

Wednesday Morning, October 17, 2007

Renewable Energy Science & Technology Topical Conference

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

Catalysis for Hydrogen Storage and the Hydrogen Economy

Moderator: G. Fisher, Delphi

8:00am EN+SS+TF-WeM1 **Catalysts for Hydrogen Production by Sulfur-Iodine Thermochemical Water Splitting Cycle**, *L.M. Petkovic, D.M. Ginosar, K.C. Burch, H.W. Rollins, S.N. Rashkeev, H.H. Farrell*, Idaho National Laboratory

Thermochemical cycles can be used to split water through a series of chemical reactions where the net result is the production of hydrogen and oxygen at much lower temperatures than direct thermal decomposition. When the primary energy source to drive the cycle is nuclear or solar heat, hydrogen can be produced without the need of fossil fuels and without generating gasses considered to be responsible for global warming. The sulfur-iodine (S-I) thermochemical cycle appears promising for producing hydrogen from water. The S-I cycle consists of three simultaneous reactions: the decomposition of hydroiodic acid (HI) to produce hydrogen and generate iodine for recycle, the decomposition of sulfuric acid to produce oxygen and generate sulfur dioxide for recycle, and a main reaction where incoming water and the recycle chemicals react to regenerate HI and sulfuric acid. Both HI and sulfuric acid decomposition reactions are facilitated by heterogeneous catalysts. The high-temperature, harsh chemical reaction conditions of the sulfuric acid decomposition reaction present a significantly challenging environment for catalytic materials. In this work a number of titania (rutile)-supported platinum-group metal (i.e., Pt, Ir, Pd, Ru, and Rh) catalysts were investigated for this reaction. To develop an understanding of the factors that cause catalyst deactivation, density-functional theory-based first-principles calculations and computer simulations for transition metal particles positioned on titania (rutile) were performed. In addition, experimental determination of the activity and stability of activated carbon catalysts for the HI decomposition reaction will also be presented. Results of activated carbon characterization analyses, including surface area, temperature programmed desorption, Boehm's titration results, and contact pH of the activated carbons will be discussed.

8:20am EN+SS+TF-WeM2 **Trends in Hydrogen Splitting on Transition Metals at 1 Bar**, *M. Johansson, O. Lytken, I. Chorkendorff*, Technical University of Denmark

Despite the fact that the interaction of hydrogen with various metal surfaces has been studied extensively under ultra-high vacuum conditions, there is very little data available for the hydrogen dissociation rate on clean surfaces at pressures on the order of 1 bar. Here we investigate the hydrogen splitting rate for a number of transition metals by measuring the rate of the H-D exchange reaction. Experiments are also carried out in the presence of CO, in order to investigate the mechanism behind CO poisoning of the anode catalyst in proton-exchange membrane fuel cells. The experiments are performed in an apparatus which combines an ultra-high vacuum chamber for sample preparation and surface analysis with a high-pressure cell.¹ Model catalysts are prepared by electron-beam evaporation of metal spots onto a highly ordered pyrolytic graphite (HOPG) substrate. Typically, the spots are 1 mm in diameter and 50 Å thick. The rate of the H-D exchange reaction for each catalyst spot is measured in the high-pressure cell with the help of a combined gas dispenser and gas sampling device. The gas is sampled 0.2 mm from the center of the spot, and the sampled gas is analyzed with mass spectrometry. Measurements were carried out at 1 bar with a gas mixture containing 1 percent D₂ in H₂, with or without the addition of 10 ppm CO. The temperature was varied in the range 40 - 200 °C. The model catalysts were characterized with Auger Electron Spectroscopy (AES) before and after exposure to gases in the high-pressure cell. In order to take the back-reaction (HD splitting) into account, a simple model for the H-D exchange reaction is used. It is assumed that the sticking probability, S, is the same for H₂, HD and D₂. Under the conditions of interest here, S is mainly dependent on the coverage of adsorbed species on the catalyst surface. Once S has been extracted from the experimental data, the dissociative adsorption/desorption rate for pure H₂ at 1 bar can be calculated. So far, the metals Co, Ni, Cu, Ru, Rh, Pd, Ir and Pt have been investigated. The measured values for S are reasonably consistent with data obtained with high hydrogen coverage under vacuum conditions. Metals which bind hydrogen strongly are expected to give lower values for S.

