

# Wednesday Morning, December 10, 2014

## Energy Harvesting & Storage

Room: Lehua - Session EH-WeM

### Characterization of Materials for Energy Applications I

Moderator: Mayo Villagran

8:00am **EH-WeM1** **Hindering Effect of Surface Point-Defects for Photoreactivity on TiO<sub>2</sub>(110)**, *Igor Lyubinsky*, Pacific Northwest National Laboratory

**Hindering Effect of Surface Point-Defects for Photoreactivity on TiO<sub>2</sub>(110)**

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While surface point-defects are expected to act as charge trapping and/or recombination centers in photoinduced processes, their direct impact of surface defects on photoreactivity is not well explored. We present the first observation of a suppressing effect of oxygen vacancy ( $V_O$ ) defects on photoreactivity of TiO<sub>2</sub>(110). Direct scanning tunneling microscopy imaging reveal a pronounced site-selectivity in the hole-mediated photooxidation of trimethyl acetate (TMA) on TiO<sub>2</sub>(110) upon ultra-violet light irradiation, wherein the reaction readily occurs at regular Ti sites but is completely inhibited at  $V_O$  defects. Utilizing electron energy loss spectroscopy and density functional theory, we show that the lack of reactivity of TMA groups adsorbed at  $V_O$ 's cannot be attributed to either a less active adsorption conformation or electron transfer from the  $V_O$  defect. Instead, we propose that the excess unpaired electrons associated with the  $V_O$  promptly recombine with photoexcited holes approaching the surface, effectively 'screening' TMA species at  $V_O$  site. We also show that this screening effect is spatially short-ranged, being predominately localized at the  $V_O$ , and only mildly affecting TMA's at adjacent Ti sites. The direct impact of O vacancies on TMA photoreactivity over TiO<sub>2</sub>(110) is expected to have similar implications for other hole-mediated (e.g., photooxidation) reactions in which adsorption at or near electronic point-defects is possible. Furthermore, the localized influence of these defects on hole-mediated chemistry offers opportunities for additional study of site-selective photocatalysis on TiO<sub>2</sub>.

\* In collaboration with Z.-T. Wang and M.A. Henderson, PNNL and N.A. Deskins, Worcester Polytechnic Institute. We acknowledge support from the US DOE BES, Division of Chemical Sciences, Geosciences & Biosciences. A portion of this research was funded by the Chemical Imaging Initiative LDRD at PNNL.

8:20am **EH-WeM2** **Atomic Structure and Intrinsic Electronic States of the In<sub>2</sub>O<sub>3</sub>(111) surface**, *Holger Eisele Eisele, R. Zielinski, A. Lenz*, Technische Universität Berlin, Germany, *Z. Galazka*, Leibniz Institute for Crystal Growth, Germany, *M. Dähne*, Technische Universität Berlin, Germany

Indium oxide as transparent semiconductor is one of the most promising materials for contact layers in photovoltaic applications. Nevertheless, due to the delicate fabrication process for single crystals only a few intrinsic properties are known about In<sub>2</sub>O<sub>3</sub>, yet. Especially the storage under air conditions may influence the surface properties. Hence it is hard to decide, which properties are intrinsic and which ones are influenced by physisorbed and/or chemisorbed atoms and molecules from the ambient air.

In this contribution for the first time we studied high quality single crystals at their freshly UHV-cleaved (111) surfaces by scanning tunneling microscopy (STM) and spectroscopy (STS). From these investigations we achieve knowledge about the atomic configuration at the surface. This configuration fits well with recent density functional theory calculations, and indicate a local charge enhancement within the surface unit cell. Furthermore, STS reveals intrinsic electronic surface states within the fundamental band gap. The Fermi level is also energetically located within the fundamental bulk band gap, which leads to the assumption that previously reported electron accumulation at this surface is not an intrinsic property, but related to extrinsic effects, such as e.g., non-stoichiometric material reorganization. After oxidation of the In<sub>2</sub>O<sub>3</sub>(111) surfaces outside the UHV their structural as well as their electronic properties look quite different: astonishingly both show much more metallic behaviour as the freshly cleaved ones kept under UHV-conditions. The processes leading to such an behaviour are still under discussions, but the data fits much better to previous observations.

