

Monday Morning, November 10, 2014

Surface Science

Room: 315 - Session SS+EN-MoM

Photocatalysis and Photochemistry at Surfaces

Moderator: Andrew Gellman, Carnegie Mellon University, Bruce Koel, Princeton University

8:20am **SS+EN-MoM1 Reaction Chemistry at Surfaces of Hematite-Based Photoelectrocatalysts**, *P. Zhao, C. Kronawitter, Bruce Koel*, Princeton University

Hematite (α -Fe₂O₃)-based photoanodes are promising materials for photoelectrochemical hydrogen generation. We report on fundamental studies of surface structure and reaction chemistry associated with the heterogeneous oxidation of water on such materials by applying a classical surface science approach. We have characterized the structure and properties of Ni-doped and mixed-oxide hematite surfaces formed by vapor deposition under controlled conditions utilizing a range of techniques for surface analysis. The structure of Ni-modified thin films of α -Fe₂O₃ model catalysts with different morphology and geometry was characterized by LEED and STM. Then, water adsorption and reaction were studied by TPD, XPS, UPS, and vibrational spectroscopy by HREELS, characterizing the influence of Ni-modification on thermal and photochemical reaction mechanisms. Ni doping is found to be associated with a new termination for the α -Fe₂O₃(0001) film. Water TPD shows that Ni doping induces new surface chemistry, as revealed by a new, higher temperature OH recombination desorption peak, which is due to more stable surface-bound OH groups as identified by UPS. These surface-science type experiments were combined with photoelectrochemical water oxidation measurements on photoanodes prepared by thin-film and nano-materials synthesis to elucidate new information on the surface phases of hematite-based photoanodes and about their specific stability and reactivity toward photoelectrochemical water splitting.

This work was supported by the Addy/ISN North American Low Carbon Emission Energy Self-Sufficiency Fund of the Andlinger Center for Energy and the Environment (ACEE) and by the Grand Challenges Program at Princeton University.

8:40am **SS+EN-MoM2 Infrared Reflection-Absorption Spectroscopy Study of Adsorption and Photo-Decomposition of Formic Acid on Reduced and Defective Rutile TiO₂ (110) Surfaces**, *Andreas Mattsson, L. Österlund*, Uppsala University, Sweden

Adsorption and photo-decomposition of formic acid on rutile TiO₂(110) have been investigated with infrared reflection-absorption spectroscopy (IRRAS) employing p- and s-polarized light along the [001] and [1-10] crystal directions. The single crystal surfaces were prepared either by sputtering and annealing in ultra-high vacuum (UHV) to obtain a reduced surface (r-TiO₂), or by sputtering alone to create a rough, highly defective surface (sp-TiO₂). Results are compared with corresponding measurements in synthetic air on rutile nanocrystals performed. IRRAS spectra obtained on r-TiO₂ and rutile nanocrystals are very similar (Fig. S1), and show that in both cases formic acid dissociates and is predominately adsorbed as a bridging bidentate formate species,¹ demonstrating that the adsorption structure on the nanocrystals is determined by interactions with majority (110) surfaces. In contrast, the IRRAS spectra on sp-TiO₂ are different (Fig. S1), with only minor spectral features associated with (110) surfaces, which can be explained by changed adsorption geometry due to bonding to low-coordinated Ti³⁺ atoms. IRRAS measurements in UHV on thin nanoporous rutile films, made by reactive DC sputtering, were performed to compare the adsorption geometry of formate with that for single crystal surfaces and nanoparticles. The UV-induced rate of formate photo-decomposition is about 30 times higher on rutile nanocrystals in synthetic air compared with sp-TiO₂ under UHV conditions, and even larger than on r-TiO₂.² These differences are explained by the lack of oxygen and limited hydroxyl coverage under UHV conditions (thus quenching electron scavenging by adsorbed O₂ and lowering OH radical formation), and by strong bonding of formate on (110) surfaces which lowers the reactivity on r-TiO₂ further. Our results suggest that surface reaction studies of formic acid conducted at elevated pressures on rutile nanocrystals can be accurately modelled with single crystal studies conducted in UHV.

