

Surface Science

Room: N - Session SS2-MoM

TiO₂ Surfaces and Interfaces

Moderator: D.A. Chen, University of South Carolina

8:20am **SS2-MoM1 Surface Structures of TiO_x Thin Films on Au (111)**, C. Wu, M.R. Castell, Oxford University, UK

Well-ordered ultrathin titanium oxide layers were grown on reconstructed Au (111) surfaces by Ti evaporation at room temperature and post-deposition oxidation at a pressure of 10-6 Pa O₂ and a temperature of around 600 °C. Depending on the amount of Ti deposited, three different structures were observed. The structures were characterized by scanning tunnelling microscopy (STM), X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES).

With Ti coverage below one monolayer (ML), an epitaxial oxide honeycomb structure is created. The herringbone reconstruction of the Au (111) substrate is lifted underneath the titanium oxide monolayer. STM reveals that the contrast between the honeycomb monolayer and the gold reconstruction is influenced by both tip termination and imaging bias. The measured periodicity and crystallographic alignment of the honeycomb structure indicates a (2 × 2) reconstruction on Au (111). XPS and AES data show the deposited titanium is fully oxidised to TiO₂. Increasing the Ti dose up to 2 MLs gives rise to a pinwheel structure that coexists with the honeycomb on the surface. The spokes of the pinwheels are parallel to the three close-packed directions of the honeycomb structure. Triangular islands start to grow and coalesce with higher Ti coverage. It is difficult to resolve the structure on the islands, but after 1.5 hours annealing of the thicker films, a row-like structure can be observed with a periodicity of 0.95 nm across the rows. XPS and AES indicate the presence of the Ti₂+ oxidation state.

8:40am **SS2-MoM2 Geometric Structure of the TiO₂(011) (2x1) Surface by Low Energy Electron Diffraction (LEED)**, S.E. Chamberlin, H.C. Poon, D.K. Saldin, C.J. Hirschmugl, University of Wisconsin - Milwaukee

The surface of TiO₂ has been extensively studied to explore its potential for many applications, including the harvesting of solar light and the photocatalysis of water [1-3]. The majority of studies have focused on the thermodynamically most stable rutile (110) face [4], however, other faces are almost as important. For example, the rutile (011) face may have enhanced activity towards water dissociation [5], but is less studied. Crucial to understanding the mechanisms by which these processes occur is determining the atomic structure and chemistry of the surface.

The (011) surface of TiO₂ is known to exhibit a (2x1) reconstruction [6] and several models of the surface have been proposed [6-9]. The present work extends quantitative low energy electron diffraction (LEED) to reconstructed oxide surfaces in order to determine which, if any, of these models are supported by LEED-IV. I-V curves, with a total energy range of ~2200 eV, were extracted for 20 beams using a novel, low-current, delay-line-detector LEED (DLD-LEED) system to minimize effects due to charging and electron beam damage. Structural refinement from the LEED-IV analysis confirms the Brookite model [8] found by surface x-ray diffraction, with agreements in atomic displacements to within 0.04 Å perpendicular to the surface and 0.12 Å parallel to the surface. The resulting Pendry R-factor is 0.29 which definitively excludes the other proposed models that give significantly higher R factors.

[1] A. Fujishima and K. Honda, Nature (London) **238**, 37 (1972)

[2] M. Gratzel, Nature **414**, 338 (2001)

[3] T.L. Thompson and J.T. Yates, Chem. Rev. **106**, 4428 (2006)

[4] M. Ramamoorthy, D. Vanderbilt, and R.D. King-Smith, Phys. Rev. B **49**, 16721 (1994)

[5] J.W. Lowekamp, G.S. Rohrer, P.A.M. Hotsenpiller, J.D. Bolt, and W.E. Farneth, J. Phys. Chem. B **102**, 7323 (1998)

[6] T. J. Beck *et al.*, Phys. Rev. Lett. **93**, 036104 (2004)

[7] T. Kubo, H. Orita, and H. Nozoye, J. Am. Chem. Soc. **129**, 10474 (2007)

[8] X. Torrelles *et al.*, Phys. Rev. Lett. **101**, 185501 (2008)

[9] X.Q. Gong *et al.*, Surf. Sci., **603**, 138 (2009)

9:00am **SS2-MoM3 Metal Oxide Surfaces: Defects, Dopants, and Reactivity**, U. Diebold, Tulane University **INVITED**

Metal oxides are versatile materials and are used in a wide variety of technical fields. In many applications, surface properties play a critical role in device functioning. Our group is investigating the atomic-scale properties of metal oxide surfaces with Scanning Tunneling Microscopy (STM) and area-averaging surface spectroscopies. DFT calculations, conducted in collaboration with theoretical groups, are instrumental in data analysis and interpretation.

In the talk we report recent results on metal oxide materials that have industrial relevance but are rarely studied with surface science techniques. We find that on a TiO₂ anatase (101) surface standard preparation procedures lead to *sub*surface rather than surface oxygen vacancies [1]. Adsorbed water shows an interesting short-range ordering that is governed by substrate-mediated repulsive/attractive interactions [2]. The surface structure of epitaxial films of Sn-doped In₂O₃ (ITO) is discussed [3].