However, S is found not to correlate with the heat of adsorption for hydrogen as determined at low coverage under vacuum conditions. The most active metal for hydrogen splitting is Ru, closely followed by Rh. For these metals, S is close to being independent of temperature. Pt and Pd give comparable values for S in the temperature range investigated, but the temperature dependence is stronger for Pd than for Pt. The activity then decreases in the order Ir, Co and Ni. No measurable activity is found for Cu. The addition of 10 ppm CO lowers the splitting rate significantly on all the metals, also at 200 °C. Among the investigated metals, Pt and Ir are the ones most sensitive to CO poisoning.

¹ M. Johansson, J. Hoffmann Jørgensen, I. Chorkendorff, Rev. Sci. Instrum., 75 (2004) 2082.

8:40am EN+SS+TF-WeM3 **Catalytic Autothermal Reforming of Renewable Fuels at Millisecond Times**, *L. Schmidt*, University of Minnesota **INVITED**

We compare the reforming of different types of biofuels by autothermal reforming at millisecond contact times to produce synthesis gas, hydrogen, and chemicals. Fuels examined are alcohols, esters, carbohydrates, biodiesel, vegetable oil, and solid biomass. Biofuels generally have higher conversions than fossil fuels because the hydroxyl and ester linkages in these fuels produce higher sticking coefficients than for saturated alkanes. Consequently, conversions of all biofuels in these processes are nearly 100%. Highly oxygenated feedstocks tend to produce mostly syngas with little olefins or oxygenated products because surface reactions dominate, and these larger products are formed predominantly by homogeneous reaction processes after all oxygen is consumed. Recent results on production of syngas by reactive flash volatilization of nonvolatile liquids and solids will also be described. We show that, by impinging cold liquid drops or small solid particles onto the hot catalyst surface, the process can be operated in steady state with no carbon formation for many hours. This occurs because, while pyrolysis of vegetable oils and carbohydrates at low temperatures produces carbon, above ~600°C the equilibrium shifts to produce syngas rather than solid carbon.

9:20am EN+SS+TF-WeM5 **Transient Kinetic Analysis of Intermediates in Steam Reforming on Oxide Supported Cu Catalysts**, *Y. Yang, R. Dissekamp*, Pacific Northwest National Laboratory, *C.T. Campbell*, University of Washington, *C. Mims*, University of Toronto, Canada, *D. Mei, J.H. Kwak, J. Szanyi, C.H.F. Peden*, Pacific Northwest National Laboratory

Formate hydrogenation was proposed to be the surface reaction channel forming methanol through reverse water gas shift by previous investigators [Chorkendorff et al., J. Vac. Sci. Technol. A, 10(4), 2277 (1992)]. The interconversion and decay of copper formates on a Cu/Gamma-Al₂O₃ catalyst are studied here using an apparatus that combines in-situ transmission-FTIR of adsorbed species and mass spectrometric detection of reactor effluent during transient kinetic analyses (transmission-FTIR/MS/TKA). At 573 K, ~ 2% CO and 0.07% methanol conversions were obtained by sending 2.5 bar H₂:CO₂ 3:1 flow at 10 sccm through the reactor. It is also observed that at lower temperature, 353 K - 433 K, surface formate species are formed with the input feed stream as observed by IR. The kinetics of their transient reactivity (e.g., titration) are examined after switching to either a reducing (H₂), oxidizing (2% N₂O in He), or inert gas (He, Ar) feed stream. The kinetics of total formate decay at 306, 363, and 433 K under H₂, He, or Ar gas exposure are observed to be comparable, suggesting that a thermal unimolecular desorption and not hydrogenation alone, is operative. However upon hydrogen exposure it is observed that within the broad formate IR band(s) there is internal species exchange which indicates two types of different formates are formed. Similar studies are presented for a SiO₂ supported polycrystalline Cu sample to help identify the formate species. Methanol steam reforming on both samples were also studied for further understanding of the reverse reaction processes.

