Energy Science and Technology Focus Topic
Room: 203 - Session EN+SE+NS+SS-MoA

Hydrogen Storage
Moderator: J.F. Herbst, General Motors R&D Center, E. Ronnebro, Sandia National Laboratories

2:00pm **EN+SE+NS+SS-MoA1 Hydrogen Storage for Automotive Vehicles: Methods and Materials**, ***J.F. Herbst***, General Motors R&D Center

Fuel cells operating on hydrogen are a strong potential alternative to internal combustion engines relying on fossil fuels for a variety of reasons. If a hydrogen fuel cell transportation future is to be realized, however, several major hurdles must be overcome, among them a light, compact, robust, and cost-effective system for storing hydrogen on a vehicle. High pressure compressed gas is a viable option, but its implementation on the commercial scale raises serious manufacturing and cost challenges. A similar statement applies to cryogenic liquid storage, for which dormancy is an additional issue. There is justifiable optimism that new materials may offer significant improvement of the prospects for two other options: (1) hybrid approaches combining compressed gas and a high surface area physisorption medium at 77K, and (2) reversible storage near ambient conditions. Progress on the broad materials front as well as recent research at GM R&D will be discussed.

2:20pm **EN+SE+NS+SS-MoA2 Response of Ultra-Thin Palladium Films to Hydrogen Exposure Studied by Low Energy Electron Microscopy and Diffraction**, ***B. Santos***, Universidad Autonoma de Madrid, Spain, *J.I. Cerda, J. de la Figuera,* CSIC, Spain, *K.F. McCarty,* Sandia National Laboratories, *J.M. Puerta*, CSIC, Spain

The ability of Palladium to store hydrogen is well known. Nevertheless surface science studies of the exposure of Pd(111) samples to hydrogen have found only a dense hydrogen layer betwen the last palladium-palladium layers, with additional hydrogen going into the bulk as a solid solution.[1,2] On Pd films a few atomic layers thick on a substrate which does not accept substantial quantites of hydrogen such as Ru, it should be possible to saturate completely the Pd film, and thus study the formation of PdH hydride with surface science techniques. In particular, as there is a substantial lattice mismatch betwen Pd and the beta-PdH hydride, the incorporation of H in Pd-intersticial places should induce a significant expansion of the Pd layers. Although H itself is basically invisible to low energy electron diffraction, the change of the Pd-Pd distances should be easily resolvable by LEED.[3] In this work, we present a low energy electron microscopy study of the hydrogren exposure of thin films of Pd on Ru(0001) and W(110). We characterize and study the growth and structure of Pd thin films. LEEM is a useful technique to monitor and control the growth of thin films in real space. Furthermore, a LEEM microscope can be used to acquire selected area diffraction (SAD-LEED) to determine the structure of such film.[4] Our experiments reveals that Pd films 2 to 6 ML thick on Ru(0001) follow the fcc sequence with the Ru in-plane lattice spacing, and present a corresponding expansion in the out-of-plane lattice spacing. Thicker films on Ru(0001) relax to a bulk-like Pd in-plane spacing. Both thick films on Ru(0001) or W(110) show a slight expansion of the last interlayer spacing, in line with reported studies on the surface of bulk Pd. We follow the dosing of atomic H on the Pd films by means of real-time LEED IV curves acquired by LEEM. We have found preliminary indications that room and low temperature exposure produce a significant expansion in the interlayer distance for a 4 ML thick film. But this expansion is smaller that the one expected for a full PdH beta-hydride formation.

[1] G.E. Gdowski, T.E. Felter and R.H. Stulen Surf. Sci. 181, L147, (1987)

[2] Sampyo Hong and Talat S. Rahman Phys. Rev. B 75, 155405 2007

[3] T. E. Felter, Eric C. Sowa, and M. A. Van Hove, Phys. Rev. B 40 num. 2, 891-899, (1989)

[4] J. de la Figuera, et al, Surf. .Sci. 600, L105 (2006)

2:40pm **EN+SE+NS+SS-MoA3 Destabilized Magnesium-based Alloy Thin Films as Model Systems for Hydrogen Storage**, ***D. Mitlin***, *J. Haagsma, C. Ophus, C.T. Harrower,* University of Alberta and NRC National Institute for Nanotechnology, Canada, *M. Saoudi, H. Fritzsche*, National Research Council Canada, SIMS, Canadian Neutron Beam Centre, Chalk River Laboratories **INVITED**

The key for achieving 100 °C - range hydrogen sorption is to have favorable thermodynamics, i.e. a hydrogen binding energy near 30 kJ/mol. Metallic magnesium possesses sufficient gravimetric and volumetric sorption capacity, but has unfavorable thermodynamics (-77 kJ/mol α-MgH2 formation energy) and poor kinetics. In this presentation I will discuss our general methodology for tuning the hydrogen sorption thermodynamics of magnesium, through alloy design. We use a thin films approach to create a range of destabilized magnesium-based alloys and of accompanying catalytic layers. Thin films make for ideal "model" systems that may be used for accurately and rapidly screening a variety of matrix and catalyst formulations. Because of the small diffusion distances, films also allow for better separation of system thermodynamics from the kinetics. The synthesized films were tested volumetrically through multiple adsorption-desorption cycles. The microstructures were characterized by neutron reflectometry and x-ray diffraction. We show that alloying magnesium with light elements that have weak hydrogen interaction, such as aluminum, is a very effective method for lowering the sorption temperature to near ambient. At certain compositions, the addition of aluminum promotes the high-pressure γ-MgH2 phase at the expense of the equilibrium α-MgH2. At other compositions, the sorbed microstructure is a composite of α-MgH2 intermixed with α-AlH3. We also demonstrate that there is critical temperature above which the palladium catalyst caps are not stable, reacting with the underlying material and losing their efficacy. Additionally, there will be a discussion of the processing and sorption kinetics of MgH2 - metal catalyst - carbon nanotube (CNT) powder composites, and of direct TEM characterization of milled MgH2.

3:20pm **EN+SE+NS+SS-MoA5 Thermodynamics and Kinetics of Hydrogen Storage in Metallic Nanoparticles Studied by Surface Plasmon Resonance Spectroscopy and Quartz Crystal Microbalance Techniques**, *C. Langhammer,* ***I. Zoric,*** Chalmers University of Technology, Sweden, *S.T. Kelly, B.M. Clemens,* Stanford University, *B. Kasemo*, Chalmers University of Technology, Sweden

Nanosized metallic particles may have advantageous hydrogen storage properties compared to the corresponding bulk material both in terms of sorption/desorption kinetics and in terms of storage capacity. In order to understand the physical principles behind the influence of nanosizing on hydrogen uptake/release properties, we have developed a novel localized surface plasmon resonance (LSPR) based optical hydrogen sensing scheme for nanoparticle storage systems. As model experiments we carried out measurements of the phase diagram and thermodynamic properties for supported Pd nanodisks, ranging in size from 30 nm to 300 nm. By monitoring the shift of the LSPR extinction peak upon hydrogen uptake/release as a function of hydrogen pressure, at different temperatures, we have mapped out a series of pressure-concentration (p-C) isotherm for a range of particle sizes. These optical studies are complemented by gravimetric studies using a quartz crystal microbalance (QCM). In the latter case the corresponding p-C isotherms were obtained by monitoring the frequency shifts when the Pd nanodisks were prepared on the QCM electrode and exposed to hydrogen environment at different temperatures. We have used Van't Hoff plots (log of the isotherm plateau pressure, in the two-phase region, versus inverse plateau temperature), to obtain the enthalpy and entropy for hydride formation in Pd nanodisks of different sizes. Furthermore, we have used Sievert's plots in the low hydrogen concentration limit (α-phase) to extract enthalpies and entropies of hydrogen dissolution. An excellent agreement was obtained for the corresponding thermodynamic variables obtained from LSPR sensing data and QCM data. Similarities and differences to the corresponding thermodynamic variables for bulk systems are discussed. In addition, we have carried out corresponding measurements with Mg nanoparticles "capped" with few nanometers of Pd to facilitate H2 dissociation. The "capping" with a Pd layer circumvents the bottleneck associated with low dissociative sticking of hydrogen on Mg. Double plateau isotherms were obtained indicating initial onset of the mixed phase formation at low hydrogen pressure in Mg nanoparticle followed by a corresponding two phase onset in the Pd cap at higher pressure, characteristic for Pd nanoparticles at a given temperature. In addition, we also present the QCM and LSPR based studies of hydrogen uptake/release kinetics at different temperatures.

4:00pm **EN+SE+NS+SS-MoA7 Atomistic Mechanisms of Reversible Hydrogen Storage in Complex Metal Hydrides**, ***P. Sutter***, Brookhaven National Laboratory **INVITED**

The storage of hydrogen in a lightweight, high-capacity medium with fast charge/discharge kinetics has been recognized as one of the primary challenges in achieving the transition to a hydrogen-based economy. Hydrogen-rich compounds, such as complex metal hydrides, offer potentially high storage capacities but the solid-state hydrogen storage reactions in these materials generally proceed slowly and in many instances are not reversible, i.e., re-hydrogenation of the depleted products cannot be realized by controlling temperature and hydrogen pressure alone. The use of doping to achieve reversibility and fast reaction kinetics has been demonstrated successfully for a particular complex metal hydride, sodium alanate ($NaAlH_4$). Here we discuss our recent efforts on identifying the atomic-scale effects of such doping by microscopy and spectroscopy experiments on well-defined model systems (e.g., single crystal surfaces), closely linked to ab-initio theory and simulations. A comprehensive understanding of important microscopic reaction mechanisms allows deriving general guidelines for the use of dopants or catalysts to accelerate hydrogen storage reactions in alanates, and possibly in a broader class of solid-state storage materials.

4:40pm **EN+SE+NS+SS-MoA9 Microwave Irradiation for the Reversible Desorption of Hydrogen from Sodium Aluminum Hydride**, ***T.A. Dobbins***, Louisiana Tech University and Grambling State University, *R. Krishnan*, Louisiana Tech University

Materials such as complex metal hydrides and hydrogen adsorbents have been the primary focus of the on-board hydrogen storage research program. Complex metal hydrides offer great potential in making it into the transportation industry due their reliable on-board reversibility. These materials can perform very well even after multiple dehydrogenation-hydrogenation cycles. Conventional heating mechanisms have been used to desorb hydrogen from complex metal hydrides. However, conventional heating processes involve high energy penalties (because the energy invested to heat the complex metal hydride is equal to or greater than the energy generated by a fuel cell using the desorbed hydrogen). This research is aimed at establishing the use of microwave irradiation to desorb hydrogen from sodium aluminum hydride (NaAlH4). Microwave heating is known to be more energy efficient than conventional heating. However, microwave fields are also known to drive order to disorder reactions in the hydrides, thus resulting in amorphous desorption products. This work reports a method to use microwave irradiation to desorb hydrogen from NaAlH4 via the reversible desorption pathway. This is the first report of using microwaves to drive a dehydrogenation reaction with the same pathway as driven by conventional heating processes. The method established in this research makes use of the energy efficiency of microwave irradiation and can be extended to other hydride systems for future research.

Funding for this project was provided by the Department of Energy, Office of Basic Energy Sciences (Contract No.: DE-FG02-05ER46246).

