to catalysis, environmental interactions and electronic devices. The (100) surface can terminate in either Sr-O or Ti-O planes. A number of reconstructions have been found on this surface depending on processing conditions. We have been able to stabilize atomically smooth (100) surfaces with unit cell (0.4 nm) and half unit cell (0.2 nm) steps assuring the presence of both types of terminations. Scanning tunneling spectroscopy of the two termination planes exhibits differences in electronic structure that are related to the proximity of Ti d orbitals near the surface. An orientational relationship between reconstructions and step edge direction is quantitatively related to strain from a systematic series of surfaces with different miscut angles. Finally the surface relaxation and electronic structure at low temperatures will be presented.

8:40am **SS2-TuM2 Oxygen Adsorption, Diffusion, and Reaction on a Reduced TiO₂ Surface**, *D. Pillay, G. Hwang*, The University of Texas at Austin

The rutile TiO₂ surface has been widely used as a catalyst for photochemical reactions and a support for transition metal catalysts. Molecular oxygen adsorption plays an important role in determining the activity of TiO₂ supported metal catalysts. Surface bound oxygen species may directly influence chemical and photochemical processes occurring on TiO₂. In addition, O₂ exposure leads to significant structural changes of supported metal particles, which may in turn affect their catalytic activity. It has been found that O₂ adsorbs on TiO₂(110) only when O-vacancies are present. Despite its importance, however the chemistry and dynamics of adsorbed oxygen species on a Au-covered reduced TiO₂(110) surface are still unclear. Using density functional theory calculations, we have investigated the adsorption and diffusion of oxygen species on the reduced TiO₂(110) surface. We have found that O₂ strongly binds not only to O-vacancies, but also to Ti(5c) neighbors, due to delocalization of unpaired electrons arising from the removal of neutral bridging oxygen atoms. Our results show that O₂ can jump across an oxygen vacancy and diffuse along a Ti(5c) row, with a moderate barrier that is significantly altered by the density of O vacancies. Based on our calculation results, we will discuss the diffusion and healing of O vacancies associated with O₂ adsorption, as a function of the vacancy density. We will also present the structure and energetics of higher coverage O₂ adsorption, as well as CO oxidation mechanisms on the reduced TiO₂(110) surface.

9:00am **SS2-TuM3 High-Resolution Scanning Tunneling Microscopy Studies of Surface Reactions on Rutile TiO₂(110)**, *F. Besenbacher*, University of Aarhus, Denmark **INVITED**

Transition-metal oxide surfaces play an important role in a wide range of applications, e.g. heterogeneous catalysis, photoelectrolysis, biocompatibility and sanitary disinfection. Defects like oxygen vacancies often dominate electronic and chemical properties of transition-metal oxide surfaces. In recent studies on a prototypical model oxide system (rutile TiO₂(110) surface) we exploited our high-resolution, variable-temperature and fast-scanning Aarhus STM to study how oxygen vacancies influence surface and interface reactions. Water dissociation on TiO₂ is of fundamental interest as an example of a simple surface chemical process with important applications. In high-resolution STM experiments, we unambiguously identify surface oxygen vacancies and hydroxyl groups. Controlled voltage STM pulses allow us to desorb OH groups only; O vacancies remain unaffected. Through STM images and time-resolved movies, we determine the active site responsible for the water molecule dissociation on TiO₂(110). At low H₂O exposures, O vacancies dissociate water molecules by transferring one proton to a nearby oxygen atom, forming two hydroxyl groups for every vacancy. At elevated exposures, a novel water dissociation channel is seen and will be described in detail. The amount of water dissociation is not limited by the density of oxygen vacancies on the clean surface as proposed earlier in literature. Extended

oxygen exposure on TiO₂(110) will lead to restoichiometrization of the support, thus markedly reducing its reactivity. An atomic-scale understanding of the healing process is still lacking, but it is thought to be a simple mechanism where a single O₂ molecule heals two vacancies subsequent to a dissociative process. Using high-resolution STM and TPD measurements, we investigate the interaction of O₂ from the gas phase with different surface defects (O vacancies, OH groups) on TiO₂(110).

9:40am **SS2-TuM5 Surface Reconstruction Variations on Barium Titanate (100)**, *R. Shao, D. Bonnell*, University of Pennsylvania

BaTiO₃ is a prototype ferroelectric compound and a simple model for interactions in complex oxides. Recently the effect of ferroelectric dipoles on interactions of surfaces has been examined as it relates to domain specific chemical reactivity. Scanning probe microscopy is the obvious probe of local surface reactions; however, it has proven difficult to obtain reproducible atomically smooth surfaces because of its tendency toward non stoichiometry and carbonate formation. In this work, we have determined the sequence of high temperature annealing in oxidizing and reducing atmospheres with which BaTiO₃ (100) surfaces can be produced with unit cell (0.4 nm) and half unit cell (0.2) step heights. These steps correspond to different lattice plane terminations. Atomic resolution STM is used in conjunction with LEED/AES and Scanning Surface Potentiometry (Kelvin Probe Microscopy) to compare the geometric and electronic structures that occur on these surfaces as a function of thermal history. Differences in electronic structure determined from tunneling spectroscopy are compared to theoretical predictions.