9:40am EN+SS+TF-WeM6 **Model Catalysts for Water-Gas Shift Reaction**, *S. Ma, X. Zhao, J.A. Rodriguez, P. Liu, J. Hrbek*, Brookhaven National Laboratory

Gold supported on ceria was shown to be very active catalyst for water-gas shift reaction and low temperature CO oxidation. Both reactions are used to purify hydrogen by removing CO, a poison of fuel cell catalysts, and are therefore of importance in the hydrogen economy. In this presentation we will describe the preparation, characterization and reactivity of an inverse model catalyst, i.e. CeOx nanoparticles supported on the Au(111) surface. Using STM and XPS we found that physical vapor deposition of Ce metal leads to formation of surface intermetallic compounds after annealing. The Ce-Au surface alloys have low reactivity toward oxygen, however, we were able to prepare CeOx by vapor-

deposition of Ce in a moderate oxygen pressure (10-7 torr). Elongated flat ceria nanoparticles are 0.5 nm thick, several nanometers long and anchored mostly to steps. Atomically resolved images of the ceria island show well-ordered CeO₂ (111) surfaces with few defects. Ce 3d photoelectron spectra were used to identify the oxidation state of Ce in oxides prepared by different methods. In general, oxidation at temperatures below 400 K leads to formation of poorly ordered nanoparticles of Ce₂O₃ and higher temperature annealing in background oxygen is needed to form CeO₂. Individually, neither Au(111) nor CeO₂(111) have any activity in the WGS reaction, while both the Au/CeO₂(111) model catalyst and the CeO_x/Au(111) inverse model catalyst show significant activity in high pressure experiments. Our photoemission data indicate that Ce₂O₃ nanoparticles supported on the gold surface dissociate water molecules even below room temperature while the CeO₂ nanoparticles are inactive. As the water dissociation could be the rate limiting step in the WGS reaction, our ability to identify dissociation products under vacuum conditions and to link them with the structural characterization at the atomic level reinforces reaction models in which the oxide support is not a simple spectator and plays an essential role in the WGS process. Acknowledgement: This research was carried out at Brookhaven National Laboratory and supported by the US Department of Energy (Chemical Sciences Division, DE-AC02-98CH10886).

10:40am **EN+SS+TF-WeM9 Double Role of Water in Fuel Cell Oxygen Reduction Reaction**, *H. Ogasawara, L.-Å Nässtrand, J.B. MacNaughton, T. Anniyev, A. Nilsson*, Stanford Synchrotron Radiation Laboratory

A management of appropriate humidity level is necessary for the fuel cell to operate. The oxygen reduction reaction (ORR) occurs at the triple phase boundary where gas, electrolyte containing water and catalytic metal particle contact forms humid and dry region on the surface of the catalyst. Using XPS and XAS, we have demonstrated active site poisoning by water, where the activation of oxygen to the adsorbed atomic phase occurs rapidly in the dry region, but not in the humid region. On the contrary, there is a promoter effect of water on the reduction of adsorbed atomic oxygen in the formation of a water-hydroxyl surface complex.

11:20am **EN+SS+TF-WeM11 Adsorption and Dehydrogenation of Carborane on Pt(111)**, *A. Tillekaratne, M. Trenary*, University of Illinois at Chicago

The techniques of reflection absorption infrared spectroscopy (RAIRS) and temperature programmed desorption (TPD) have been used to explore the dehydrogenation on a Pt(111) surface of 1,2-dicarba-closo-dodecaborane, C₂B₁₀H₁₂, also known simply as carborane. Complex hydrides, such as the boranes and carboranes, are of interest as possible hydrogen storage materials because of their high hydrogen content. Many hydrides are quite stable and catalysts are needed to promote the release of hydrogen at low temperatures. The carbon and boron atoms of the C₂B₁₀H₁₂ carboranes occupy the vertices of a slightly distorted icosahedron and have a hydrogen weight percentage of 8.3. There are three isomers of these icosahedral carboranes, of which the ortho form (the 1,2 isomer) is the most readily available. The icosahedral structure of the boron-carbon cage structure of carborane is also adopted by the boron-rich solid boron carbide. The similarity in the structures of carborane and boron carbide has led to the successful use of carborane as a precursor gas for the growth of boron carbide thin films. However, the detailed mechanism by which carborane dehydrogenates to form boron carbide has not been previously investigated. At submonolayer coverages at 85 K the RAIRS spectrum of carborane displays strong B-H stretching vibrations near 2600 cm⁻¹, and a weak C-H stretch at 3090 cm⁻¹ that indicate molecular adsorption at low temperature. The molecule is stable on the surface up to 250 K, where it is transformed into a new intermediate with a strongly red-shifted B-H stretch vibration at 2507 cm⁻¹. This intermediate is stable up to 400 K, above which no B-H stretch vibrations are observed. Hydrogen is released in stages as the carborane monolayer is heated from 85 to 800 K, which is also indicative of the formation of partially hydrogenated surface intermediates. Further analysis of the data may permit definitive identification of the surface intermediates formed during the course of carborane dehydrogenation on the Pt(111) surface.