8:40am **EH-WeM3** **Laser-Excited Scanning Tunneling Spectroscopy of Materials for Solar Cell Application**, *Verena Portz, M. Schnedler, R.E. Dunin-Borkowski, P. Ebert*, Forschungszentrum Jülich GmbH, Germany

Materials for solar cell and optoelectronic applications are critically affected by defects. The defects can give rise to deep gap states, which can lead to non-radiative carrier recombination centers. These are detrimental to both the electron-light and light-electron conversion efficiencies in optoelectronic and solar cell devices, respectively. In order to understand the physical processes involved at the atomic scale, the materials used in the device structures need to be investigated under illumination with atomic resolution.

Therefore, we investigated the prototype group III-V semiconductor GaAs as a model system by light-excited scanning tunneling microscopy and spectroscopy. We used GaAs(110) cleavage surfaces, which are free of intrinsic surface states in the band gap, and hence the surface potential is governed by the underlying bulk doping. The effect of the laser irradiation on the scanning tunneling spectra was determined on the clean defect-free surface, at dopant sites, and close to defects, using a newly developed measurement methodology, whose advantages will be discussed. The atomically-resolved spectra show distinct changes of the local potential at the different sites, which can be related to the local distribution of the illumination-induced carrier concentration. In order to analyze the spectra in detail, we developed a simulation program, which allows us for the first time to calculate quantitatively the effect of laser irradiation on the tunnel current. The physical models used for the simulation will be discussed. Fits of the simulated spectra to the measured ones allow the determination of the local redistribution of light-excited carriers and the identification of atomic scale carrier recombination centers

9:00am **EH-WeM4** **TEM Observation of Nano Porous Gold in Reaction Environment**, *Takeshi Fujita*, Tohoku University, Japan  
**INVITED**

Nanoporous gold (NPG) produced by dealloying possesses a self-organized, self-supporting three-dimensional (3D) nano-architecture, which gains increased attentions as a multifunctional material for a wide range of applications. Similar to small gold nanoparticles, NPG has been demonstrated to be catalytically active for a number of important chemical/electrochemical reactions, but at a much larger characteristic size (>20 nm) for both gold ligaments and nanopores. While many factors have been suggested to explain the nano-size chemical effect of gold nanoparticles, such as quantum size effects, charge transfer between gold nanoparticles and oxide supporters, and enhanced concentration of low-coordination atoms, on the other hand the self-supported NPG indicates that the unique morphological characteristics alone is responsible for the catalytic activity of NPG.

We characterized the microstructure of NPG using spherical-aberration-corrected transmission electron microscopy (Cs-corrected TEM). The atomic structure of the internal surfaces of NPG, responsible for the catalytic activity, was imaged by scanning transmission electron microscopy (STEM) using a high-angle annual dark-field (HAADF) detector. The arrangement of near-surface atoms was also measured accurately by Cs-corrected high-resolution TEM (HRTEM), which provides phase-contrast images with high displacement sensitivity. On the basis of extensive HRTEM and STEM characterization, the high catalytic performance of NPG was suggested to originate from surface strains and a high concentration of low-coordination atoms stabilized by the complex geometry of bicontinuous nanoporosity of NPG. In addition to the static observation in inert vacuum environment, we also characterized the surface atomic structure evolution during CO oxidation in a reactive atmosphere using a newly dedicated environmental HRTEM [1].

Our key observation also provided the first direct atomic observations of the coarsening process of the porous catalyst, which shows completely different mechanisms of catalytic degeneration when compared to conventional nanoparticulate catalysts. More importantly, the atomic observation provides compelling evidence that planar defects such as twins can effectively prevent structure coarsening, suggesting a new strategy for developing chemically active and structurally sound catalysts. The effect of planar defects on catalysis has been highlighted recently and our observation offers the first direct experimental evidence of this important phenomenon [2].

[1] Fujita, T. et al., Nature Materials, 11 (2012) 775-780.

[2] Fujita, T. et al. Nano Letters 14 (2014) 1172-1177.

9:40am **EH-WeM6 Characterizing Automotive Fuel Cell Materials by Soft X-Ray Scanning Transmission X-Ray Microscopy (STXM)**, *Adam Hitchcock, V. Lee*, McMaster University, Canada, *V. Berejnov, D. Susac, J. Stumper*, AFCC, Canada