10:00am **SS2-TuM6 Defects Modeled with Vicinally-Stepped Oxide Surfaces: the Adsorption of Bromobenzene on NiO(100)**, *E.M. Marsh, S.C. Petitto, M.A. Langell*, University of Nebraska-Lincoln

The chemical reactivity of a metal oxide surface is often dominated by its defect properties. However, at naturally-occurring levels these defects are often present in low concentrations and as only one of a range of defect types making their effect on surface reactivity difficult to isolate. We have modeled oxide step defects with periodically-stepped NiO(100) substrates, where the predominant defect type and concentration can be readily controlled, and have investigated the ability of the stepped substrates to adsorb and dissociate bromobenzene (C₆H₅Br). The surfaces were characterized using Auger electron (AES) and x-ray photoelectron (XPS) spectroscopies, low energy electron diffraction (LEED), high resolution electron energy loss spectroscopy (HREELS) and thermal desorption mass spectrometry (TDS). In particular, the geometry of the adsorbate is correlated with short terrace widths and this in turn affects the dissociative nature of the adsorbate interaction.

10:20am **SS2-TuM7 Structure, Defects, and Adsorption on Metal Oxide Surfaces**, *U. Diebold*, Tulane University **INVITED**

In recent years, the surface science of metal oxides has experienced a remarkable increase in terms of research papers published, systems studied, and level of detail of the obtained information. A long-standing paradigm -- that surface defects on oxides are dominant reactivity centers -- is now scrutinized with scanning probe techniques. In this talk, I will give a representative overview of surface structural and adsorption studies on various surface orientations of TiO₂, ZnO, and SnO₂. Our experimental investigations are significantly enhanced through collaborations with theoretical groups.

11:00am **SS2-TuM9 Controlling Surface Reactivity of SnO₂(101): Dissociative and Molecular Water Adsorption**, *M. Batzill, U. Diebold*, Tulane University

Water adsorbs dissociatively on many oxide surfaces. In such cases undercoordinated surface oxygen atoms accept a proton and the remaining water-OH⁻ adsorbs on surface cation sites. Thus the surface reactivity towards water dissociation may be tuned by controlling the number of undercoordinated surface oxygen atoms (Bronsted base sites). On SnO₂(101) such a control over the surface composition can be exerted and the surface can be prepared with and without terminating oxygen atoms. Here we show by valence band photoemission that these two surfaces show different activity towards water adsorption. Surfaces without bridging oxygen adsorb water weakly while dissociation is observed on surfaces exhibiting terminating oxygen. The different activity of the surfaces is also apparent from water induced band bending. Dissociative adsorption causes downward band bending of ~0.35 eV which consequently causes a large increase in the surface conductivity of the SnO₂ sample. The latter is measured using a novel approach utilizing surface charging as a conductivity probe.

Tuesday Morning, November 1, 2005

@FootnoteText@ @footnote 1@ M. Batzill, A.M. Chaka, U. Diebold, Europhys. Lett. 65, 61 (2004).

11:40am SS2-TuM11 **The Reaction of Water over the Stoichiometric and Defected Surfaces of Uranium Dioxide: a High Resolution XPS Study**, S.D. Senanayake, G.I.N. Waterhouse, The Univ. of Auckland, New Zealand; A.S.Y. Chan, Rutgers, The State Univ. of New Jersey; D.R. Mullins, Oak Ridge National Lab.; T.E. Madey, Rutgers, The State Univ. of New Jersey; H. Idriss, The Univ. of Auckland, New Zealand

The chemistry of the uranium oxides is complex and historically been important to many aspects of nuclear technology. A recent study has shown using XPS that argon ion sputtering of the UO_2 surface can form a stable reduced oxide surface (UO_{2-x}) due to creation of oxygen defects. @footnote 1@ This work uses high resolution photoelectron spectroscopy (HRXPS) performed at the beam line U12a at the National Synchrotron Light Source/BNL to investigate the effect of this defect formation process. Sputtering at 300 and 95K gave different defect distributions. The reduced surface has a complex set of oxidation states lower than that of U^{+4} including U metal (U^0). Previous investigations made on the reactivity of water vapor on polycrystalline UO_2 @footnote 2@ and defected single crystal UO_{2-x} surface have revealed complex reaction pathways to the production of H_2 and XPS has further confirmed adsorbate induced oxidation of the surface. @footnote 1@ This work aims to further examine the effect of D_2O adsorption on the stoichiometric and sputter reduced surfaces of UO_2 at 300 and 95K. The effects of the thermal chemistry and oxidation of the surface is studied using temperature programmed XPS (TPXPS). In particular, the formation of D_2O ice at low temperature and dissociated OD species versus the role of defects in this heterogeneous interplay is examined. @FootnoteText@ @footnote 1@ Senanayake S.D., Idriss H., Surf. Sci. 563 (2004) 135. @footnote 2@ Senanayake S.D., Rousseau R., Colegrave D., Idriss H, J. Nucl. Mater. In press.

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