¹ A. Mattsson, S.-L. Hu, K. Hermansson, L. Österlund, *Journal of Chemical Physics* 140 (2014) 034705

² L. Österlund, *Solid State Phenomena* 162 (2010) 203-219

9:00am **SS+EN-MoM3 Molecular Beam Epitaxy of Highly Mismatched GaN Alloys with GaAs, GaSb and GaBi for Potential Water Splitting and Other Solar Energy Conversion Applications**, *Sergei Novikov*, University of Nottingham, UK, *K.M. Yu*, Lawrence Berkeley National Laboratory, *W.L. Sarney*, US Army Research Laboratory, *Z. Liliental-Weber*, Lawrence Berkeley National Laboratory, *R.W. Martin*, University of Strathclyde, UK, *S.P. Svensson*, US Army Research Laboratory, *W. Walukiewicz*, Lawrence Berkeley National Laboratory, *C.T. Foxon*, University of Nottingham, UK **INVITED**

We have grown GaN layers alloyed with GaAs, GaSb and GaBi compounds using plasma-assisted molecular beam epitaxy (PA-MBE) and extensively characterized their structural, optical and electrical properties.

Electronic band structures of these so-called highly mismatched alloys (HMAs) are described by the band anticrossing (BAC) model which predicts that the alloys should exhibit a wide range of direct energy gaps. We have shown previously that the energy gap of GaN_{1-x}As_x alloys varies from 0.7eV to 3.4eV. An even larger modification of the band structures is anticipated for more extremely mismatched GaN_{1-x}Sb_x and GaN_{1-x}Bi_x alloys. The large band gap range and controllable conduction and valence band edge positions makes the HMAs promising materials for efficient solar energy conversion devices. For example, these HMAs may be suitable for solar water splitting applications for hydrogen production. As efficient photoelectrodes, the bandgap of the semiconductor must be >2 eV to induce electrochemical decomposition of water but still small enough to absorb a significant portion of the solar spectrum. In addition the band edges must also straddle the H₂O redox potentials.

At dilute doping levels, substitutions of As, Sb and Bi into the N sublattice results in formation of localized energy levels above the valence band in GaN. Our measurements on GaN doped with As and Sb have demonstrated that the As and the Sb impurity levels lie at about 0.7eV and 1.2eV above the valence band edge of GaN, respectively.

The BAC model predicts that at a higher concentration of the group V elements the interaction of the impurity levels with the extended states of the valence band leads to formation of an impurity-derived, fully occupied narrow band that plays a role of the new valence band edge. This results in an abrupt upward shift of the valence band edge and a reduction of the optical gap of the HMAs. We have achieved the enhanced incorporation of As, Sb and Bi by growing the layers at extremely low temperatures (down to about 100°C). Although the layers become amorphous for high As, Sb and Bi content, the measured composition dependence of the optical absorption edge are consistent with the predictions of the BAC model, indicating that the amorphous HMAs samples have a short-range order resembling random crystalline alloys. The large band gap range and controllable positions of the conduction and valence bands make these HMAs promising materials for efficient solar energy conversion devices.

9:40am **SS+EN-MoM5 Photochemistry of Acetone on Reduced Rutile TiO₂(110)**, *Nikolay Petrik, M.A. Henderson, G.A. Kimmel*, Pacific Northwest National Laboratory

TiO₂ is an important photocatalyst with many practical applications. However, fundamental understanding of thermal and non-thermal reactions on TiO₂ surfaces is still lacking. We have investigated the ultraviolet (UV) photon-stimulated reactions acetone and oxygen adsorbed on reduced rutile TiO₂(110). Previous research suggests that a thermal reaction between acetone and chemisorbed oxygen forms acetone diolate – a photochemically active product.¹ During UV irradiation, a methyl radical is ejected leaving acetate on the surface. Using infrared reflection absorption spectroscopy, we have identified the acetone diolate, which degrades during UV irradiation forming a new product. We have also measured the angular distribution of the photodesorbing methyl radicals, which is consistent with their ejection from the acetone diolate. Specifically, a peak in the distribution near ~60° to the surface normal is detected in the plane perpendicular to the BBO rows. However, we have also observed a second channel for photo-ejection of methyl radical for larger acetone:O₂ ratios. It manifests itself with a photodesorption peak normal to the surface and slower signal decay kinetics. These studies provide new insights into mechanisms responsible for the photochemistry of small molecules on TiO₂ and other oxide surfaces. This work was supported by the US Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences & Biosciences. The work was performed using EMSL, a national scientific user facility sponsored by the Department of Energy's Office of Biological and Environmental Research and located at Pacific Northwest National Laboratory (PNNL). PNNL is a multiprogram national laboratory operated for DOE by Battelle under Contract DE-AC05-76RL01830.

(1) Henderson, M. A. Relationship of O₂ Photodesorption in Photooxidation of Acetone on TiO₂. *J. Phys. Chem. C*, 2008, 112, 11433-11440.