Low temperature, hydrogen-fueled, proton exchange membrane fuel cell (PEM-FC) based engines are being developed rapidly for near-term implementation in mass production, personal automobiles. Materials and process research aiming to further optimize these systems is focused on understanding and controlling various degradation processes (carbon corrosion, Pt migration, cold start), and reducing cost by reducing or eliminating Pt in the electro-catalyst, especially for the oxygen reduction reaction (ORR). We are using soft X-ray scanning transmission X-ray microscopy (STXM) at the S 2p, C 1s, O 1s and F 1s edges to study a variety of issues related to optimization of PEM-FC materials for automotive applications. STXM provides spectroscopic identification and quantitative mapping of chemical components with 30 nm spatial resolution in both 2D projection and 3D spectro-tomography. Themes of our studies include: mapping ionomer in cathodes of beginning-of-life and end-of-life membrane electrode assemblies [1,2, 3]; investigating Pt-in-membrane [4] and carbon corrosion degradation [3]; studies of alternate electrode technologies (3M nanostructured thin films [5], ink-jet print [6]); and measuring water distributions *in situ* [7]. The O 1s spectra of the 3 phases of water differ from those of membrane electrode assemblies (MEA) constituents allowing direct *in-situ* visualization of water uptake and quantitative mapping of gas and liquid/sorbed water. A newly developed environmental cell for *in situ* studies with controlled humidity and temperature will be described and its current performance will be outlined.

Research funded by AFCC and NSERC. Measurements were made at the Canadian Light Source (supported by NSERC, NRC, CIHR, and the University of Saskatchewan) and at the Advanced Light Source (supported by the Division of Basic Energy Sciences of U.S. DoE).

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- [4] V. Berejnov, et al, Phys. Chem. Chem. Phys. **14** (2012) 4835
- [5] V. Lee, V. Berejnov, M. West, S. Kundu, D. Susac, J. Stumper, R.T. Atanasoski, M. Debe and A.P. Hitchcock, J. Power Sources **263** (2014) 163
- [6] M.S. Saha, M. Tam, V. Berejnov, D. Susac, S. McDermid, A.P. Hitchcock and J. Stumper, ECS Transactions, **58** (2013) 797
- [7] V. Berejnov, D. Susac, J. Stumper and A.P. Hitchcock, ECS Transactions **41** (2011) 39

10:20am **EH-WeM8 New Insights into Energy-Related Materials from Advanced Electron Microscopy Methods**, *Gianluigi Botton*, McMaster University, Canada **INVITED**

Electron Microscopy and electron energy loss spectroscopy are invaluable techniques to study the detailed structure and the chemical state of materials at unprecedented spatial resolution. In today's modern electron microscopes, it is possible to tackle problems requiring the highest energy resolution, down to 60meV, and highest spatial resolution, down to the angstrom level, so that atomic resolved spectroscopy with high spectroscopic sensitivity and resolution can be obtained. This leads to the potential of covering excitation phenomena from the mid-infrared, soft-X-rays and even hard-X-ray regime.

In this presentation, various examples of applications of electron microscopy will be given based on a modern electron microscope. After an overview of the imaging conditions used to detect core-shell ordering changes in PtFe, PtRu, PtAu alloy nanoparticles [1,2] graphene and single atoms on doped graphene [3] used for fuel cell catalysts, using a combination of high-angle annular dark-field STEM imaging, EELS elemental mapping and simulations, we will discuss the application of atomic-resolved EELS mapping in to study complex oxide and oxide support materials used to promote strong metal support interaction [4]. Here we demonstrate how electron energy loss spectroscopy can be used to probe the valence change of the oxide following the interaction with the catalyst. This powerful technique can also be used to study of the structure and substitutional effects from single atom dopants in phosphors [5] and metallic alloys.

Additional examples will highlight the application of microscopy technique to the analysis of perovskite structures. These examples demonstrate that compositional and chemical state (valence and coordination) information can be obtained down to the Ångstrom level on surfaces [6].

References

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- 6) G.-Z. Zhu, G. Radtke, G.A. Botton, *Nature*, **490**, 384, (2012)

11:00am **EH-WeM10 The Use of Massive Ar Clusters for the Sub-Surface Characterization of Organic and Inorganic Materials**, *David Surman*, Kratos Analytical Inc., *J. Counsell, S. Hutton, H. Brannon*, Kratos Analytical Ltd., UK

Over the last several years massive Argon gas cluster ion sources as accessories for sputter depth profiling of organic materials have increased in popularity. These sources utilize Argon cluster ions formed via adiabatic isentropic expansion of Argon gas into a vacuum followed by subsequent electron impact ionization and cluster size selection. In ideal cases the aforementioned massive cluster ions efficiently sputter the surface of organic materials revealing undamaged subsurface structure for analysis. More recently, developments in the technology have expanded the use of these sources to allow for the sputtering of inorganic materials.