11:40am **EN+SS+TF-WeM12 Short Range Order of Ti Dopants in Al(111): Implications for Hydrogen Storage**, *E.M. Muller*, Brookhaven National Laboratory, *C.V. Ciobanu*, Colorado School of Mines, *P. Zahl, P. Sutter*, Brookhaven National Laboratory

Complex metal hydrides can potentially satisfy the need for lightweight, high-capacity hydrogen storage materials, a key requirement for the Hydrogen Economy. However, for most known complex hydrides the solid-state reactions involved in hydrogen release are not reversible, and their rates are low under moderate ambient conditions. The discovery that small amounts of Ti make the decomposition of sodium alanate (NaAlH₄) to NaH

and Al reversible at moderate temperatures and pressures¹ has demonstrated doping with catalysts as a promising route to induce reversible hydrogen storage and fast reaction kinetics. A fundamental understanding of the catalytic effect of Ti in NaAlH₄ could form the basis for rational strategies to optimize a broader class of complex hydride hydrogen storage materials. We combine experiments on single crystal model surfaces and density-functional theory (DFT) to establish the role of near-surface Ti in the rehydrogenation of NaH and Al to NaAlH₄. A likely primary effect of Ti is the formation of catalytically active surface sites enabling the facile dissociative chemisorption of H₂ on Al, which itself has very low affinity to H₂. Using chemically specific scanning tunneling microscopy and DFT we identify the stable configurations of Ti atoms incorporated into Al(111) surfaces as a first step to identifying potential catalytically active sites. Surprisingly, despite a higher surface energy of Ti (i.e., a driving force for diffusion into sub-surface sites), our observations show a pronounced stabilization of Ti at the Al surface where its catalytic effects are maximized. STM shows a large population of a specific Ti-atom pair complex, which has been predicted to catalyze H₂ dissociation.² We discuss the origin of this pairing, and the interaction of atomic and molecular hydrogen interactions with these surface Ti complexes.

¹ B. Bogdanovic and M. Schwickardi. *J. Alloys Comp.* 253-254, 1 (1997).

² E. Muller, E. Sutter, P. Zahl, C.V. Ciobanu and P. Sutter., *Appl. Phys. Lett.* 90, 151917 (2007).

12:00pm **EN+SS+TF-WeM13 Alane Formation on Al(111) and Ti-doped Al(111)**, *S.C. Chaudhuri*, Washington State University, *J.-F. Veyan, S.C. Schaeffer*, Rutgers, The State University of New Jersey, *J.T. Muckerman*, Brookhaven National Laboratory, *Y.J. Chabal*, Rutgers, The State University of New Jersey