5:00pm **EN+SE+NS+SS-MoA10 Alane Formation on Al(100) and Ti-doped Al(100)**, ***I.S. Chopra***, *J.-F. Veyan, Y.J. Chabal,* University of Texas at Dallas, *S. Chaudhuri*, Washington State University

Complex metal hydrides, such as $NaAlH_4$, are candidates for hydrogen storage as they can reversibly release and recapture hydrogen. Alane Clusters (Al_xH_y) are believed to be the mass transport intermediate in the hydrogen storage reactions involved in hydrogen uptake and release. Understanding the surface chemistry behind the formation and evolution of alane clusters is therefore important to lower the temperatures needed for these processes. Since doping metallic Al is critical for H_2 dissociation, we have undertaken a comprehensive study of H interaction with Al(100) and Ti-doped Al(100) surfaces to better understand the atomic scale mechanisms underlying this reversible hydrogen storage behavior. The results have been compared with similar study performed earlier on the Al(111) and Ti doped Al(111) surface. In-situ infrared absorption spectroscopy had previously shown[1] that the nature of alanes (size, bonding configuration) formed on Al(111) depends on both H exposure and sample temperature. At low temperatures (~90K), small alanes such as AlH_3 and Al_2H_6 are predominant. At higher temperatures (~ 250K), larger alanes are formed. The study of alane formation on the Al(100) surface as a function of H exposures and substrate temperatures make it possible to explore the dependence of the alane formation on the crystal orientation. The effect of Ti doping is also explored as a function of both Ti concentration and H_2 pressures. Our first-principles calculations indicate that Ti atoms should occupy hollow sites of the (100) unit cell. We are therefore using LEED to test whether this site is indeed the most favorable and IR spectroscopy to explore whether Ti in that site does dissociate H_2. On Al(111), no dissociation was observed for H_2 pressure up to 10^{-6} Torr. We are therefore exploring dissociation up to 10^{-4} Torr on Al(100). Finally, we are using TPD to probe the nature of desorbed species from both Al(100) and Ti – doped Al(100) surfaces.

[1] Santanu Chaudhuri, Sylvie Rangan, Jean-Francois Veyan, James T. Muckerman,Yves J. Chabal, J.Am. Chem. Soc. (submitted).

5:20pm **EN+SE+NS+SS-MoA11 Infrared Spectroscopy Studies of Hydrogen Interaction in Metal Organic Frameworks**, ***N. Nijem***, *J.-F. Veyan*, University of Texas at Dallas, *J. Li*, Rutgers University, *Y.J. Chabal*, University of Texas at Dallas

Hydrogen storage is one of the most challenging problems in hydrogen-based energy technology. One of the goals of hydrogen storage is the ability to store a high volumetric density of hydrogen at room temperature. As a result, studies exploring hydrogen interaction in storage materials are important to facilitate further development of materials. Metal-organic Frameworks are promising candidates for hydrogen storage because their high surface area and porosity facilitate high hydrogen physisorption on specific sites of the structures. This work explores the incorporation of hydrogen into the structure using infrared (IR) absorption spectroscopy. IR spectroscopy can distinguish possible H_2 binding sites based on the perturbation of the internal H_2 stretch mode. The measurements are performed at room temperature on three different types of MOF structures, two of which have the general formula $[M(bdc)(ted)_{0.5}]$-2DMF-0.2H_2O, differing in the metal core M (Ni and Zn). These two compounds are isostructural and crystallize in the tetragonal phase (space group P4/ncc), they construct a 3D porous structures with relatively large pore size (~7-8Å, pore volume (~0.63-0.84 cc/g) and BET surface area (~1500-1900 m^2/g). Another type of MOF is the $[Ni_3(HCOO)_6]$-DMF structure which crystallizes in space group P21/c and features a 1D open channels with smaller pore diameters (~5-6 Å). Preliminary results show perturbation of the H_2 gas vibrational modes leading to a ~30 cm^{-1} shift of the ortho- and para- peaks of the unperturbed H_2. This perturbation is due to the interaction of the hydrogen with the MOF and can be seen as evidence of the hydrogen adsorbed onto specific sites of the MOF. Although the data are taken for high pressure H_2 gas at room temperature, the shift is consistent with previous observation of Bordiga et al.[1] performed at very low pressures and temperatures. The intensities of the perturbed ortho- and para- H_2 peaks have a linear dependence with pressure, indicating that the perturbation of the H_2 with the MOF lattice is dominant, i.e. H_2-H_2 interactions are much less important than in the pure H_2 gas.

[1] S. Bordiga, J. G. Vitillo, G. Ricchiardi, et al., Interaction of hydrogen with MOF-5 Journal of Physical Chemistry B 109, 18237 (2005).

Energy Science and Technology Focus Topic
Room: 203 - Session EN+BI+SS+SE-TuM

Catalysis for Energy Sustainability
Moderator: D.E. Ramaker, George Washington University

8:00am **EN+BI+SS+SE-TuM1 Size, Shape, and Support Effects in Oxidative Coupling Reactions**, ***C.L. Marshall***, *W. Setthapun, S. Mucherie,* Argonne National Laboratory*, H.S. Kim,* Northwestern University*, J.A. Libera, J.W. Elam,* Argonne National Laboratory*, P.C. Stair*, Northwestern University **INVITED**

In this paper we describe the characterization and catalytic performances in the reaction of ODH of propane over new nanostructured membrane catalysts composed of vanadium species supported on different metal oxides (Al2O3, Nb2O5, TiO2), which have been fabricated using the combination of anodic aluminum oxide (AAO) and atomic layer deposition (ALD).1 The aim of this study is to determine the role played by the nanostructured materials and the nature of the support oxide on the reactivity of these AAO membrane catalysts in terms of activity and selectivity to propylene.

8:40am **EN+BI+SS+SE-TuM3 Application of Single-Wall Carbon Nanohorns**, ***M. Yudasaka***, Advanced Industrial Science and Technology (AIST), Japan **INVITED**

The discovery of spherical aggregates of single-wall carbon nanohorns (SWNHs) was reported in 1999. The aggregates were called dahlia-like, bud-like, and seed-like SWNHs based on their forms. Since the dahlia-type aggregate (D-NHag) was obtained with the highest purity (about 90%) among the three types, SWNH applications have been studied mainly using the D-NHag. The individual SWNH has a structure similar to SWNTs, namely, a tube-like structure made of a graphene sheet, but with larger diameters (2-5 nm), shorter length (40-50 nm), and horn-shaped tips with a cone angle of about 19o. Studies of various applications of D-NHag revealed that they are a unique medium for adsorption, support, and storage of materials. This uniqueness mainly comes from mountain-valley structure of the D-NHag surfaces and wide inner-hollow spaces. The mountain-valley surface morphology was suitable for supporting material clusters with small sizes. The reason for this may be because migration on the SWNHag surface was suppressed, so coalescence of the clusters was avoided. In fact, the sizes of Pt-particles supported on D-NHag were small, about 1 nm. When the Pt/SWNHag was used as fuel-cell electrodes, the battery characteristics were significantly improved. The inside spaces of SWNHs were made accessible by making holes at the tips and defects of sidewalls. It was easy to incorporate various materials (C60, metals, inorganic and organic molecules including drugs, etc.) inside SWNHs in the liquid-phase at room temperature, where the incorporating quantities were controllable. The materials were moderately bound inside SWNHs, which enabled the rate-controlled release of the incorporated materials. It was also easy to individually disperse D-NHag in various solvents. They were well dispersed even in aqueous solutions, which will make possible biological applications of D-NHag. We previously reported that dexamethasone, a drug, was loaded in/on SWNHs in aqueous solutions and released in cell culture medium, exhibiting its drug effect in several ways. SWNH is quasi-SWNT, but, its usefulness is different from that of SWNT. We believe that D-NHag will be suitable for a catalyst support and material-delivery medium. Acknowledgement: I am grateful to all the collaborators, especially Professor Iijima, and JST for supporting this research through ICORP and SORST schemes.

[1] S. Iijima, et al., Chem. Phys. Lett. 309 (1999) 165.

9:20am **EN+BI+SS+SE-TuM5 Reducing Carbon Dioxide to Methane under Visible Light Illumination by Non-stoichiometric Mixed Phase Titania Thin Films**, ***L. Chen****, M.E. Graham, P.A. DeSario, K.A. Gray*, Northwestern University

Non-stoichiometric mixed phased titania composites were deposited by reactive DC magnetron sputtering. Previously we[1-3] demonstrated that there are solid-solid interfaces with highly reactive interfacial sites created within mixed phase titania thin films, and we observed by EPR measurement that the bulk composition of the films was not fully stoichiometric. The objective of this study is to explore the role of non-stoichiometry in mixed phase titania in terms of photoresponse and photocatalytic performance in reducing CO_2 to methane. The control of oxygen partial pressure during film deposition yielded different levels of non-stoichiometry in films deposited mostly in the transition mode. Trace amounts of nitrogen were introduced during the sputtering process to stabilize the reactive sputtering process at the turning point of the transition mode and metallic mode and without incorporation in the films. The photocatalytic results showed that there was an optimal non-stoichiometry of titania films in terms of methane yield from CO_2 reduction. Under UV illumination, the best CO_2 conversion percentage was around 22%. In addition, both from reaction tests under visible light and the optical measurements, we determined that non-stoichiometric mixed phase titania films showed a strong light absorption shift into the visible range compared to commercial standard Degussa P25, which has a similar phase composition. SEM and TEM results showed film morphology with a high density of solid-solid interfaces developed in the films. Both EELS and XPS results identified the Ti^{3+} species in addition to Ti^{4+}. Most of the Ti^{3+} species were located at the interfaces of titania columns, where they might serve as the reactive interfacial sites for visible light harvesting or electron trapping.

[1] L. Chen, et al., Photoreduction of CO_2 by TiO_2 Nanocomposties Synthesized through Reactive DC Magnetron Sputter Deposition. Thin Solid Films, 2008. in review.

[2] L. Chen, et al., Fabricating Highly Active Mixed Phase TiO_2 Photocatalysts by Reactive DC Magnetron Sputter Deposition. Thin Solid Films, 2006. 515(3): p. 1176-1181.

[3] Hurum, D.C., et al., Probing reaction mechanisms in mixed phase TiO_2 by EPR. Journal of Electron Spectroscopy and Related Phenomena, 2006. 150: p. 155-163.

