

Thursday Morning, October 18, 2007

Renewable Energy Science & Technology Topical Conference

Room: 602/603 - Session EN+SS+TF-ThM

Surface Science Challenges for Solar Energy Conversion

Moderator: M.A. Henderson, Pacific Northwest National Laboratory

8:00am **EN+SS+TF-ThM1 Thermal and Photoreactions of Catechol on TiO₂.** *P. Jacobson*, Tulane University, *X.-Q. Gong*, *M. Connors*, *A. Selloni*, Princeton University, *U. Diebold*, Tulane University

The wide band gap of titanium dioxide limits its use as a photocatalytic and photovoltaic material with solar radiation as its source. One method to increase the absorption of light at visible wavelengths is by attaching metallo-organic dye complexes. These dyes frequently use catechol and phosphonic or carboxylic acids to link the dye to the titanium dioxide surface. In an attempt to better understand the adsorption of these complex dyes, we have studied the adsorption of catechol (1,2-benzenediol) on the (110) and (011) faces of rutile titanium dioxide. Catechol was preferred over 'real' dye complexes for its ease of deposition under high vacuum conditions and simple chemical makeup. Ultraviolet photoemission spectroscopy shows a gap state introduced to the TiO₂ upon catechol adsorption. Increases in the Oxygen 1s shoulder in XPS indicate dissociative adsorption of catechol and formation of surface hydroxyls. For catechol adsorption on the rutile (110) surface a 3x1 overlayer results. Similarly, adsorption on the (011) surface forms a 2x1 overlayer. Formation of surface hydroxyls upon adsorption is believed to play a role in the formation of these ordered structures. To further study the catechol - titanium dioxide complex, temperature dependent measurements using STM, XPS, and UPS were made in the presence and absence of molecular oxygen. The difference in decomposition and intermediates formed will be discussed. These techniques were also used to study UV induced photoreactions of catechol on TiO₂.

8:20am **EN+SS+TF-ThM2 N Incorporation and Electronic Structure in High-Quality Epitaxial N-doped TiO₂ Anatase Grown by Molecular Beam Epitaxy.** *S.H. Cheung*, *P. Nachimuthu*, *M.H. Engelhard*, Pacific Northwest National Laboratory, *M.K. Bowman*, The University of Alabama, *S.A. Chambers*, Pacific Northwest National Laboratory

N doping in TiO₂ is of potential interest for bandgap reduction and enhanced visible light absorption for water splitting. We have previously investigated high-quality N-doped TiO₂ rutile grown homoepitaxially by molecular beam epitaxy (MBE) on TiO₂(110) and α -Al₂O₃(0001).¹ To gain broader understanding of N-doped TiO₂, we now report a detailed study of N incorporation and the associated electronic structure in high-quality TiO₂ anatase grown by MBE on LaAlO₃(001). A mixed beam of atomic N and O was prepared in an electron cyclotron resonance plasma source while Ti was supplied from an effusion cell. The much higher thermodynamic stability of Ti-O bonds compared to Ti-N bonds resulted in N incorporation being limited to less than 1 at. %. The high degree of structural quality was evidenced by the observation of finite thickness fringes in the vicinity of the (004) Bragg peak in high-resolution X-ray diffraction. A formal charge of -3 on substitutional N was deduced from high-resolution XPS. Photoconductivity measurement capability is being set up at the time of abstract preparation and experimental results elucidating the role of substitutional N in reducing the bandgap will be presented at the meeting.

¹ S.H. Cheung, P. Nachimuthu, A.G. Joly, M.H. Engelhard, M.K. Bowman, S.A. Chambers, Surf. Sci. 601 (2007) 1754.

8:40am **EN+SS+TF-ThM3 Lattice Site Location for N in Homoepitaxial N-doped TiO₂ (110).** *V. Shutthanandan*, *S.H. Cheung*, *S. Thevuthasan*, *P. Nachimuthu*, *S.A. Chambers*, Pacific Northwest National Laboratory