Complex metal hydrides, such as NaAlH₄, are candidates for hydrogen storage because they can reversibly release and recapture hydrogen under near ambient conditions. Surface processes in the hydrogen storage reaction in NaAlH₄, starting from a depleted phase consisting of NaH and metallic Al, and proceeding via cryolite Na₃AlH₆ to the hydrogen-rich NaAlH₄, are considered as the basis for understanding reversible hydrogen storage in the chosen prototype system. Since metallic Al, particularly when doped with other metals, appear key to H₂ dissociation, we have undertaken a comprehensive study of H interaction with Al(111) and Ti-doped Al(111) surfaces to better understand the atomic scale mechanisms underlying this reversible hydrogen storage behavior. We have combined in-situ infrared absorption spectroscopy with first principles calculations to investigate the reaction of atomic hydrogen reacts with Al surfaces. As previously observed,¹ IR spectra show that alanes are formed upon H exposure. Alanes are highly mobile species at or near room temperature and desorb from Al(111) surfaces at higher temperatures mainly as AlH, AlH₃ and Al₂H₆.² Using FT-IR we show that the size of the alanes formed on Al(111) depend on the temperature of the sample. For low temperatures (Å90K), small alanes such as AlH₃ and Al₂H₆ are predominant. At higher temperatures (Å250K), bigger alanes are formed. When the Al(111) surfaces are doped with 5% Ti, the Ti containing sites are reactive, dissociating molecular hydrogen, and thus act as a pump to generate hydride species on Al surfaces that subsequently convert into alanes. LEED is used to test the validity of first principles calculations predicting that Ti atoms occupy hollow sites on the Al(111) surface. Using TPD, the nature of desorbed species from Al(111) and Ti-doped Al(111) surfaces have been analyzed as a function of the sample temperature after either atomic H or H₂ exposures. This presentation summarizes hydrogen dissociation on Ti/Al(111), and alane formation and mobility on both Al(111) and Ti/Al(111) surfaces.

¹ Eden P. Go, Konrad Thuermer, Janice E. Reutt-Robey, *Surf. Sci.* 437 (1999) 377

²Hara, M.; Domen, K.; Onishi, T.; Nozoye, H., *J. Phys. Chem.*, 95, (1), (1991) 6-7

Wednesday Afternoon, October 17, 2007

Renewable Energy Science & Technology Topical Conference

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

Photovoltaics, Fuel Cells, and Alternative Energy Materials and Applications

Moderator: J.S. Lewis, RTI International

1:40pm **EN+TF+SS-WeA1 ENABLE-based Low Temperature Growth of In-rich InGaN Films**, *T.L. Williamson, M.A. Hoffbauer*, Los Alamos National Laboratory, *N. Miller, R.E. Jones, K.M. Yu*, Lawrence Berkeley National Laboratory, *P. Flanigan, J. Wu*, University of California, Berkeley, *J.W. Ager, Z. Liliental-Weber, E.E. Haller, W. Walukiewicz*, Lawrence Berkeley National Laboratory

The different optimum growth temperatures for the group III-nitride compounds (e.g. GaN >900C and InN ~550C) make the growth of In-rich and fully compositionally graded InGaN films by MOCVD or MBE a considerable technological challenge. Recently, energetic neutral atomic-beam lithography & epitaxy (ENABLE) has been developed at LANL that makes possible isothermal low-temperature growth of high-quality GaN and $\text{In}_x\text{Ga}_{1-x}\text{N}$ alloys over the entire composition range ($0 < x < 1$). ENABLE uses a large flux of neutral nitrogen atoms to activate surface chemical reactions, thereby mitigating the need for high substrate temperatures and allowing the growth of high quality III-nitrides at substrate temperatures far below those of other conventional techniques (<600C) at rates exceeding 2 microns/hr. We will present recent results for ENABLE-grown InN and In-rich InGaN showing spectroscopic, X-ray diffraction, Rutherford backscattering spectrometry (RBS), transmission electron microscopy, and Hall effect measurements to assess the thickness, composition, crystalline quality, and optical and electrical properties of the films. InN films show intense luminescence at the bandgap of ~0.7 eV with electron mobilities exceeding $700 \text{ cm}^2/\text{Vsec}$. We will also present characterization results for compositionally graded films grown from pure GaN and grading to InN and from pure InN and grading to GaN. These results establish ENABLE as a new technique uniquely capable of growing InGaN films of widely varying composition including compositionally graded InGaN films and InN/GaN heterostructures.