10:00am **SS+EN-MoM6 STM Spectroscopic Studies of TMAA Photocatalysis on TiO₂**, *Denis Potapenko, Z. Li, R.M. Osgood*, Columbia University

Titanium oxide is a versatile photocatalytic material and it has been the subject of much research throughout the last two decades. Scanning Tunneling Microscopy (STM) allows explorations on the single molecule basis thus providing important insight into the physical phenomena involved in photocatalysis. Our experiments examine the tip-induced chemistry of tri-methyl acetic acid (TMAA) molecules adsorbed on TiO₂ rutile(110) surface; this system was chosen as a model for light-driven catalysis since it is easily imaged with STM and since this system has been the subject of many earlier studies of photo and thermal chemistry. In the present work we combine three methods of initiation of surface chemistry: a) excitation of charge carriers in bulk TiO₂ with monochromated light from a UV-vis lamp, b) injection of the charge carriers from the STM tip directly into an adsorbed molecule, and c) injection of hot carriers into the substrate from the STM tip. In the latter case the surface reactions are initiated in the vicinity of the injection point by the electrical charges diffusing in the bulk of TiO₂, thus giving a unique insight into the charge dynamics. We show that there is a threshold energy for a hot hole below the edge of the TiO₂ valence band that is required for TMAA photo-decomposition.

11:00am **SS+EN-MoM9 Photoluminescence Response of p-GaInP₂ Photocathodes to Vapor and Solution Ambients**, *James Young*, University of Colorado, Boulder, *H. Doscher, T.G. Deutsch, J.A. Turner*, National Renewable Energy Laboratory, *S.M. George*, University of Colorado, Boulder

III-V photoelectrochemical (PEC) devices have achieved high solar-to-hydrogen water splitting efficiencies but corrosion greatly limits their operating lifetime. A dynamic three-phase semiconductor-electrolyte-hydrogen (oxygen) system exists at a photocathode (photoanode) surface during operation. Understanding the interaction of water, hydrogen, and oxygen with III-V surfaces is critical to optimizing device performance and applying corrosion-resistant surface modifications. In this work, we use photoluminescence (PL) to probe the surface response of p-type GaInP₂ to several gas and solution ambients *in-situ*. X-ray photoelectron spectroscopy and photoelectrochemical techniques are used to characterize surface changes *ex-situ*. Pretreating p-GaInP₂ with sulfuric acid removes surface oxide and doubles p-GaInP₂ band-to-band PL yield when measured in air. Measurements in vacuum show that PL of pretreated samples increases reversibly with adsorption isotherm dependence on water vapor at partial pressures below 2 Torr while samples without the pretreatment show no PL response to water vapor. A comparison of water to other vapor phase ambients suggests that PL response increases with the dipole strength and involves dissociative adsorption. In oxygen ambient, the PL decays irreversibly which we attribute to photo-oxidation of the p-GaInP₂ surface. We will also present results from measurements in hydrogen ambient and PL measurements and monitoring in electrolyte solutions with a discussion of their relevance to PEC device performance and usefulness in characterizing corrosion resistant surface modifications.

Authors Index

Bold page numbers indicate the presenter

— D —

Deutsch, T.G.: SS+EN-MoM9, 2
Doscher, H.: SS+EN-MoM9, 2

— F —

Foxon, C.T.: SS+EN-MoM3, 1

— G —

George, S.M.: SS+EN-MoM9, 2

— H —

Henderson, M.A.: SS+EN-MoM5, 1

— K —

Kimmel, G.A.: SS+EN-MoM5, 1
Koel, B.: SS+EN-MoM1, **1**
Kronawitter, C.: SS+EN-MoM1, 1

— L —

Li, Z.: SS+EN-MoM6, 2
Liliental-Weber, Z.: SS+EN-MoM3, 1

— M —

Martin, R.W.: SS+EN-MoM3, 1
Mattsson, A.: SS+EN-MoM2, **1**

— N —

Novikov, S.V.: SS+EN-MoM3, **1**

— O —

Osgood, R.M.: SS+EN-MoM6, 2
Österlund, L.: SS+EN-MoM2, 1

— P —

Petrik, N.G.: SS+EN-MoM5, **1**

Potapenko, D.V.: SS+EN-MoM6, **2**

— S —

Sarney, W.L.: SS+EN-MoM3, 1
Svensson, S.P.: SS+EN-MoM3, 1

— T —

Turner, J.A.: SS+EN-MoM9, 2

— W —

Walukiewicz, W.: SS+EN-MoM3, 1

— Y —

Young, J.L.: SS+EN-MoM9, **2**
Yu, K.M.: SS+EN-MoM3, 1

— Z —

Zhao, P.: SS+EN-MoM1, 1