9:40am **EN+BI+SS+SE-TuM6 Variations in Metal-Ligand Effects on Pt in Pt_nM (M = Ru,Mo,Sn) Electrocatalysts as Exhibited by in situ XANES and EXAFS Measurements in Methanol**, ***D.E. Ramaker****, F.J. Scott,* George Washington University*, S. Mukerjee*, Northeastern University

Metal-ligand effects on Pt are commonly utilized to decrease the CO poisoning of the anode in methanol as well as to increase the activity for oxygen reduction at the cathode. However, these effects are not clearly understood because of the general lack of information on the particle morphology (M island size, homogeneity, etc.) and CO or OH adsorbate coverages. In this work, in situ X-Ray Absorption Spectroscopy (XAS) measurements, in the near edge and extended regions (XANES and EXAFS) at the Pt L_3 edge, were carried out on three different carbon-supported electrocatalysts (Pt_3Mo, Pt_4Mo, and PtSn) in an electrochemical cell in 1 M $HClO_4$ along with 0.3 M methanol. The CO, OH, O, and H_{upd} relative adsorbate coverages on Pt are determined as a function of the applied potential via the ΔXANES technique and compared with comparable data reported for three different PtRu electrocatalysts (PtRu Etek, PtRu Watanabe, and Pt_3Ru) reported previously[1]. The average particle morphology of each catalysts is determined from EXAFS coordination numbers and a modeling technique.[1] The onset of the n-fold O atom coverage between 0.5 and 0.9 V (RHE) tracks essentially with the particle size. The more reactive Sn and Mo atoms interact more strongly with Pt, and hence the ligand effect for the M and MO_n islands are comparable, in contrast to that for Ru vs. RuO_n. Our results are correlated with the extensive electrochemical results found in the literature on similar Pt_nM catalysts. The results suggest that the strength of the ligand effect increases in the order $Ru < Mo, MoO_n < Sn, SnO_n \leq RuO_n$, where the relative Pt-CO bond strength is found to decrease and the Pt-OH bond strength increases with ligand effect. In the Sn and Mo bimetallics, the ligand effect is found to be sufficiently strong to allow CO replacement by H_2 at low currents.

[1] F. J. Scott, S. Mukerjee, and D. E. Ramaker, J. Electrochem. Soc. 154, A396-A406 (2007).

10:40am **EN+BI+SS+SE-TuM9 Controlling the Activity of Fuel Cell Electrode Materials by Tuning the Surface Electronic Structure**, ***J.K. Norskov***, Technical University of Denmark **INVITED**

The performance of low temperature fuel cells based on proton conducting membranes is severely hampered by an overpotential at the cathode where molecular oxygen combines with protons and electrons to form water. To understand the origin of this problem a method has been developed that allows a theoretical treatment of chemical reactions at the water-solid interface in the presence of an electrical bias on the basis of electronic structure calculations. Extensive density functional calculations have allowed an identification of the origin of the overpotential for the commonly used electrode material, platinum, as well as insight into the way alloying can change the surface electronic structure of platinum to reduce the overpotential. The reverse reaction, electrochemical water splitting, is also discussed, and it is shown that the performance of different classes of inorganic materials as electrocatalyst as well as the catalytic center for biological water splitting in photosystem II can be understood within the same conceptual framework.

11:20am **EN+BI+SS+SE-TuM11 Resolving the Electronic Properties of Catalytically Important Pd/Au Alloys at the Sub-Nanometer Level**, ***A.E. Baber****, H.L. Tierney, E.C.H. Sykes*, Tufts University

Palladium/gold (Pd/Au) bimetallic alloys have been used to catalyze important processes such as the synthesis of vinyl acetate and hydrogen peroxide as well as some oxidative reactions (methanol, formic acid, CO).

Low temperature, ultra-high vacuum scanning tunneling microscopy (LT-UHV STM) is used not only to image bimetallic alloys, but also to spectroscopically probe the local electronic changes in both Pd and Au atoms when the two are alloyed. We have used STM to evaluate the surface composition of a real bimetallic alloy system and have found that the unique herringbone reconstruction of Au{111} provides entry sites for the incorporation of Pd atoms. We were able to differentiate between surface, subsurface and overlayer Pd atoms and study the temperature dependence of the preferred Pd destination. As the deposition temperature increases, the location of Pd changes from mostly overlayer to surface to subsurface. Scanning tunneling spectroscopy was used to examine the local density of states (LDOS) of individual Pd and Au atoms in both surface and subsurface sites in order to investigate the changes in the LDOS of a reactive metal alloyed in a more noble metal. It was found that in both surface and subsurface sites, Pd atoms displayed a LDOS very similar to the surrounding gold atoms, except for a small region at the band edge of the Au surface state in which the electron density was depleted. Pd atoms act as scattering sites for the surface electrons but do not fully quench the surface state. This is the first example of a simultaneous atomic-scale geometric and electronic characterization of a real PdAu catalytic system.

11:40am **EN+BI+SS+SE-TuM12 Water-Gas-Shift Reaction on Metal-Oxide Catalysts**, ***P. Liu***, *S. Ma, J.A. Rodriguez, J. Hrbek*, Brookhaven National Laboratory

The water-gas shift (WGS) reaction ($CO + H_2O \rightarrow H_2 + CO_2$) is a critical process in providing pure hydrogen for fuel cells and other applications. However, current industrial catalysts (Fe-Cr or Zn-Al-Cu oxides) are pyrophoric and require complex activation steps before usage. A fascinating puzzle has recently emerged: Au/CeO_2 and Au/TiO_2 nanomaterials show high activity for WGS catalysis. This is remarkable since in bulk form Au, ceria and titania are not known as WGS catalysts. The nature of the active phase(s) in these metal-oxide nanocatalysts is unclear at the present time, which impedes the design and optimization of WGS catalysts. We have carried out coordinated experimental and theoretical studies to address this problem. The experiments show that the model catalysts, Au/CeO_2(111) or TiO_2(110) and inverse CeO_2 or TiO_2/Au(111), display activities comparable to good WGS catalysts (i.e., Cu(100) and Cu(111)). Theoretical calculations based on density functional theory (DFT) are also carried out to understand the active sites in the oxide-gold catalysts, by probing reaction scenarios on Au, titania, and Au-TiO_2 (Au/TiO_2 and TiO_2/Au(111)) catalyst model structure. In accordance with experiments, our calculations show a very high barrier for the dissociation of water on Au and the formation of very stable formate species on titania that prevents the production of H_2 and CO_2. The model Au-TiO_2 catalyst overcomes these bottlenecks: the moderate chemical activity of gold is coupled to the more reactive oxide. The dissociation of water takes place on the oxide easily, a reaction that extended surfaces and nanoparticles of Au cannot perform. CO adsorbs on gold sites located nearby (bifunctional catalyst). Then all the subsequent steps occur at the oxide-metal interface at a reasonable speed. Our results imply that the high activities of Au/CeO_2 and Au/TiO_2 nanocatalysts in the WGS reaction depend heavily on the direct participation of oxide-metal interface. The diversity of nanoparticle structures and the interplay with the support highlight the importance of identifying critical structural motifs to model catalyst function. This research was carried out at Brookhaven National Laboratory and supported by the US Department of Energy (Chemical Sciences Division, DE-AC02-98CH10886).

Energy Science and Technology Focus Topic
Room: 203 - Session EN+EM+NS+PS-TuA

Photovoltaics
Moderator: B.J. Stanbery, Helio Volt Corporation, J. Xue, University of Florida

1:40pm **EN+EM+NS+PS-TuA1 Thin films, Plasmas and Solar Cells**, ***M.C.M. van de Sanden***, Eindhoven University of Technology, The Netherlands **INVITED**

Solar cells, devices which can convert sunlight directly into electricity by the photovoltaic (PV) effect, is now recognized as one of the options to provide a significant fraction of the energy mix in 2050 to power the world. Presently the PV industry is booming and two important challenges lie ahead: increasing the efficiency of conversion of sunlight into electricity and obtaining the required scale in terms of the surface area produced. The latter requires high throughput processing of solar cells in all its aspects. Increasing the efficiency is scientifically attaining the most attention, but history has shown that more cost reduction can be obtained by improving processes and increasing the scale of the industry. This talk will address both challenges by discussing the role of thin film and plasma technology. Presently the solar cell market is dominated by solar cells based on crystalline silicon. In this solar cell technology, where the photo-active material is wafer based silicon, thin films still play an important role to increase efficiency by effectively passivating bulk and surface defects and enhancing light trapping in the solar cell. The high rate deposition of a-SiNx:H as passivation and anti-reflection coating, by means of the expanding thermal plasma technique, will be shortly reviewed. Possible combinations with novel concepts to convert the solar spectrum will be addressed. Recently, we also introduced plasma assisted atomic layer deposition of Al_2O_3, a high k dielectric containing a large amount of negative charge, to passivate future p-type emitters on n-type silicon based solar cells. Demonstration of improved performance of n-type solar cells using this type of passivation layer with an efficiency as high 23.2 % will be discussed. To obtain the required large scale by 2050 further improvement of thin film solar cell technology will be essential, both in terms of materials as well as in terms of processes. Apart from the need for high throughput deposition of the photo-active materials, additional thin film technologies will be needed for barrier layers on substrates to limit impurity transport, for efficient light trapping (textured surfaces and anti-reflection layers) and last but not least encapsulation layers to guarantee the lifetime of the thin film solar cell. Apart from the further development of improved materials and device concepts, process monitoring and control to improve quality and throughput becomes more and more important. I will discuss here the monitoring of high rate deposition of microcrystalline silicon by means of optical emission spectroscopy. This optical probing method also enables the in situ detection of the crystallinity of the material deposited as well as fundamental insights in the growth mechanism.

2:20pm **EN+EM+NS+PS-TuA3 Effects of Nanostructures formed by Plasma Etching on Reflectance of Solar Cells**, ***S.H. Ryu***, *C. Yang, W.J. Yoo,* Sungkyunkwan University, Korea, *D.-H. Kim, T. Kim*, Samsung Advanced Institute of Technology, Korea

We investigated the lithography-free plasma etching methods to modify surface of single crystalline Si which was widely used for manufacturing of solar cells. Experiments were performed using SF6/O2 gases dry etching for the purpose of reducing the reflectivity at the Si surface. Upon inductively coupled plasma etching in SF6/O2 pillar-shaped nanostructures were formed on the surface which changed to black in color. The absorption factor was estimated by measuring reflection and transmission on the surface across near UV to near IR. Before etching, reflectance of Si wafer was ~ 35% in the wavelength range of 600-1000 nm and > 50% in the wavelength range of 200-400nm, whereas it decreased to < 5% after performing SF6/O2 plasma etching. The absorption factor of Si wafer after etching was increased up to ~ 90% from 65% compared to that without etching, in the wavelength range of 600-1000 nm. Furthermore, various etching methods and conditions to suppress reflectivity in a broad spectral range were investigated for optimization of the surface property of the solar cells, ie, enhancement of solar cell efficiency. We investigated the effects of various processing parameters on surface property by changing gas ratio, bias power and etching time. The current-voltage characteristics on the surface textured solar cells showed that short circuit current (Isc) and open circuit voltage (Voc) changed sensitively depending on the surface treatment. The relation between the surface morphology and the absorption factor was analyzed.

2:40pm **EN+EM+NS+PS-TuA4 Nanoscale Heterojunction Engineering to Grow High-Quality Ge on Si for Multijunction Solar Cells**, ***D. Leonhardt***, *J. Sheng, T.E. Vandervelde,* University of New Mexico, *J.G. Cederberg, M.S. Carroll,* Sandia National Laboratories, *S.M. Han*, University of New Mexico

In an effort to reduce the manufacturing cost of multijunction solar cells, we have scaled up a process to grow low-defect-density Ge films on 2-inch-diameter Si substrates. This growth technique makes use of nanoscale heterojunction engineering to minimize the interfacial strain density. The engineered substrates may potentially replace the Ge wafers that are currently used in multijunction solar cell fabrication, if the Ge film's bulk and surface quality can match that of the epi-ready Ge wafers. We will present results for the scaled-up process of Ge film production, including key aspects of the nucleation process and film characterization, using transmission electron microscopy and etch pit counting. Next, we present our efforts to produce a high-quality surface finish, using chemical-mechanical planarization, and method for cleaning and passivating the Ge surface. Additionally, results of GaAs film growth on our engineered substrates will be presented and compared to growth on Ge and GaAs wafers, both offcut and nominal. We find that the offcut wafers effectively eliminate anti-phase domains in the GaAs. We also observe room-temperature photoluminescence from GaAs epilayers grown on our engineered Ge/Si substrates. Lastly, future work and directions will be discussed in light of our findings.