2:00pm **EN+TF+SS-WeA2 Tandem-Junction Solar Cells using BeTe Buffer Layers for AlGaAs Molecular Beam Epitaxy on Silicon Substrates**, *K.P. Clark, E. Maldonado, F. Amir, W.P. Kirk*, University of Texas at Arlington

Monolithically-stacked tandem-junctions allow solar cells with conversion efficiencies above the single-junction limit. An optimal bandgap combination of 1.7 eV and 1.1 eV has a theoretical efficiency above 30% for a series-connected cell. Aluminum gallium arsenide epitaxially grown on silicon is a natural implementation, but has long-standing crystal-quality challenges due to lattice mismatch, thermal expansion mismatch, and island growth of AlGaAs. We report investigations of AlGaAs molecular beam epitaxy on prelayers of the wide-bandgap II-VI compound beryllium telluride BeTe on arsenic-passivated silicon. AlGaAs is nearly lattice matched to BeTe but has a strong tendency for island formation, which is suppressed by low-temperature growth initiation. $\text{Al}_{0.15}\text{Ga}_{0.85}\text{As}$ -GaAs multiple quantum-well p-i-n junction structures were processed and characterized electrically under illumination. The short-circuit photocurrent J_{SC} and open-circuit voltage V_{OC} for the Si/BeTe based junction approach within 15% and 30% respectively of those for a similar junction grown on a GaAs substrate. We report techniques for initial AlGaAs growth including solid-phase epitaxy, BeTe termination, and germanium adlayers studied using RHEED diffraction, X-ray diffraction, and transmission electron microscopy.

Supported in part by NASA.

2:20pm **EN+TF+SS-WeA3 Gaseous Deposition of Lead Sulfide Nanoparticle/Ti-Phthalocyanine Composite Films**, *I.L. Bolotin, D.J. Asunskis, A.M. Zachary, A.T. Wroble, L. Hanley*, University of Illinois at Chicago

Composite materials composed of inorganic semiconductor nanoparticles (NPs) dispersed in organic matrices may find use in photovoltaics, photodiodes, nonlinear optical devices, and other applications. This interest arises from the possibility of tuning the optoelectronic properties of the composite by varying the NP size and concentration within the organic

matrix. Bulk PbS is a group IV-VI semiconductor with a narrow band gap of 0.41 eV at room temperature. Strong quantum size effects occur for <20 nm PbS NPs. Among the other potential advantages of PbS NPs is their high electron affinity, which will enhance charge transfer from an intermingled organic phase. Most of the lead salt NP photovoltaics devices produced to date have been prepared from the solution phase using colloidal techniques. However, gaseous deposition techniques possess certain advantages for the synthesis of nanocomposites: it is inherently suited to film deposition, is compatible with traditional methods of fabricating semiconductor devices, allows control of oxidation during deposition, and it can reduce the agglomeration of NPs. This work demonstrates that gaseous deposition can synthesize a composite film with <5 nm diameter PbS NPs of narrow size distribution embedded within a titanyl phthalocyanine (TiPc) organic matrix. Composite film samples were fabricated here using a cluster beam deposition source combining magnetron DC-sputtering and gas-agglomeration techniques in a fashion similar to that originally developed by Haberland and coworkers. X-ray photoelectron spectroscopy showed that PbS was successfully incorporated into the TiPc matrix during co-deposition. Transmission electron microscopy (TEM) was used to measure the size, shape, distribution, and crystallinity of the NPs in these composite films. Soft-landing of PbS clusters into the TiPc organic matrix allowed the clusters to maintain their three-dimensional structure upon deposition. In the absence of the TiPc matrix, PbS showed the aggregation into much larger, irregularly-shaped particles. PbS NPs appeared homogeneously distributed in the TiPc matrix, with particle spacings of several times the particle diameter. TEM also showed that at least some NPs deposited into TiPc were crystalline. This method also allows for deposition of composite films composed of any evaporable organic and inorganic nanoparticles that can be formed by sputtering and reaction within the cluster source.

2:40pm **EN+TF+SS-WeA4 Plastic Bulk-Heterojunction Solar Cells and Near-Infrared Photodetectors**, *G. Li, Y. Yao*, University of California, Los Angeles, *L. Yu, Y. Liang, S. Xiao*, University of Chicago, **Y. Yang**, University of California, Los Angeles

Polymer based solar cells and photodetectors have tremendous application in harnessing solar energy and photodetection in a cost-effective way. Here we studied the self-organization effect in polymer solar cells and first demonstrated plastic near-infrared photodetectors using low band-gap polymer. The self-organization effect in polymer solar cells based on regioregular poly(3-hexylthiophene) (RR-P3HT):[6,6]-phenyl-C61-butyric acid methyl ester (PCBM) is studied in an evolutionary way, with the difference being spin-coating time t_s (20 to 80 sec) which controls solvent annealing time (t_a) by the solvent residue. Photoluminescence (PL), ultraviolet-visible (UV-vis) absorption spectroscopy, scanning atomic force microscopy (AFM), and grazing-incidence X-ray diffraction (GIXD) were conducted on these blend films and linked to the device performance. In addition to the high performance polymer solar cells, we also demonstrated a fast response near-infrared detector using a new low band gap material. With promising results shown in this presentation, we believe the low band gap materials will open up a new perspective in near-infrared detection.