TiO₂ is one of the most heavily studied materials for photocatalytic water splitting even though the optical absorption spectrum of TiO₂ has poor overlap with the solar spectrum, and the e⁻/h⁺ pair recombination rate is high. Bandgap reduction is one approach to enhancing visible light absorption. N doping causes a redshift of the bandgap into the visible and visible-light-induced photochemistry has been observed in this material. We have grown TiO_{2-x}N_x rutile epitaxial films on rutile TiO₂ (110) single crystal substrates using oxygen plasma assisted molecular beam epitaxy. The N concentration (x) was varied by careful control of the atomic fluxes. The N

dopant site location was studied using nuclear reaction analysis (NRA) and Rutherford backscattering spectrometry (RBS) in channeling and random geometries. ¹⁴N(d, α)¹²C and ¹⁶O(d,p)¹⁷O nuclear reactions were used to identify the locations of N and O, respectively. NRA measurements in a channeling geometry for x = 0.04 and 0.05 clearly show that N substitutes for O in this concentration range. The x = 0.04 film shows a higher degree of N substitution (~98%) than the x = 0.05 film (~75%). Angular scans obtained around <110> for the x = 0.04 film exhibit a N angular half width that is slightly narrower (~0.05°) than that of host O. This narrowing is an indication that the N atoms are slightly displaced from the idealized anion lattice sites. The angular yield scan obtained for the x = 0.05 film exhibits a slightly larger angular half width for O, indicating that O positions are perturbed by N incorporation. In contrast, NRA and RBS measurements performed on the x = 0.12 film reveal that most of the N occupies random positions within the film, and glancing incidence XRD reveals limited Ti₂N secondary phase formation. These results clearly demonstrate that the upper limit of N solid solubility in crystalline TiO₂ rutile is ~3 at. % of the anions. Higher N concentrations can be incorporated by varying the growth conditions to facilitate defect formation, but the quality of the materials drops considerably and secondary phase formation occurs.

9:00am **EN+SS+TF-ThM4 Photochemically Activated Tethering of Molecular Monolayers to Anatase and Rutile TiO₂ Surfaces.** *H.J. Kim*, *E.C. Landis*, University of Wisconsin-Madison, *S.H. Cheung*, *S.A. Chambers*, Pacific Northwest National Laboratory, *T.F. Kuech*, *R.J. Hamers*, University of Wisconsin-Madison

Molecular interfaces to TiO₂ are an important component of dye-sensitized solar cells and other emerging systems for solar-to-electrical and solar-to-fuel conversion. Using X-ray photoelectron spectroscopy and Fourier-transform infrared spectroscopy, we demonstrate that organic alkenes will link to the surfaces of titanium dioxide in both anatase and rutile forms when illuminated with ultraviolet light. This provides a versatile way to covalently link functional organic molecules directly to oxide semiconductors. Measurements have been performed on epitaxial thin films of anatase (001), bulk crystals of anatase(101), rutile (001), rutile (110), and nanocrystalline anatase. Quantitative XPS measurements have been used to investigate the kinetics of functionalization and its dependence on the structure of the bulk samples and the dependence on exposed crystal face. We will compare the functionalization of these surfaces and discuss the mechanism of the modification. Implications for tethering of photochemically active molecules to these surfaces will be discussed.

9:20am **EN+SS+TF-ThM5 Progress and Challenges in Solar Energy Conversion Using Semiconductor/Liquid Junctions.** *N.S. Lewis*, California Institute of Technology

INVITED

Semiconductor/liquid contacts are useful in photoelectrochemical cells as well as for probing the fundamental surface chemistry and surface physics of semiconductors. In this talk, we will discuss the thermodynamics and dynamics of charge flow across semiconductor/liquid interfaces with an emphasis on comparison of theory and experiment for charge transfer in 1-electron outer-sphere redox systems. In addition, we will discuss the principles of surface modification to control the electrical, electronic, and chemical properties of Si surfaces. Finally, we will discuss the use of photoelectrochemistry in transport, localization, and movement of charge molecules in three dimensions in solution in real time.

10:00am **EN+SS+TF-ThM7 An Organic Donor/Acceptor Lateral Superlattice at the Nanoscale: Towards an Optimum Morphology for Photovoltaic Devices.** *R. Otero*, *D. Eciija*, Universidad Autonoma de Madrid, Spain, *G. Fernandez*, Universidad Complutense de Madrid, Spain, *J.M. Gallego*, ICMN-CSIC, Spain, *L. Sanchez*, *N. Martin*, Universidad Complutense de Madrid, Spain, *R. Miranda*, Universidad Autonoma de Madrid, Spain