3:00pm **EN+EM+NS+PS-TuA5 On a New Concept of Tandem Photovoltaic Cells Based on III-V Semiconductor Materials**, ***M. Emziane***, Masdar Institute of Science and Technology, UAE, *R.J. Nicholas*, University of Oxford, UK

We have investigated single-junction and double-junction photovoltaic devices using ternary and quaternary InGaAs(P) semiconductor materials. These were designed and optimized for potential applications in conventional photovoltaics, thermophotovoltaics and concentrator photovoltaics.Different bandgaps were considered for single-junctions, and various bandgap combinations were simulated for the top and bottom cells of the tandem devices where the structure comprises two single-junction cells connected back to back and separated by a middle common contact. For both single and double-junctions, the device structures were modeled and optimized as a function of the doping concentration and thickness of the active layers, and the simulations show that optimum device performance can be achieved by using relatively thin structures and low doping concentrations in the emitter and base layers. The variation of the device performance with the black-body source temperature, incident intensity and operating temperature was also simulated and discussed. Due to the split of the incident spectrum, the bottom cell response is found to be different from that expected for a single-junction cell having the same bandgap. The optimal bandgap combination that delivers the best total efficiency for the tandem device was also determined and the data discussed.

4:00pm **EN+EM+NS+PS-TuA8 Thin Film Preparation of Chalcopyrites for Solar Cells and Fundamental Material Physics**, ***S. Siebentritt***, University of Luxembourg **INVITED**

Thin film solar modules are expected to be the next generation of photovoltaics technologies. Their cost reduction potential has been estimated much higher than that of Si wafer technologies. Among the various thin film technologies solar cells based on chalcopyrite ($CuInGaSe_2$, CIGS) absorbers show the highest efficiencies, reaching 19.9% in the lab. These record solar cells are prepared by a high vacuum co-evaporation process that proceeds in three stages with different composition. A simplified two stage co-evaporation process is used in the first mass production of chalcopyrite solar modules. Further industrial processes are the sputter deposition of metallic precursors which are reacted in an annealing process to the semiconductor compound. Recently electrochemical deposition has appeared as a low cost approach to the precursor deposition. In all cases the knowledge on fundamental growth processes, nucleation behaviour and detailed reaction is limited. The details of the processes and their advantages and disadvantages for solar module production will be discussed. The afore mentioned deposition processes result in polycrystalline films with grain sizes of approximately 1 micrometer. For the investigation of the fundamental material physics it is necessary to obtain grain boundary free material. The lattice mismatch between $CuInSe_2$ and $CuGaSe_2$ on one side and GaAs on the other side is between 2.2 and -0.7% and allows epitaxy of chalcopyrite films on GaAs. Several methods for the epitaxy have been developed: metal organic vapour phase epitaxy (MOVPE), molecular beam epitaxy (MBE) and a hybrid sputter/evaporation process. The specifics of these processes will be briefly discussed and some results of epitaxial films will be presented.

4:40pm **EN+EM+NS+PS-TuA10 Influence of a Single Grain Boundary on Epitaxial CuInSe$_2$ Film Growth**, ***A.J. Hall***, *D. Hebert*, *A. Rockett*, University of Illinois at Urbana-Champaign

Very large multigrain copper indium diselenide (CuInSe2) films were grown on gallium arsenide (GaAs) multigrain wafers using a hybrid sputtering/effusion growth process. Scanning electrom microscopy (SEM) morphology shows excellent epitaxial grain growth on the substrate with intimate grain boundary contact. Electron backscatter diffraction analysis shows a crystal misorientation common axis and misorientation angle for a high-angle, non-twin, boundary. Atomic force microscope and transmission electron microscope images are presented which confirm the surface morphology and the atomic intimacy of the grain interface. Kelvin probe force microscopy shows that the grain-boundary has little electrical influence on the film in comparison to other features present in the crystallites. Growth of large multicrystalline or bicrystalline CuInSe2 films allows more careful study of both physical and electrical influence of grain-boundaries on film properties. Current work on the physical influence of a single boundary on film growth is discussed.

Energy Science and Technology Focus Topic
Room: Hall D - Session EN-TuP

Energy Focus Topic Poster Session

EN-TuP1 Resistive Oxygen Gas Sensor Using Pure and Doped CeO_2, ***S. Gupta***, Portland State University, *S.V.N.T. Kuchibhata, M.H. Engelhard, P. Nachimuthu, V. Shutthanandan, L.V. Saraf, S. Thevuthasan,* Pacific Northwest National Laboratory, *S. Prasad*, Portland State University

Oxygen sensors have come into wide use in automotive and industrial applications as leak detectors, industrial process flow evaluators, as well as in life science industry in diagnostic applications such as respiratory vital signs monitoring, and metabolic rate monitoring. All these applications require the fast monitoring of the oxygen gas. Hence we have explored the possibilities to develop an oxygen sensor operating on the chemiresistive principle at aggressive environments with a reduced response time. Ceria is known for its unique ability to lose or gain oxygen based on the ambient environment. The doping of trivalent elements including Y, Sm and Gd in ceria is expected to create oxygen vacancies and eventually influence virtually all types of transport properties like ionic and electronic properties. The overarching objective of this project is to study the effects of changes in surrounding conditions such as temperature, pressure, dopant concentration on the transport properties of doped ceria films. High quality, epitaxial, pure and doped ceria thin films were grown on sapphire (0001) substrates using oxygen plasma assisted molecular beam epitaxy (OPA-MBE) and characterized them using several bulk and surface sensitive techniques. Conductivity in these films was measured as a function of temperature (room temperature to 700C) under various oxygen partial pressure (1 torr to 100 torr) and vacuum conditions. Preliminary results show that response of the doped ceria film is much faster than the pure ceria films under the same conditions of temperature and pressure. Moreover response time of these films is few milliseconds with the change in the oxygen partial pressure. It was observed that the samarium concentration of approximately 4-6 atom% is the optimum doping content.

EN-TuP2 A Closer Look at H-CO Interaction on the Platinum Surface, ***T. Roman***, *H. Nakanishi, H. Kasai*, Osaka University, Japan

The system comprised of coadsorbed hydrogen and carbon monoxide on platinum has been the subject of a number of experimental work due to its high relevance in heterogeneous catalysis, particularly in relation with hydrogen fuel cells. Several studies have asserted the strong repulsion between these two species on the solid surface, especially in high pressures, wherein the formation of homogeneous islands of CO have been reported. On the other hand, theoretical work specifically addressing the H/CO coadsorption system on Pt is rather limited. To fully understand the physical mechanisms involved at the atomic scale, it would be beneficial for example to quantify the extent to which H and CO interaction on Pt is repulsive, knowing that H-CO interaction in the gas phase is actually partly attractive, and comment on possibilities for H and CO closely coexisting on Pt. It is in this light that we in this study describe the behavior of hydrogen near a Pt surface-adsorbed carbon monoxide molecule using a potential energy term constructed from ab initio calculations. The considerable asymmetry of the repulsion extent around CO suggests that while incoming hydrogen experiences strong obstacles to adsorption even before the Pt surface is reached, adsorbed H can remain stable even in relatively compact conditions. Inhibiting effects of CO greater than what is expected from simple adsorption site exclusion are discussed with regard to adsorption/desorption and mobility on platinum, as well as possibilities of COH and HCO formation on platinum. A quantum mechanical treatment of the H atom behavior similar to what we have used before[1] is also performed on the obtained potential term. Theoretical results are lastly discussed with available experimental data on the H-CO coadsorbate system on transition metal surfaces.

[1] T. Roman, H. Nakanishi, W. A. Diño, H. Kasai, e-J. Surf. Sci. Nanotech. 4 (2006) 619.

EN-TuP3 Electronic Energy Level Alignment in Dye Sensitized Oxide Substrates, ***J.P. Theisen***, *S. Rangan, E. Bersch, R.A. Bartynski, J.D. Sorge, D.P. Birnie, Z. Duan, Y. Lu*, Rutgers University

In dye-sensitized solar cell applications, the HOMO-LUMO gap of dye molecules determines the useful portion of the solar spectrum, and charge transfer of photoexcited electrons to the substrate depends on the alignment of the LUMO to the substrate conduction band edge. We have used direct and inverse photoemission to measure the occupied and unoccupied electronic states of several dye-related molecules and determine their alignment with the band edges of single crystal and nanostructured TiO_2 and ZnO substrates. On well characterized rutile $TiO_2(110)$ and wurtzite ZnO(11-20) single crystal surfaces, we have compared the position of the HOMO and LUMO levels of the N3 Ruthenium based-dye, of isonicotinic acid and catechol molecules. Isonicotinic acid, as a simpler form of the linker that binds the N3-dye on TiO_2, is found to have a very similar electronic structure as the N3-dye in the unoccupied states. This is consistent with the electronic transfer scheme where N3 excitation occurs from the HOMO localized on its Ruthenium center, to the LUMO delocalized on the dye linker to the surface. Catechol on $TiO_2(110)$ however has no electronic states degenerated with the bottom of the conduction band edge. As a consequence the lower energy excitation process occurs via a HOMO to conduction band process. We have also measured the electronic structure of N3 adsorbed on more technologically relevant TiO_2 anatase nanoparticle and ZnO nanorod substrates.

EN-TuP4 High Efficiency Down Converting Powder Phosphors for Solid Sate Lighting Applications, ***S. Maslov***, *D. Bera, L. Qian, P.H. Holloway*, University of Florida

High performance blue and white organic light emitting diodes (OLED) offer improved efficiencies for solid state lighting. A down converting phosphor layer allows color tuning capabilities when coupled with a blue emitting OLED, and leads to improved efficacies approaching 80 lm/watt. The efficacy, CIE color coordinates, color rendering index, and angle resolved photoluminescence intensity were characterized versus film thickness and phosphor weight fraction. Due to scattering by phosphor particles, the initially forward focused light is converted to a Lambertian distribution of intensity. The method for applying powder thin films will be illustrated and discussed. The advantages and disadvantages of PMMA versus silicones for the dispersion matrix will be reported. Optimum phosphor layers were those with high quantum yield and maximum light out coupling.