4:00pm **EN+TF+SS-WeA8 Defect Characterization of CdTe and CdMgTe Solar Cells and Their Correlation to the Device Properties**, *R.G. Dhere, D. Young, J. Scharf, A. Duda, B. To, R. Noufi*, National Renewable Energy Laboratory

CdTe solar cells are at the forefront of commercial thin-film solar cells because of the high laboratory efficiencies and relative ease of fabrication. The current losses for these devices are well understood, with very small room for improvement. On the other hand, open-circuit voltage (V_{oc}) of champion devices is much lower than its potential and presents the only path to improve device performance. In this paper, we present our work on the CdTe and CdMgTe devices fabricated by close-spaced sublimation and physical vapor deposition on glass/SnO₂/CdS substrates. The devices are heat-treated in chloride vapor after deposition, in a controlled ambient, in temperature range of 390°-440°C. The treatment results in recrystallization of the samples deposited at low temperature (~400° C) and selective recrystallization at the CdS/CdTe interface in samples deposited at higher temperatures. The post-deposition treatment also improves the electronic properties of the absorber due to reduced defect density and results in improved device performance. Our investigation studies the effect of bandgap variation and defect density within the space-charge region in the absorber on the device properties, particularly V_{oc} . The bandgap of the alloy is varied by changing the alloy composition of CdS_{1-x}Te_x alloy formed at the CdS/CdTe interface and CdMgTe alloy composition. We examine the bandgap range of 1.45-1.65 eV for the absorber layer. We have varied defect density in the absorber layer by adjusting the substrate temperature and degree of post-deposition chloride treatment. The structural properties

of the samples are studied by atomic force microscopy. The devices have been characterized using drive-level capacitance profiling in combination with capacitance-voltage analysis, in addition to conventional photovoltaic analysis. We will present the data on the devices with a wide range of performance and investigate the correlation between device parameters and the material properties such as bandgap and defect density. This abstract is subject to government rights.

4:20pm EN+TF+SS-WeA9 Electron Backscatter Diffraction of CdTe Thin Films - Effects of CdCl₂ Treatment, H.R. Moutinho, R.G. Dhere, C.-S. Jiang, B. To, M.M. Al-Jassim, National Renewable Energy Laboratory
Electron backscatter diffraction (EBSD) utilizes the electron beam of a scanning electron microscope (SEM) to investigate the crystallographic orientation of materials with high spatial resolution. In EBSD, some of the electrons of the SEM beam are diffracted by the crystalline planes of the sample and collected by a detector, where they form a pattern of Kikuchi lines. These patterns are characteristic of the crystal structure and orientation, and they are collected while the electron beam is being scanned, forming maps of crystallographic orientation. In contrast to X-ray diffraction, which gives the crystallographic orientation of a macroscopic volume of the bulk sample, EBSD provides the individual orientation of volumes with nanometer dimensions. To optimize the EBSD signal, the sample must be inclined by about 70° in relation to the electron beam. Consequently, in rough samples, topographic features shadow some of the diffracted electrons from reaching the detector; thus surface preparation is a common requirement. In this work, we describe the surface processing of CdTe thin films deposited by close-spaced sublimation and physical vapor deposition (PVD). Most of the films studied were too rough to produce good EBSD data. Polishing flattened the sample, but created an amorphous layer on the surface, resulting in no diffraction patterns. Ion-beam milling was not as effective in flattening the surface, but removed rough surface features, resulting in high-quality EBSD data. Etching and light ion milling after polishing also produced good results. After optimizing the sample preparation process, we studied PVD CdTe samples after CdCl₂ treatment using dipping or vapor processes, with different parameters. We observed a striking difference in the sample microstructure depending on the CdCl₂ process and parameters—with grain sizes varying from a few to several dozen micrometers. Our results showed that maintaining a steady source of CdCl₂ during the treatment, compared to a fixed amount, results in completely different recrystallization dynamics. We also studied the grain structure from the substrate to the surface by doing EBSD in cross sections of the samples, as well as analyzing samples after different degrees of polishing.