Advanced software controlled ion sources and flexible sample handling equipment allow a wide range of experimental conditions to be routinely employed during sputter depth profiling with these massive Argon clusters. In this study we have investigated a variety of parameters such as incident ion energy and cluster size distribution on the effectiveness of the sputtering process and the degree of chemical damage that is induced using X-ray Photoelectron Spectroscopy (XPS) as the monitor. A range of both organic and inorganic materials have been analysed. It has been observed that for most organic materials large cluster sizes with a medium beam energy (typically less than 10keV) are very effective for sputtering with no observable chemical damage. This is in contrast to sputtering of inorganic materials where typically high beam energies (greater than 10keV) and small cluster sizes are required for effective sputtering. The identification of a minimum partition energy for sputtering will be discussed. In addition, it will be demonstrated that, although preferential Oxygen sputtering can be observed on many oxides resulting in the formation of reduced chemical states, this effect is substantially reduced when compared to the use of monoatomic Ar ions.

11:20am **EH-WeM11 Recent Applications and Results in Near Ambient Pressure XPS - In-situ Cell Designs for Liquid Environments**, *Thomas Schulmeyer, A.T. Thissen*, SPECS Surface Nano Analysis, Inc.

Modern devices are often only functional in environments far away from ultrahigh vacuum, which is still considered the standard operating condition for all Surface Science techniques. Due to miniaturization down to the nanoscale, surfaces are increasingly important for device performance. In order to contribute to advanced material analysis in future Photoelectron spectroscopy, Scanning Probe Microscopies and related techniques must be performed in generic or near generic device environments. Such an environment would mean high, elevated or near ambient pressures of defined working gas mixtures, liquid media, potentials or magnetic fields; extremely low or high temperatures might also be necessary. Of course, all standard Surface Science Techniques did not work under these extreme environments previously. This work summarizes and presents existing solutions for present and future development routes to new instruments, and displays how material analysis methods are functional under these working conditions. The opportunities and limitations will be discussed from the perspective of suppliers of scientific instruments. And finally, application examples and results from existing In situ methods will be demonstrated. These methods include: high pressure treatment cells, complete High Pressure or Near Ambient Pressure Photoelectron Spectroscopy or Scanning Probe Microscopy Systems (NAP-PES or NAP-SPM), liquid and electrochemical cells, Liquid sample "manipulators", and concepts and status of equipment working in the highest or lowest temperatures, high magnetic fields and static or dynamic potentials.

11:40am **EH-WeM12 Dynamic H<sub>2</sub>O/GaP (111) Interfacial Chemistry Monitored by Near-Ambient Pressure XPS in Real Time**, *Xueqiang Zhang, S. Ptasinska*, University of Notre Dame

A photoelectrochemical (PEC) solar cell for water splitting can convert solar energy into chemical energy and store it in the form of hydrogen, a molecule regarded as a promising candidate for sustainable and clean fuels [1]. PEC solar cells using phosphide-based III-V semiconductors are known to have higher efficiency than other materials. They are, however, usually limited by issues such as photocorrosion or decreased electron extraction efficiency due to formation of interfacial oxide species, which becomes

especially critical when operating electrodes (typically, semiconductors) are exposed to aqueous electrolytes [2]. Therefore, It is desirable to understand the process of water interactions with semiconductors and possible oxidation and reduction mechanisms at the H<sub>2</sub>O/semiconductor interface, especially under near realistic conditions.

In the present study, water dissociative adsorption on a GaP (111) surface was investigated using near ambient pressure X-ray photoelectron spectroscopy (NAP XPS) at various pressures and temperatures. The interfacial chemistry was tracked by recording high resolution photoemission spectra of Ga 2p<sub>3/2</sub>, O 1s and P 2p. In the pressure-dependent study (room temperature, ~300 K), enhanced surface Ga hydroxylation and oxidation were observed with an increase of water vapor pressure, which was also mirrored by the photoemission spectra of O 1s. In the temperature-dependent study, surface Ga hydroxylation and oxidation were further enhanced at temperatures below 673 K. While a large-scale conversion of surface O-Ga-OH species into Ga hydroxide, along with surface P oxidation, was observed at a temperature of 773 K. The formation of Ga and P oxide/hydroxide networks with a schematic formula of Ga<sub>a</sub>P<sub>b</sub>O<sub>c</sub>(OH)<sub>d</sub> (a, b, c and d represent a ratio of different elements and groups) is suggested. Our results can be compared with recent theoretical findings [3, 4] and lead to a better understanding of water splitting mechanisms and photo-corrosion on semiconductor surfaces.

#### Reference

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