EN-TuP5 Ionic Conductivity of Scandia Doped Zirconia Thin Films by Oxygen-Plasma-Assisted Molecular Beam Epitaxy, ***M.H. Engelhard***, Pacific Northwest National Laboratory, *Z.Q. Yu,* Nanjing Normal University, China, *S.V.N.T. Kuchibhatla, C.M. Wang, O. Marina, W. Jiang, V. Shutthanandan, P. Nachimuthu, R. Devanathan, L.V. Saraf, S. Thevuthasan*, Pacific Northwest National Laboratory

The development of electrolyte materials with high oxygen ion conductance at relatively low temperatures is essential to increase the efficiency and lifetime of electrochemical devices, such as solid oxide fuel cells (SOFC). Recently, there has been considerable interest in scandia stabilized zirconia (SSZ) since it shows high oxygen ionic conductance in comparison to commonly used ytrria stabilized zirconia (YSZ) in SOFCs. We have used oxygen plasma assisted molecular beam epitaxy (OPA-MBE) to synthesize high quality SSZ thin films on sapphire (0001) substrates and systematically investigated the conductivity as a function of temperature and Sc concentration. The epitaxial films have been characterized using various surface and bulk sensitive capabilities to determine their structure and composition. The ionic conductivity of SSZ depends not only on the dopant concentration, but also on the crystalline structure of the thin films. The optimum Sc dopant concentration for the highest conductivity was observed as 18 cation % in the temperature range of 500-900 °C. Conductivity appears to be significantly high in high quality cubic SZZ films in comparison to mixed phases of cubic and monoclinic. Molecular dynamics simulations of oxygen diffusion in cubic SZZ between 1125 and 2500 K show that the oxygen vacancy has no preference between Sc and Zr first neighbors, but the activation energy for O diffusion changes with Sc dopant concentration. Insights into the role of Sc dopant concentration on conductivity of SZZ obtained from experiments and simulations will be presented

EN-TuP6 Chemical Mechanical Polishing Characteristics of CdS for CdS/CdTe Thin Film Solar Cell Applications, ***H.-Y. Na***, *J.-S. Park, P.-J. Ko,* Chosun University, Korea, *N.-H. Kim,* Chonnam National University, Korea, *J.-T. Yang,* Gwangju College of Korea Polytechnic V, *W.-S. Lee*, Chosun University, Korea

CdS is widely used for the window layer material for the various thin film solar cells including CdS/CdTe, CdS/Cu_2S, and $CdS/CuInSe_2$ due to its excellent permeability with band gap of 2.42 eV while CdTe is one of the most promising photovoltaic materials with a direct band gap of about 1.45 eV, high optical absorption coefficients, the low cost, high efficiency and stable performance. The surface morphology of window layer materials was well known to affect the performances including the gain in photocurrent by increase of light scattering.[1] Therefore the surface morphology of CdS thin film as an window layer must be enhanced by the improved processes. Sputtering method was employed for preparation of CdS thin film, but it showed the rough surface morphology. Chemical mechanical polishing

(CMP) processing was firstly proposed for improving the surface morphology of CdS thin film on behalf of the plasma treatment reported in some researches. Removal rate was estimated by the obtained results through the application to Hernandez power law as a generalization version of Preston's equation for a better description of removal rate. Surface roughness and within-wafer non-uniformity (WIWNU%) of the sputtered CdS thin film was also examined with a change of CMP process parameters including table speed and down force. The optimized process condition was selected considering to both the surface roughness and the hillock-free surface with the good uniformity.

[1] M. Phyton et al., J. Non-Cryst. Solids 2008.

EN-TuP7 High Quality TCO Deposition using New DC Power Supplies, ***D. Ochs***, HUETTINGER Elektronik GmbH + Co KG, Germany, *P. Ozimek*, HUETTINGER Electronic Sp z o. o., Poland

The main application of magnetron sputter processes for thin film solar cell production is the deposition of transparent conductive oxides (TCO). The most significant example for this TCO material class is ZnO:Al (AZO) which is of great importance as a transparent conductive layer for photovoltaic applications. Since this material has an especially high arcing rate, pulsed DC power processes have been used for deposition in the past. A new DC power supply family has been developed with the goal of replacing these pulsed DC processes with economic standard DC processes. The most important feature of this power supply is an extremely fast and advanced arc management with the capability to run stable processes with high arcing rates. The arc management has three different detection criteria: a voltage, a current and a combined voltage/current criteria. After detecting an arc, a positive voltage is applied to the cable between the power supply and cathode. This so-called Cable Length Compensation compensates the stored energy of the cable and reduces the energy supplied into the arc after power shut off. In this way residual arc energies of less than 0.5 mJ/kW, are achievable. Stable processes over a long time with arcing rates of up to 20,000 arcs/s become possible. The fast arc management with adaptable parameters results in superior film quality, and homogeneity of the deposited film. The new economic DC power supplies replace pulsed DC power without any disadvantages.

EN-TuP8 Vacuum Insulating Glass: Window of the Future, ***P.J. Petit***, V-Glass LLC

This paper provides a brief summary of the past, present and potential near-term future of energy efficient windows, based on vacuum insulating glass, for residential buildings. It presents a brief history of window technology to the present day, summarizes known efforts around the world today to develop improved insulating window technology, and describes a "Window of the Future"[1] that might reasonably be assumed to be available in 2015. This "Window of the Future" consists of a Vacuum Insulating Glass (VIG) unit mounted in a low-heat-loss frame. Using a 3 ft by 5 ft window assembly as a representative "average" size for the purpose of this exercise, the overall U-value for a window of this design and size is estimated to be about 0.091 Btu/hr-sq ft-°F, which is equivalent to a wall rated at R11. Barriers which have prevented vacuum windows from being realized over the past two decades will be described, as well as the current strategies intended to overcome them.

[1] "Window of the Future", Swing Research LLC, April, 2008.

EN-TuP9 Characterization of the Photovoltaic Heterostructure CdS:F/CdSTe*, ***F. de Moure-Flores***, *M. Meléndez-Lira, J.G. Quiñones-Galván, E. Mota-Pineda, S. Cerón-Gutiérrez,* CINVESTAV-IPN, México, *A. Hernández-Hernández,* Escuela Superior de Fisica Matemáticas-IPN, México, *M. González-Alcudia, M. Zapata-Torres,* CICATA-IPN Unidad Altamira, México, *C. Davet-Lazos, M.delaL. Olvera*, CINVESTAV-IPN, México

We present results of the characterization of the structural, electronic and electrical properties of the photovoltaic heterostructure: ITO / CdS:F / CdSTe. The ITO film was deposited by the technique of rf sputtering. The CdS layer was deposited employing chemical bath deposition adding fluorine to increase n-type doping. The top CdSTe layer was deposited by the modified laser ablation technique.[1] The motivation to deposit a CdSTe layer, instead just CdTe, is to limit the S interdiffusion at the CdS/CdTe interface in order to improve the characteristics of the interfacial electric field.[2] We report the characteristic I vs. V, the spectral response, as well as the efficiency of the photovoltaic heterostructure. These results are correlated with those obtained from the chemical, structural and electronic characterization obtained through EDX and X-ray diffraction and UV-Vis and Raman spectroscopies.

[*] This work is partially supported by CONACyT-Mexico

[1] M. González-Alcudia, A. Márquez-Herrera, M. Zapata-Torres, M. Meléndez-Lira and O. Calzadilla-Amaya, Adv. in Tech. of Mat. And Mat. Proc. J. 9, 81 (2007).

[2] M.A. Santana-Aranda, M. Meléndez-Lira, Applied Surface Science, 175-176 (2000) 538-542.

EN-TuP10 Photoconduction Properties of Titanium Dioxide Films Prepared by Reactive Magnetron Sputtering, ***H.A. Shukur***, Kogakuin Univeristy, Japan, *H. Nagai, I. Takano, M. Sato*, Kogakuin University, Japan

Since TiO_2 has been used as one of lower cost materials and is harmless to the environment, it is expected to use as a material of a clean energy system in future. Furthermore its photocatalysis have antifouling and antibacterial properties. At the same time, the electric property shows n-type semiconductor characteristics and is classified as a high dielectric material. However, details of electric property for TiO_2 have not been researched on the relations between the oxygen deficit state and light. Generally the resistance of TiO_2 is decreases by the excitation of electrons due to the light irradiation. We anticipate that these properties are applied to a photo sensor of electronic parts. In this study the electrical property of TiO_2 thin film was investigated under irradiation with the ultraviolet or visible light. The formation conditions was changed the substrate temperature 100 and 200°C. Furthermore O_2 flow rate was changed from 0.1 to 1.7 sccm for each substrate temperature. I-V property of films on a slide glass was measured by using an unresisted current meter under fluorescence light (FL), a black light (BL) or a sterilizing light (SL). The measurement size of the film was 200nm in thickness, 10 mm in length and 8 mm in width. The resistivity of films depends on O_2 flow rate. On the other hand the films resistivities in both temperature conditions hadn't a large different property until 1.3 sccm, but the films formed under substrate temperature 200°C showed a large resistvity. The microstructure of these films investigated by X-ray diffraction showed clearly that the both of O_2 flow rate and substrate temperature affected films in crystalline structure. In case of high substrate temperature and large O_2 flow rate, the crystalline structure of films changed to an anatase type and films resistivity was raised. The measurement of photoconduction current under each light irradiation showed two important results. Firstly the TiO_2 thin films obtained a large effect of photoconduction current under BL irradiation in all formation conditions. The second point was that the photoconduction current reduced with increase of the film resitivity and the maximum photoconduction current was obtained at the film of 0.5 sccm with both of a substrate temperature.

[1] Akira Fujishima, Kazuhito Hashimoto and Toshiya Watanabe, "TiO_2 Photocatalysis Fundamental and Applications".

EN-TuP11 Effects of Pulse Sputtering Condition on Al: ZnO's Uniformities of TCO Properties for Solar Cell Application, ***W.K. Yang***, *J.E. Jee, J.H. Joo*, Kunsan National University, Korea

Bipolar pulsed magnetron sputtering is used to deposit Al doped ZnO on a glass substrate for a TCO (transparent conducting oxide) in a solar cell structure. A 5"x25" AZO target was sputtered by 50 – 250 kHz bipolar pulsed dc power supply to deposit 400x400mm area by swinging back and forth. Sheet resistance, surface morphology and optical transmittance were measured at 16 slide glasses (1"x3") to evaluate uniformity. In the thickness of 800nm, the average value of sheet resistance was 37Ω/□ and uniformity was 21.4% in 400×400mm area. The thickness of AZO thin film was 800nm and the resistivity was 2.9×10-3 Ω•cm. Generally, magnetron sputtering plasma is thought to be well confined above a target's race track. As substrate carrier is swinging, plasma is observed to be severely disrupted to go around to the back side at 5cm of target-substrate distance. To fully address these phenomena, we must use self consistent plasma model incorporating pulsed dc not just a simple dc cathode. As a first approach, we analyzed gas flow using a 3D fluid model as a substrate carrier is moving around a target and a gas distribution pipe. In here, we found that the gas flow distribution affected the plasma. Also we thought that this plasma might affect the deposited thin film. So, we expected that the uniform gas flow distribution could improve the plasma uniformity and the characteristics of AZO thin film.