[1] Y. He *et al.*, Phys. Rev. Lett. **102**, 106105 (2009).

[2] Y. He *et al.*, Nature Mater. in press (2009).

[3] E. H. Morales *et al.*, New Journal of Physics, **10** (2008) 125030

9:40am **SS2-MoM5 Controlled Manipulation of Oxygen Vacancies on TiO₂(110)-1x1 Using LT-STM**, D. Acharya, P.W. Sutter, Brookhaven National Laboratory

Titanium dioxide (TiO₂) – widely used in, photocatalysis, heterogeneous catalysis, gas sensors, and solar cells – has become the prototype material for studying the chemical reactivity of metal oxide surfaces. Oxygen vacancies are among the primary chemically active defects on this surface, as well as on other reducible transition metal oxides. We report the controlled manipulation of individual O-vacancies (O_v) on reduced TiO₂ (110)-1x1 in low temperature scanning tunneling microscopy. Using localized voltage pulses, the hopping of oxygen vacancies can be controlled precisely along the bridging oxygen rows. We apply this single-vacancy manipulation to study the interaction of closely spaced vacancies, and to establish the possibility of forming highly reactive double and triple O_v clusters. The occurrence of such defects with exposed low-coordinated Ti atoms has implications on the reactivity of TiO₂(110) and of similar metal-oxide surfaces.

10:00am **SS2-MoM6 Oxygen Reactivity on Reduced TiO₂(110)**, N.G. Petrik, G.A. Kimmel, Pacific Northwest National Laboratory

The interaction of oxygen with TiO₂ is critical for a variety of applications including the photooxidation of organic materials, purification of water and air, and (potentially) photocatalytic water splitting. In this paper, the thermal and non-thermal (photon- and electron-stimulated) reactions of molecular oxygen are studied versus oxygen coverage on reduced TiO₂(110). At low temperatures, two O₂ can chemisorb per oxygen vacancy (V_O).¹ Hydroxylation of the vacancies (via dissociative water adsorption) does not affect the amount of chemisorbed O₂. Most of the chemisorbed molecules do not desorb upon annealing to 700 K, but react. The thermal reactions of the chemisorbed O₂ depend strongly on the oxygen coverage. When 1 O₂ is adsorbed in an oxygen vacancy, the molecule dissociates upon annealing above ~200 K, healing the vacancy and depositing an oxygen adatom on the Ti row. At an oxygen coverage of 2 O₂ per oxygen vacancy, the oxygen converts to another species (perhaps tetraoxygen or ozonide) in temperature range of 200 K < T < 400 K. This species subsequently decomposes at higher temperatures. The photon- (and electron-) stimulated desorption of chemisorbed oxygen are also very sensitive to the oxygen coverage. The results demonstrate that the reactivity of TiO₂(110) with O₂ is primarily controlled by the amount of electron-donating surface species on the surface (V_O's and/or hydroxyls).²

¹ G.A. Kimmel and N.G. Petrik, Phys. Rev. Lett. **100**, 196102 (2008).

² N.G. Petrik, Z. Zhang, Y. Du, Z. Dohnalek, I. Lyubinetsky, G.A. Kimmel, JCP submitted

10:40am **SS2-MoM8 Oxygen Interactions with Hydroxylated TiO₂(110) Surfaces**, Y. Du, A. Deskins, Z. Zhang, N.G. Petrik, G.A. Kimmel, Z. Dohnalek, M. Dupuis, I. Lyubinetsky, Pacific Northwest National Laboratory

Reactions leading from O₂ to H₂O on catalytically active surfaces often involve intricate mechanisms with a number of possible surface-bond intermediates, such as OH, HO₂, or H₂O₂. Such reactions on surfaces are challenging to explore with ensemble-average techniques because of the

extremely small number of participating molecules and the difficulty in resolving intermediates spectroscopically.

In this work, the reaction of O₂ with both partially and fully hydroxylated TiO₂(110) surface was directly followed by STM. The consecutive steps of both primary and secondary site-specific reactions have been tracked by comparing the atomically resolved STM images of same surface area before and after O₂ exposure. As a result, we have directly imaged two chemical intermediates, terminal OH and OOH, which have been proposed to play key roles in the interconversion of oxygen and water. By combining the site-specific STM and ensemble-averaging TPD/ESD studies, we also find that H₂O can participate in the reaction process in multiple ways – as a reactant, product, and catalyst. Specifically, water mediates the diffusion of surface species that would otherwise be stationary, and thus brings reactants together, catalyzing the reactions with O₂. As a result, most of the OH₂ can be removed via reaction with O₂ such that a fully hydroxylated surface can be converted to a nearly stoichiometric surface.