4:40pm EN+TF+SS-WeA10 Effect of Selenization Temperature on the Grain Growth of Absorber Layer in Ultra Thin CIGS/CdS Solar Cells, S.A. Pette, N.G. Dhere, Florida Solar Energy Center

Solar cells based on CuIn_xGa_{1-x}Se₂(CIGS) have achieved efficiencies of 19.5% and therefore are promising candidates for economic, large-scale production. CIGS thin film solar cells having absorber thickness of 2.5 μm have shown good performance. However, CIGS being a direct bandgap material, theoretically efficient cells could be prepared with absorber thickness as low as 0.5 μm. The rationale behind decreasing the CIGS thickness is to reduce consumption of the scarce and costly resource, indium. It has been observed that the performance of the solar cells degrades as the thickness goes below 0.75 μm. 0.9 μm thick absorber layer are prepared at PV Mat Lab facility at Florida Solar Energy Center (FSEC) with device conversion efficiency of 6.26% as measured at FSEC. The reason for this degradation can be attributed to the defects in the bulk of the absorber material. We know from the Movchan&Demchishin zone model that the rate of grain growth becomes almost negligible once the grains with favored texture and orientation have consumed all the unfavorable grains. This results in columnar grain structure with parallel boundaries. Similar grain structure was observed for the CIGS absorber layers with thickness of about 2.5 μm. It was observed that the grains were finer towards the back contact and larger at the surface and as the thickness goes on reducing there is not enough material for the grains to grow and coalesce. This results in smaller grains and so larger grain boundaries. Another factor affecting the grain size is the mobility of the deposited species which can be increased by increasing the annealing temperatures during selenization. But in case of ultra thin film absorber layer the higher temperatures adversely affect the molybdenum back contact layer thus introducing higher series resistance issues. Hence, in case of ultra thin CIGS absorber layer the selenization time - temperature profile needs to be optimized to obtain a favorable columnar grain structure. The material characterization of the different absorber layers will be carried out using scanning electron microscopy and transmission electron microscopy. The absorber layers would be further fabricated on to complete the device and current-voltage characteristics would be carried out to understand the effect of different temperature-time

profiles on the device parameters such as open circuit voltage, short circuit current, fill factor and finally the conversion efficiency.

5:00pm EN+TF+SS-WeA11 Thin Film Epitaxial Growth of CuInSe₂ Bicrystals for Grain-Boundary Studies, A.J. Hall, D.N. Hebert, A. Rockett, University of Illinois at Urbana-Champaign

Photovoltaics based on CuInSe₂ and related materials have the highest performance of any thin film devices. The nature and role of grain-boundaries in CuInSe₂ devices is currently poorly understood. Previous studies on the influence of grain-boundaries in Cu(In,Ga)Se₂ devices have shown that they exhibit little to no detrimental effect on photovoltaic device performance. Polycrystalline CuInSe₂ devices currently outperform single crystal CuInSe₂ devices. Past studies have been focused on average electrical properties or local surface electrical measurements for observation of the influence of boundaries on film properties. Since polycrystal devices have crystal sizes on the order of 1 micron, optoelectrical measurements are difficult. In order to alleviate these difficulties, a single high-angle grain-boundary in epitaxial CuInSe₂ has been grown on a GaAs bicrystal substrate using a hybrid sputtering and evaporation technique. Electron backscatter diffraction and x-ray diffraction show that film growth is epitaxial across all boundaries (high-angle and twin) in the bicrystal substrates. Atomic force microscopy, profilometry, and focused ion beam cross-sectioning results indicate that surface polarity and termination have a strong influence on film thickness and morphology. Near grain boundary morphology suggests mass transport leading to boundary migration is occurring. It is proposed that high surface energy anisotropy (on the opposing {111}_{A,B} surface facets) motivates mass transport during the growth of CuInSe₂ at crystal boundaries.

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. Ecija*, 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 nanoscale 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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