EN-TuP12 Germanium Nanowires: Applications in Photovoltaics and Electronics, *L.A. Klein*, ***D.D.T. Mastrogiovanni***, *A. Du Pasquier, E. Garfunkel*, Rutgers University

Single crystal germanium nanowires are grown via vapor-liquid-solid methods in a hot-wall chemical vapor deposition reactor. We present the results of nanowire growth and discuss potential applications of nanowires grown on a variety of substrates. The relatively low growth temperature required for germanium nanowire formation combined with the enhanced semiconducting properties such as higher carrier mobility of germanium over silicon makes these wires an attractive building block in the rapidly expanding field of nanotechnology. In addition to our investigations into how growth conditions and substrates can affect the shape and orientation of the nanowires, we have investigated various chemical passivation methods, including chlorination, H-termination, and thiol and alkene passivation. Passivation becomes of utmost importance for germanium devices as germanium does not possess a stable native oxide as does silicon. These chemistries are also used to facilitate further surface functionalization and ohmic formation, and to improve device electrical performance. Most recently, the germanium nanowires were also used to enhance the properties of organic photovoltaic devices through the creation of a bulk heterojunction solar cell with poly(3-hexylthiophene) (P3HT). This hybrid-inorganic/organic device exhibits a significant increase in exciton dissociation and photocurrent when compared to pure P3HT. The photoelectrical properties of this device are characterized by measuring absorbance and photoluminescence spectra, current-voltage curves, and AM 1.5 filtered external quantum efficiency. In addition to the aforementioned techniques, other studies utilizing x-ray diffraction, Rutherford backscattering spectroscopy, and inductively coupled plasma mass spectroscopy enable us to observe how variations in nanowire concentration can affect the relative crystallinity and crystallite orientation of P3HT. We conclude with a discussion of our plans to improve the performance of these devices through surface passivation and the controlled introduction of phosphine impurities.

Energy Science and Technology Focus Topic
Room: 203 - Session EN+AS+EM+TF-WeM

Electrochemical Storage
Moderator: S. Haile, Caltech, K. Thornton, University of Michigan

8:00am **EN+AS+EM+TF-WeM1 Molybdenum Oxide Nanoparticles for Improved Lithium Ion Battery Technologies**, ***A.C. Dillon***, National Renewable Energy Lab., *S.-H. Lee,* University of Colorado, *Y.-H. Kim,* National Renewable Energy Lab., *R. Deshpande,* Lam Research, *P.A. Parilla, D.T. Gillaspie, E. Whitney,* National Renewable Energy Lab., *S.B. Zhang,* Rensselaer Polytechnic Institute, *A.H. Mahan*, National Renewable Energy Lab. **INVITED**

Lithium-ion batteries are current power sources of choice for portable electronics. Further improvement of performance and simultaneous reduction in cost could allow for the deployment in hybrid electric vehicles or plug-in hybrid electric vehicles (PHEVs). The development of PHEVs will enable reduced oil consumption in the transportation sector. Importantly, PHEVs will also enable increased use of intermittent renewable energy resources such as solar and wind. By charging PHEVs during peak solar generation times, the load on the grid is effectively “leveled”, and the average output of coal-fired power plants will be decreased. Recent efforts for electric vehicle applications are focused on new anode materials with slightly more positive insertion voltages to minimize any risks of high-surface-area Li plating while charging at high rates, a major safety concern. The state-of-the-art anode is graphite with a reversible capacity of ~ 350 mAh/g and a potential of 0.1 V relative to lithium metal. Metal oxides have long been known as Li-insertion compounds and typically operate at higher potential than graphite. Unfortunately they suffer from poor kinetics and/or capacity fade with cycling, especially at higher rates. Hot-wire chemical vapor deposition has been employed as a scalable method for the deposition of crystalline metal oxide nanoparticles at high density. Under optimal synthesis conditions, only crystalline nanostructures with a smallest dimension of ~ 10 - 40 nm are observed. Anodes fabricated from crystalline MoO3 nanoparticles display both an unprecedented reversible capacity of ~ 630 mAh/g and durable high rate capability. Porous thin film nanoparticle anodes, deposited by a simple electrophoresis technique, show no degradation in capacity for 150 cycles when cycled at high rate (C/2 corresponding to one discharge in 2 hrs.). Micron sized MoO3 particles are shown to fail after several cycles, under the same conditions. Both x-ray diffraction and in situ Raman spectroscopy studies reveal that upon Li-ion insertion the crystalline nanoparticles become highly disordered. Density functional theory calculations elucidate the complex Li-ion insertion process and reveal a novel mechanism confirming the nanoscale, high-rate, reversible capacity despite the loss of structural order. The synthesis of these novel nanostructured materials and their potential for improving lithium-ion battery technologies will be discussed in detail.

8:40am **EN+AS+EM+TF-WeM3 Boron Oxynitride: An Emerging Dielectric for High Temperature Capacitor Applications**, *N. Badi,* ***S. Vijayaraghavan***, *A. Bensaoula,* University of Houston, *A. Tempez, P. Chapon,* Horiba Jobin Yvon, France, *N. Tuccitto, A. Licciardello,* University of Catania, Italy

Among the many technical challenges encountered in the development of high temperature electronics, the role of a passive component like capacitor is very important. Dielectric integrity at temperatures greater than 250 °C has however, up till now, been one of the major impediments to bringing out a capacitor with suitable performance characteristics at these high temperatures. In this work, we investigate applicability of boron oxynitride (BO_xN_{1-x}) thin films to fabricate capacitors for high temperature applications. Deposited BO_xN_{1-x} layers by a filamentless ion source assisted physical vapor deposition technique show a high thermal stability up to 400 °C and a very high breakdown voltage (BDV) above 400 V/µm. BO_xN_{1-x} samples of thickness varying from 70nm – 200nm were grown in a high vacuum reactor. Prototype capacitors with boron oxynitride dielectric and titanium metal electrodes have been fabricated on 3" Si wafers followed by electrical and thermal characterization. Preliminary results indicate a very small variation (~3%) of capacitance over the frequency range of 10 KHz – 2 MHz and <10% variation in capacitance for the temperature range of 25 °C-400 °C. The device electrical characteristics studies (capacitance, leakage current, breakdown voltage), as a function of temperature and frequency for (BO_xN_{1-x}) dielectrics with varying oxygen to nitrogen ratio, are currently underway and their results will be presented at the conference.

This research was supported in part by USDOE grant # DE-FG02-05ER84325 to Integrated Micro Sensors, Inc.

9:00am **EN+AS+EM+TF-WeM4 Improving Efficiencies of Electrochemical Systems Through Microstructure Optimization**, *H.Y. Chen,* University of Michigan, *J.R. Wilson, P.W. Voorhees,* Northwestern University, *S.B. Adler,* University of Washington, *S.A. Barnett,* Northwestern University, ***K. Thornton***, University of Michigan

The properties and performance of a wide range of materials depend on their microstructures. This is especially true in multifunctional, multiphase or composite materials in which different phases perform different functions. Therefore, controlling microstructures in these materials is one of the main routes for materials design to achieve optimal performance. Various simulation methods that can be applied to examine processing, property, and degradation during operation, including the phase-field simulations and finite element modeling, will be discussed. Through coupling of simulations of microstructural evolution and transport that use realistic microstructures, microstructural design for optimized performance is investigated. Specific examples will include microstructures found in solid oxide fuel cell electrodes and those resulting from phase separation.

9:20am **EN+AS+EM+TF-WeM5 Layer-By-Layer Approaches to Electrochemical Energy and Storage**, ***P.T. Hammond***, MIT **INVITED**

New advances in multilayer assembly have involved the development of ionically conductive multilayer thin films and the introduction of electrochemical functionality. These systems have allowed the formation of a range of ultrathin electrochemical devices including electrochromic displays, proton exchange membranes in fuel cells, and the use of these multilayers in other power and micropower devices. The use of this water based electrostatic assembly method has enabled the use of simple processing conditions, such as salt content and solution pH, to act as tools for the manipulation of ion and electron transport characteristics in the film, as well as the morphology of these unique nano-assemblies. Examples of this approach include the ability to integrate highly water soluble polymers with large sulfonic acid content into mechanically stable ultrathin films has led to new membranes with ionic conductivity approaching that of Nafion, and methanol permeability two orders lower, thus lowering fuel crossover and leading to large enhancements in methanol fuel cell performance with the application of nanometer thick thin films. On the other hand, the incorporation of both organic and inorganic nanoscale objects using the electrostatic assembly approach has enabled the incorporation of genetically engineering virus biotemplates in collaborations with the Belcher research group that have resulted in new developments in battery electrodes, and the integration of titania and other materials systems for reactive electrodes. Ultimately, the use of layer-by-layer systems have led to a range of organic and inorganic materials systems that have incorporated metal oxide nanoparticles, semiconducting carbon elements, and organic polymers to yield systems of interest for solar cells, capacitor/battery and electrochemical energy electrode and separator applications.

10:40am **EN+AS+EM+TF-WeM9 Material Solutions for Solid State Energy Storage**, ***L.F. Nazar***, University of Waterloo, Canada **INVITED**

The increasing demand for energy world-wide and inherent pressing environmental needs, have jump-started efforts to develop energy storage systems that can be coupled to renewable sources, and/or viable energy conversion systems. Traditional electrode materials for lithium-ion storage cells are typically crystalline, single-phase layered structures such as metal oxides, and graphitic carbons. These materials power billions of portable electronic devices in today’s society. However, large-scale, high-capacity storage devices capable of powering hybrid electric vehicles (HEV’s) or their plug-in versions (PHEV’s and EV’s) have much more demanding requirements. This in turn, means that demands are on chemists to create novel materials, and address fundamental scientific issues relating to mass (ion) and electron transport at rapid rates. Recently, nanostructured solid state materials comprised of two more compositions, are being increasingly exploited. These can take the form of “surface modified nanocrystallites”, or stuffed nanoporous materials. For example, we employ porous frameworks as electrically conductive scaffolds to encapsulate active electrode materials, where both components play a role in controlling the electrochemical performance. This presentation will provide an overview of how the nanostructured approach provides benefit over the bulk, using selected examples from a range of promising new solid state materials with targeted, and tuneable structures.

11:20am **EN+AS+EM+TF-WeM11 Platinum Nanorods as PEM Fuel Cell Electrodes**, ***M. Gasda***, *R. Teki, T.-M. Lu, N. Koratkar, G. Eisman, D. Gall*, Rensselaer Polytechnic Institute

Platinum catalyst layers were deposited by magnetron sputtering from a variable deposition angle α onto gas diffusion layer (GDL) substrates and were tested as cathode electrodes in polymer electrolyte membrane (PEM) fuel cells. Layers deposited at normal incidence (α = 0°) are continuous, and approximately replicate the rough surface morphology of the underlying GDL. In contrast, glancing angle deposition (GLAD) with α = 85° and continuously rotating substrates yields highly porous layers consisting of vertical Pt nanorods. At 0.40 mg/cm^2 total Pt loading, the rods are 100-500 nm long and ~300 nm wide, separated by 20-100 nm wide voids. The dramatic difference in microstructure is due to atomic shadowing during GLAD that causes Pt flux from highly oblique angles to preferentially deposit on surface protrusions, leading to nucleation and columnar growth on substrate mounds while surface depressions remain uncoated. Fuel cell testing at 70°C using Nafion 1135 membranes, Teflon-bonded Pt-black electrodes (TBPBE) at the anode, and atmospheric pressure hydrogen and air reactants shows a monotonic increase in performance of GLAD cathodes from 0.05 to 0.40 mg/cm^2 total Pt loading. Nanorod cells exhibit approximately 2x higher mass activity than continuous layers at 0.50V (corrected for iR, shorting, and gas crossover); for example, GLAD and continuous layers with approximately the same Pt loading (0.18 and 0.25 mg/cm^2, respectively) show 1.7 and 0.8 A/mg. In contrast, at low current density of 0.10 A/cm^2, the continuous layers (0.70 V with 0.25 mg/cm^2 Pt) outperform GLAD cells even with relatively high Pt loadings (0.65 V with 0.40 mg/cm^2 Pt). The GLAD cells' higher mass-specific performance at high current densities is due to their high porosity which facilitates reactant transport, while the low-current performance of the continuous layer is attributed to a higher active Pt surface area. The sputter-deposited electrodes exhibit a higher platinum utilization in comparison to TBPBE reference cathodes, with GLAD cells (1.7 A/mg) performing better than TBPBE (0.75 A/mg) at high current densities (0.50 V), while continuous layers (0.07 A/mg) outperform TBPBE (0.035 A/mg) at 0.80 V. These results indicate the promise of nanoengineering to boost catalyst utilization in PEM fuel cells.