One of the major factors limiting the efficiency of organic photovoltaic devices is the fact that, instead of free electron-hole pairs, photon absorption usually leads to the formation of tightly bound excitons (bound states of an electron-hole pair) which can diffuse only for a characteristic length of about 10 nm before radiative recombination occurs. The hitherto most successful approach to promote the dissociation of the photogenerated excitons is to use blends of phase-segregated electron-donor/electron-acceptor molecules; the so-called bulk heterojunction concept. At the interface between electron-donor and electron-acceptor areas, the difference in electron affinities drives the exciton dissociation by injecting free electrons (holes) into the electron-acceptor (electron-donor) areas. Provided that continuously connected paths between the interfaces and the electrodes exist, the free electrons and holes will be collected therein. From these considerations a number of morphological criteria can be extracted for

optimum solar cell performance: first, the segregated electron-donor and acceptor domains must have a typical size of the order of the exciton diffusion length, in order to avoid wasteful radiative recombination events; second, the interface area between donor and acceptor domains, where exciton dissociation takes place, must be maximized; and, finally, donor (acceptor) domains must be continuously connected to the cathode (anode) to favour efficient charge transport. A morphology that would satisfy these three criteria could be a lateral superlattice of donor and acceptor areas with typical dimensions of some 10 nm. In this work we describe variable-temperature Scanning Tunneling Microscopy (STM) experiments that show how monolayer-thick blends of the electron donor molecule (exTTF) with the electron acceptor (PCBM) on a reconstructed Au(111) surface, segregates laterally into 'nanostripes' whose width is of the order of the exciton diffusion length; it thus corresponds closely with the morphology for optimum solar cell performance. The reason for such a peculiar nano-scale morphology can be traced back to the different interactions between the two molecular species and the herringbone reconstruction of Au(111). Our results demonstrate the potential of atomistic studies about the growth of organic semiconductors to open new directions for the design and construction of highly-efficient organic electronic devices.

10:20am **EN+SS+TF-ThM8 Solar Water Splitting for Renewable Hydrogen Production: The Role of N and Surface Modification in the Improved Stability of III-V Nitride Photoelectrodes**, *T. Schiros, J. Leisch, L.-Å Näslund, H. Ogasawara*, Stanford Synchrotron Radiation Laboratory, *T. Deutsch, J. Geisz, S. Kurtz*, National Renewable Energy Laboratory, *R. Kirby, A. Nilsson*, Stanford Synchrotron Radiation Laboratory

III-V semiconductors are promising materials for photoelectrochemical (PEC) hydrogen production, however, material stability is a serious issue. The addition of dilute amounts of nitrogen to GaP and surface modification such as platinization result in dramatic increases in photocorrosion resistance, but the underlying mechanism is not known. We combine surface-sensitive core-level x-ray spectroscopy and microscopy with electrochemical measurements to study changes in the chemical environment and local morphology at the semiconductor-electrolyte interface during PEC hydrogen production and reveal the role of nitrogen and the platinum catalyst treatment in preserving the integrity of the surface. A detailed understanding of the interface is essential to improve control of photocorrosion and increase device stability.

10:40am **EN+SS+TF-ThM9 Surface Nanostructure and Nanochemistry of CuInSe₂ by Scanning Tunneling Microscopy**, *M. Mayer, L. Ruppalt, J. Lyding, A. Rockett*, University of Illinois

Results of the characterization of the surface physical, chemical and energy band structure of CuInSe₂ (CIS) are reported based on scanning tunneling microscopy (STM) studies of epitaxial CIS thin films. Cu(In, Ga)Se₂ (CIGS) is the absorber layer in the highest efficiency thin-film solar cells. However, this material does not perform as well as expected, most likely due to local defects and composition fluctuations. These lead to the formation of electronic defect levels in the energy gap and band edge fluctuations, both of which can cause carrier recombination. STM images compare the structure of cleaved (110) type surfaces, which have been shown previously to be energetically unstable, with epitaxial layers of various stable surface orientations that had been cleaned by sputtering and annealing. The energetically favorable close-packed tetragonal (112) surface showed triangular facets in agreement with AFM and SEM images. The (110) face showed structural and chemical correlations with the local density of states and evidence of a Cu-deficient surface consisting of extended In-rich rows. The surface structure of the cleaved surface is consistent with suggestions that the surfaces of group III rich CIGS should be highly In-rich and should contain Cu vacancies. No significant reconstruction associated with the Se sublattice was observed. The local density of states obtained from tunneling spectroscopy exhibited large fluctuations in the energy gap and Fermi energy, providing direct evidence of the band edge fluctuations observed by photoluminescence. The gap fluctuations are correlated with the surface topography and have direct implications for the device performances.

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