11:00am **SS2-MoM9 The Photochemistry of Trifluoroacetone on TiO₂(110)**, *R.T. Zehr, M.A. Henderson*, Pacific Northwest National Laboratory

The ultraviolet (UV) photon induced photodecomposition of 1,1,1-trifluoroacetone (TFA) adsorbed on the rutile TiO₂(110) surface has been investigated with photon stimulated desorption (PSD) and thermal programmed desorption (TPD). TFA adsorbed on the reduced surface (8% oxygen vacancies) showed a molecular desorption peak at 260 K that shifts to 220 K with increasing TFA coverage, indicative of inter-adsorbate repulsion in the adsorbed layer. Adsorption of TFA on a reduced TiO₂ surface pre-exposed to 20 L O₂ leads to the formation of a TFA peak at 350 K accounting for 2/3rd ML coverage. A second peak at 250 K (1/3rd ML) completes the monolayer. Irradiation of the TFA covered oxidized surface by UV light at 90 K reduces the intensity of the 350 K TPD peak, with the 250 K state unaffected. Post-irradiation TPD shows evidence of the formation of small amounts of acetate (evolving as ketene at 650 K) as a surface bound decomposition product. UV irradiation of TFA causes the near complete photodecomposition of the photoactive species, leading to PSD of CH₃, CF₃, and CO during irradiation. This result is in contrast to the photochemical behavior of acetone, butanone and acetaldehyde on TiO₂(110), where the gas phase ejection of only one of the two carbonyl substituent groups is observed and a stoichiometric amount of carboxylate is left on the surface. We conclude that fluorination alters the electronic structure of adsorbed carbonyls on TiO₂(110) in such a way as to promote complete fragmentation of the adsorbed carbonyl complex.

(This work was supported by the DOE Office of Basic Energy Sciences, Division of Chemical Sciences and performed in the Environmental Molecular Sciences Laboratory at PNNL.)

11:20am **SS2-MoM10 TiO₂ with Subsurface Metallic Nanoclusters for Stimulating Photochemistry**, *F. Womack, F. Wang, Z. Zhang, P. Sprunger, R.L. Kurtz*, Louisiana State University

Metallic nanoclusters can be buried within nanometers of the surface of TiO₂ and can enhance photoabsorption to produce hot electron-hole pairs for surface chemistry. When Ag is grown on TiO₂(110), STM shows that it forms ~ 5nm clusters, and HREELS shows a plasmon resonance at 3.7 eV. AFM shows that these clusters remain after coating with a thin layer of titania and conducting probe AFM shows that the conductivity in the vicinity of the clusters is enhanced consistent with their metallic nature and increased defect densities in the oxide. HREELS shows that the plasmon resonance of the nanocluster is red-shifted and broadened to 1.5-2 eV when encapsulated in titania and these findings are supported by optical measurements. The nanoclusters induce defects within the surrounding titania and the role that Ti³⁺ defects, O-vacancies, and Ti-interstitials play in Ag/TiO₂ interactions as probed with synchrotron-based photoemission will be discussed. Electrochemical measurements have been conducted to test photochemical performance in electrolyte, and subsequent surface analysis provides information on the changes induced in morphology, defect densities, and oxidation states.

We acknowledge the support of NSF through CHE-0615606.

11:40am **SS2-MoM11 Switching of Sulfur Lattice Sites in S-doped TiO₂(110) Under Controlled Annealing Environments**, *N. Athavan, Portland State University, V. Shuthanandan, P. Nachimuthu, S. Thevuthasan*, Pacific Northwest National Laboratory

TiO₂ is one of the most heavily studied materials for photocatalytic water splitting even though it has a poor overlap of its optical absorption spectrum with the solar spectrum and high e⁻/h⁺ pair recombination rate. Band gap reduction is one approach to enhance visible light absorption in TiO₂. Anion (N, C and S) doping causes a red shift of the absorption edge into the visible

region and visible-light-induced photochemistry has been observed on these materials. Recently, we have investigated S doped TiO₂(110) rutile by ion implantation as a function of substrate temperatures and dopant concentrations. Subsequently high-temperature annealing was carried out on selected samples to heal the implantation damage as well as to understand the location and mobility of the dopants in the rutile lattice. Following implantation and annealing, the samples were characterized using several surface and bulk sensitive techniques such as x-ray photoelectron spectroscopy (XPS), Rutherford backscattering spectrometry (RBS), nuclear reaction analysis (NRA) and proton induced x-ray emission (PIXE) in both random and channeling directions. Depth profile of S implanted TiO₂ was obtained using XPS. PIXE was used to locate the lattice sites of S while NRA and RBS were used to measure the lattice sites of oxygen and titanium atoms, respectively. PIXE measurements along the channeling and random geometries clearly demonstrate the substitution of sulfur for oxygen in TiO₂ lattice under certain implantation conditions. Angular scans obtained around <110> were used to investigate the lattice site locations of sulfur at different annealing conditions. When the implanted sample is further annealed at 700°C for 1 hour at 100 Torr of oxygen, the sulfur atoms moved from the substitutional sites to interstitial sites. Subsequent annealing in vacuum (1 x10⁻⁵ Torr) at 800°C for 1 hour showed that the displaced sulfur atoms reoccupied the substitutional sites. Additional vacuum annealing at 900°C is not only retained the S atoms at the oxygen lattice sites but also improved the overall crystalline quality of the implanted region.

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