Energy Science and Technology Focus Topic
Room: 203 - Session EN+AS+TF+VT+NC-WeA

Energy: Tools and Approaches
Moderator: T.A. Dobbins, Louisiana Tech University and Grambling State University

1:40pm **EN+AS+TF+VT+NC-WeA1 Continuous, In-Line Processing of CdS/CdTe Devices**, ***W.S. Sampath***, Colorado State University, *R.A. Enzenroth, K.L. Barth,* AVA Solar Inc., *V. Manivannan,* Colorado State University, *K. Barricklow, P. Noronha*, AVA Solar Inc. **INVITED**

A continuous, in-line process suitable for high throughput manufacturing of CdS/CdTe photovoltaic devices has been demonstrated. Utilizing this process, devices with efficiencies of 13% has been fabricated with a low iron soda lime glass (3"x3") with ant-reflection coatings. The process has been extended to large area devices (16" x16" substrate size). After $CdCl_2$ treatment, devices showed $V_{oc} > 700$ mV and $J_{sc} > 20$ mA/cm^2. This performance is similar to the performance of small area devices which showed good stability. Also we have employed many methods including Spectroscopic Ellipsometry (SE) as a non-destructive tool to characterize CdS/CdTe heterojunction specifically studying the effects of processing on the optical properties of the thin-film layers.

2:20pm **EN+AS+TF+VT+NC-WeA3 Molecular Dynamics and Experimental Investigations of Reversible Absorption of H_2, CH_4, and CO_2 in Calixarenes**, ***J.L. Daschbach***, *P.K. Thallapally, B.P. McGrail, L.X. Dang*, Pacific Northwest National Laboratory

Molecular solids based on calix[4]arenes have been shown to exhibit reversible absorption of small gas molecules, and remain stable, at temperatures above 400 K. As such, they are interesting as prototypical molecular systems for storing guests like hydrogen and methane, and potentially selectively trapping carbon dioxide in hydrocarbon based systems. We have conducted high-pressure and temperature gas absorption experiments with low density p-tert-butylcalix[4]arene (TBC4) in which calixarenes are slightly offset to form a skewed capsule with an estimated free volume of 235 Å^3. Hydrogen and methane absorption near 300 K were 1.0 and 2.2 wt% respectively. Carbon dioxide is absorbed at a 1:1 loading per TBC4 molecule at 3 atm. In recent work we have shown that the high density form of TBC4 will absorb CO_2 at 3 atm, undergoing a phase transformation in the process, and it can be reversibly cycled between these states using moderate combinations of temperature and pressure. Somewhat surprisingly, we have found that TBC4 can be loaded with up to two CO_2 per TBC4 molecule. We have used empirical molecular simulation techniques to study the dynamics of CO_2 and CH_4 in TBC4. The rattling motion of the absorbed small molecules have been characterized using velocity autocorrelation. The coupling to the host lattice is probed by temperature dependent calculations. The effects of increased loading are studied up to the 2:1 loading of CO_2, and clearly show differences in the host-guest coupling for molecules outside the cavities relative to the cage entrapped molecules. The free energy of absorption of CH_4 and CO_2 is studied under range of conditions by thermodynamic integration. These data support the experimental observations that these molecules can be reversibly absorbed at moderate pressures and temperatures.

2:40pm **EN+AS+TF+VT+NC-WeA4 Sustainable Energy and the Role of Advanced Electron Microscopy**, ***D.J. Stokes***, *B. Freitag, D.H.W. Hubert*, FEI Company, The Netherlands

Advanced electron microscopy, using the latest aberration-corrected and monochromated (scanning) transmission electron microscopes (S/TEM) is helping to bring new scientific and technological insights that are advancing progress in areas such as health, energy and the environment. Specifically, with global energy resources under increasing pressure, great efforts are being made to develop new nanomaterials that will lead to renewable energy sources and increased efficiency, to sustain energy supplies into the long term future whilst helping to preserve and protect the Earth's environment. To get there, we are being taken to atomic realms such that, to tailor new nanomaterials for specific functions, it is essential to precisely understand, accurately control and truly visualize structure-property relations at an unprecedented level. The atomic structure of nanomaterials and the energy needed for their function can be optimized by the fundamental understanding of catalytic behavior of nanoparticles and by a better understanding of the physical properties on the atomic level of systems such as solar cells, fuel cells and light sources (LEDs). This requires advanced tools that allow us to see down to the individual atoms and sense their chemical environment. It means having the ability to perform experiments in situ, to follow specific chemical reactions and physical processes, and there is a need to be able to do this in multi-dimensions, both spatial and temporal. We discuss and demonstrate the role of advanced electron microscopy in answering some of the most challenging and fundamental scientific questions in the field of catalysis, ranging from electron tomographic 3D reconstruction of the crystal facets of catalyst nanoparticles and aberration-corrected imaging correlated with density functional theory for elucidating precise atomic positions, to in situ studies of catalytic reactions for visualization of otherwise unseen intermediate nanostructures. These examples relate the nanostructures investigated to the property manifested by that particular structure, enabling us to gain new information about catalytic function.

3:00pm **EN+AS+TF+VT+NC-WeA5 Investigation of Low Temperature-Annealed TiO_2 Electrodes Prepared by Sol-Gel Technique for the Fabrication of Dye-Sensitized Solar Cells**, *M.F. Hossain, S. Biswas, M. Shahjahan, A. Majumder,* ***T. Takahashi***, University of Toyama, Japan

Dye sensitized solar cells (DSCs) are considered as a low cost alternative to conventional p-n junction solar cell devices. The high light-to-energy conversion efficiencies achieved with dye sensitized solar cells (DSCs) may be attributed to the nanoporous TiO_2 electrode. Among the various techniques for the preparation of TiO_2 photo-electrode, the relatively simple sol gel method is the most widely used because of its ability to obtain films with tailored properties on large, curved substrates, and also it is a low temperature process. Crystallinity is one of the key factors behind the photovoltaic performances of TiO_2; therefore achievement of better crystallinity at relatively low temperature is an important issue. In our present study, the titanium dioxide porous films were deposited on SnO_2:F coated glass by sol–gel technique; where, an alcoholic solution of tetra-buthylorthotitane was hydrolysed in a water/alcohol/acetic acid mixture. These films were transparent and crack free. For this investigation; annealing temperature and number of coating layers were varied. All the films were annealed at different annealing temperatures, ranging from 350 to 500°C. Sufficiently good crystalline samples were obtained by annealing at 350°C. The X-ray diffraction patterns of all TiO_2 films confirmed the anatase structure. The surface morphology of the films has been observed by atomic force microscope and field emission scanning electron microscope. The morphology of TiO_2 thin films strongly depends on annealing temperatures and number of coatings. Incident photon-to-current conversion efficiency is calculated for all the solar cells with different TiO_2 thin films to evaluate the economic viability of this technique. It has been observed that the photoelectric conversion efficiency of DSCs increases with the optimization of annealing temperature as well as with the increase of the numbers of layers.

Thursday Morning, October 23, 2008

Energy Science and Technology Focus Topic
Room: 203 - Session EN+EM+NS+P+A+T+V-ThM

Energy: Tools and Approaches
Moderator: S.P. Williams, Plextronics, Inc.

8:00am **EN+EM+NS+P+A+T+V-ThM1 Nano-Structured and Micro-Structured Semiconductors for Better Efficiency of Solar Cells**, ***C.-F. Lin***, *J.-S. Huang, S.-C. Shiu, J.-J. Chao, C.-Y. Hsiao, K.-H. Tsai*, National Taiwan University **INVITED**

The foreseeable depletion of fossil fuel and the global warming caused by the carbon dioxide had led to the increasing attention of alternative renewable energy, especially photovoltaic. Therefore, crystalline Si-PV devices are quickly spreading. Unfortunately, the large consumption of Si materials hinders their vast applications. Many efforts have been switched to developing thin-film PV devices. In this talk, we will discuss the use of nano-structured and micro-structured semiconductors that enable the fabrication of thin-film solar cells with improved efficiency. Several types of such thin-film solar cells will be discussed, including the organic-semiconductor-nanowire composite film, organic-semiconductor micro-structure composite film, nano-wire semiconductor thin film, and micro-structured semiconductor thin film. In the thin-film solar cells using organic-semiconductor-nanorod composite film, different types of semiconductor nanowires such as ZnO, Si, and GaAs nanowires are used to replace the accepter-type organics for two purposes: increasing the electron mobility and assisting the formation of nano-morphology for better inter link between the donor organics and acceptor materials. The fabrication procedures of those nanowires as well as the formation of the organic-semiconductor-nanowire composite film with controlled nano-morphology will be presented. For the other solar cells using nano-structured and micro-structured semiconductors, we will particularly describe the technique of nanowire/micro-structure transfer. In our approach, the nanowires and micro-structures are made from the bulk semiconductors or epitaxial semiconductors, so they will have much better crystal quality than the usual thin-film materials. In addition, after nanowires and micro-structures are transferred to other transparent substrates, the original wafer can be reused, so the material cost can be lowered considerably. In addition, it offers the advantages of the bending flexibility, not being limited by the brittle property of semiconductors. Furthermore, in comparison with current III-V tandem solar cells taken by monolithic approach, which requires lattice match and current balance, our approach enables mechanically stacking. Thus each cell could be designed individually to match the entire solar spectrum for optimal solar usage. Therefore, such new-type thin-film solar cells are expected to be potentially efficient and low cost.

8:40am **EN+EM+NS+P+A+T+V-ThM3 Endohedral Metallofullerenes as Improved Acceptor Materials for Organic Solar Cells**, *M. Drees,* Luna Innovations Incorporated*, R. Ross,* Georgetown University*, C. Cardona,* Luna Innovations Incorporated*, E. Van Keuren,* Georgetown University*, D. Guldi,* Friedrich-Alexander-Universitat Erlangen-Nurnberg, Germany*,* ***B.C. Holloway***, Luna Innovations Incorporated

Cost factors in inorganic solar cells have opened up a new path to less expensive manufacturing techniques using bulk heterojunction polymer/fullerene based solar cells. Using empty cage fullerene derivatives as the acceptor material, state-of-the-art organic photovoltaics currently display ~5% overall conversion efficiency. One of the main factors limiting the efficiency in organic solar cells is the low open circuit voltage. The open circuit voltage is governed by the molecular orbitals of the donor and acceptor material; therefore better matching of the orbitals will lead to improved voltages. Here we present a novel acceptor material based on Trimetasphere® carbon nanomaterials (TMS). Trimetaspheres® are endohedral metallofullerenes that consist of a trimetal nitride cluster enclosed in a C80 cage. First-generation Trimetasphere® carbon nanomaterial derivatives have been synthesized and show behavior consistent with C60 but with improved molecular orbitals. Electrochemical data suggests a maximum voltage increase of up to 280 mV over C60-PCBM-based devices and photophysical characterization of shows efficient and stable charge separation. Initial bulk-heterojunction devices have been synthesized with open circuit voltages that are 280 mV higher than reference devices using C60-PCBM and conversion efficiencies exceeding 3.1%.

9:00am **EN+EM+NS+P+A+T+V-ThM4 Morphology Study of Vacuum-Deposited Pentacene:C60 Mixed Thin Films for Photovoltaic Applications**, ***J. Xue***, *Y. Zheng, J.D. Myers, J. Ouyang*, University of Florida

The efficiency of organic photovoltaic (PV) devices has gained steady increase in past 20 years, showing a potential to provide clean and low-cost electrical energy in the near future. Bulk heterojunction (HJ) composed of nanoscale percolation of donor and acceptor phase have been demonstrated to improve the efficiency of organic PV device. Such improvement is attributed to the creation of a spatially distributed interface, which enhances exciton dissociation, and the presence of continuous conducting paths for efficient charge collection. However, ideal nanoscale percolation is not readily achievable. Therefore, understanding the morphology inside the bulk heterojuncion plays an important role on achieving efficient PV device. Here, phase separation in donor-acceptor (D-A) mixture composed of pentacene:C60 and how it contributes to a percolated morphology are studied. The pentacene:C60 mixed films are fabricated by co-deposition of two molecules with vacuum thermal evaporation (VTE) method. The mixing ratio of pentacene and C60 is controlled by varying the deposition rate of each species. X-ray diffraction (XRD), scanning electron microscopy (SEM) and atomic force microscopy (AFM) are used to characterize the vacuum deposited pentacene:C60 mixed film. XRD patterns of pentacene:C60 mixed films indicate phase separation inside the mixture, which is reflected by appearance of characteristic diffraction peaks of thin film phase pentacene. SEM and AFM images reveal the change of surface morphology of the mixed films with varied mixing ratio and deposition rate, suggesting different degree of phase separation inside. Base on these information, PV devices are fabricated and their performance is investigated. It is found that by suppressing the phase separation between pentacene and C60 to nanoscale the PV performance is improved significantly. The open circuit voltage (Voc) and short circuit current (Jsc) increase from 0.45 V and 9.7 µA/cm2 in pentacene:C60 = 1:1 (by weight) device to 0.58 V and 1.3 mA/cm2 in pentacene:C60 = 1:5.5. All these suggest that degree of phase separation of molecular mixtures can be controlled by varying the process conditions, which may lead to new pathways to generate nanoscale percolation for application in efficient organic PV devices.

9:20am **EN+EM+NS+P+A+T+V-ThM5 Tailoring the Morphology of Organic Solar Cells with Surface Templates**, ***S. O'Donnell***, University of Virginia and The MITRE Corporation*, P. Reinke*, University of Virginia

One of the most important applications of fullerenes is their incorporation in organic solar cells, where they function as an electron acceptor in conjunction with photoactive molecules such as porphyrin. The photoyield is intimately linked to the morphology, which determines the efficiency of exciton diffusion and separation, and the effectiveness of charge transport to the electrodes. Control of the morphology across lengthscales, spanning the range from the molecule to the several hundred nm, is critical to optimization of solar cell functionality. We control the morphology by using tailored substrate templates on which we assemble ultrathin films with well-defined regions of acceptor and photoabsorber molecules. This approach enables us to measure the morphology and interface structure with atomic resolution with scanning probe methods, and to subsequently investigate the photocurrent distribution. A pattern with variable geometry is written on the surface of highly oriented pyrolitic graphite (HOPG), our model surface, with a focussed ion beam (Ga+, 30 keV ion energy), which creates regions with a high density of surface defects interspaced with largely undamaged graphite surface. The surface defect structure, its extension and density within the pattern is characterized prior to molecule deposition. Surface defects interact strongly with the fullerene molecules, and thus provide nucleation centers for the formation of fullerene islands whose position is in registry with the artificial pattern. The boundary of the ion damaged region serves as the primary nucleation center for the formation of C60 islands, whose shape is controlled by the pattern geometry and the diffusion length of the molecules. We will describe how the artificial pattern can be used to tailor the morphology across lengthscales and discuss the extension of this method to other, technically relevant surfaces such as quartz which possesses a natural patterning in the form of ledges. The complete 2D nanostructure can be built by deposition of fullerene on the templated HOPG, and the remaining "empty" graphite surface is then filled with photoabsorber molecules. We will show the movement of porphyrin molecules into the pattern, and how the interfacial region between fullerenes and porphyrins evolves, and discuss the resultant morphologies. This hierarchical assembly of organic solar cells will enable us to tailor morphologies and link them uniquely to the photophysical processes.

9:40am **EN+EM+NS+P+A+T+V-ThM6 Photoemission Studies of Lead Sulfide Nanocrystals in Organic Films**, ***A.T. Wroble****, D.J. Asunskis, A.M. Zachary, I.L. Bolotin,* University of Illinois at Chicago*, D.J. Wallace, M. Severson,* University of Wisonsin-Madison*, L. Hanley*, University of Illinois at Chicago

Lead sulfide (PbS) nanocrystals have shown potential for use in optoelectronic applications including photovoltaics. PbS nanocrystals are grown directly into polymers or organic oligomer matrices to control the size and surface chemistry of the resulting nanocrystals. Transmission electron microscopy is used to determine the size distribution of PbS nanocrystals in organic films grown by either colloidal synthesis in polymer solutions or gaseous deposition using a cluster beam deposition source. Both the colloidal and cluster beam deposition methods are described in detail. Various techniques in photoemission spectroscopy are then applied to these PbS nanocrystal-organic films. X-ray photoelectron spectroscopy (XPS) confirms that PbS nanocrystals are present. Soft-XPS using 200 eV photon energies available at a synchrotron radiation source provides surface sensitivity to observe the interaction of the PbS nanocrystal surface with the organic matrix and is compared to XPS results obtained using 1487 eV photon energy. Little or no bonding between the PbS nanocrystals and the organic phase is observed. The core of the nanocrystals are found to be 1:1 Pb:S, but their surfaces are enriched in Pb. Finally, core level binding energy shifts in XPS under simulated solar irradiation are used for contact-free evaluation of element-specific photovoltaic electrical response of these PbS nanocrystal-organic thin films.

10:40am **EN+EM+NS+P+A+T+V-ThM9 Rational Design of Nanostructured Hybrid Materials for Photovoltaics**, ***S.B. Darling****, I. Botiz,* Argonne National Laboratory*, S. Tepavcevic, S.J. Sibener,* The University of Chicago*, T. Rajh, N. Dimitrijevic*, Argonne National Laboratory

Efficient conversion of photons to electricity in organic and hybrid materials depends on optimization of factors including light absorption, exciton separation, and charge carrier migration. Bulk heterojunction devices target these processes, but disorder on the nanoscale results in inefficiencies due to exciton recombination and poor mobility. By rationally designing the morphology at appropriate length scales, one can enhance the effectiveness of internal processes and, therefore, the performance of photovoltaic devices. In this work, we have implemented this approach in two hybrid material systems—both of which may provide pathways to low-cost, large-area fabrication.[1] The first involves a rod-coil block copolymer which is used both as an optoelectronically active material and as a structure-directing agent to pattern active material into ordered nanostructures. The second system uses electrochemically prepared titania nanotube arrays in concert with in situ polymerization of electron-donating material. In both cases, the characteristic donor-acceptor length scale is controlled to be comparable to the exciton diffusion length throughout the active layer, and the domains are oriented perpendicular to the incident light direction to encourage efficient charge migration.

[1] Use of the Center for Nanoscale Materials was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract #DE-AC02-06CH11357. Parts of this work were also supported by the NSF-MRSEC at the University of Chicago.

11:00am **EN+EM+NS+P+A+T+V-ThM10 Electronic Energy Level Alignment in Dye Sensitized Oxide Surfaces**, ***S. Rangan****, J.P. Theisen, E. Bersch, R.A. Bartynski*, Rutgers University

We have used direct and inverse photoemission to measure the occupied and unoccupied electronic states of N3 dye and determine their alignment with the band edges of single crystal and nanostructured TiO_2 and ZnO substrates. In dye-sensitized solar cell applications, the HOMO-LUMO gap of the dye molecule determines the useful portion of the solar spectrum, and charge transfer of photoexcited electrons to the substrate depends on the alignment of the LUMO to the substrate conduction band edge. We have compared the N3 dye properties on well characterized rutile TiO_2(110) and wurtzite ZnO single crystal surfaces to adsorption on more technologically relevant TiO_2 anatase nanoparticle and ZnO nanorod substrates. Samples were prepared and passivated with a pivalate layer in UHV, then sensitized ex-situ in a solution of N3 dye in acetonitrile. STM measurements show that the pivalic acid forms an ordered overlayer on the TiO_2(110) surface and that the N3 dye molecules can be imaged after sensitization. For N3 on TiO_2(110) as shown below, our spectroscopic measurements show that passivation significantly reduces contamination (presumably from water in the ambient) and that the N3 HOMO occurs at 0.9 eV above the TiO_2 valence band edge, while the LUMO is found 0.5 eV above the conduction band edge. On ZnO , the N3 HOMO occurs at 1.3 eV above the ZnO valence band edge but the N3 LUMO occurs 2.1 eV above the conduction band edge, much higher than what is measured on TiO_2. Comparison with experimental and theoretical values from the literature will be discussed.

11:20am **EN+EM+NS+P+A+T+V-ThM11 Preparation of Nanoporous ZnO Photoelectrode using PEG Template for the Fabrication of Dye-Sensitized Solar Cells**, ***M.F. Hossain****, S. Biswas, M. Shahjahan, T. Takahashi*, University of Toyama, Japan

Recently, great attention has been paid to dye-sensitized solar cells (DSCs) due to their low fabrication cost. The high light-to-energy conversion efficiencies achieved with dye sensitized solar cells (DSCs) may be attributed to the nanoporous TiO_2 electrode. Zinc oxide (ZnO) is a wide band gap semiconducting material with a similar band gap and electron affinity to those of TiO_2 and has been considered as an alternative material in DSCs applications. Among the various techniques for the preparation of ZnO photo-electrode, the relatively simple sol gel method is the most widely used because of its ability to obtain films with tailored properties on large, curved substrates. In our present study, the nanoporous ZnO films were deposited on SnO_2:F coated glass by sol–gel technique with polyethylene glycol (PEG) as organic template, $Zn(CH_3COO)_2.2H_2O$ as precursor, ethanol as solvent and $NH(C_2H_2OH)2$ as chelating agent. The ZnO films have been characterized by the TG-DTA, XRD, SEM AFM, FTIR and UV-VIS systems. The surface morphology of the nanoporous ZnO films strongly depend on the $Zn(CH_3COO)_2$ concentrations, PEG contents and number of coatings. It was revealed from optical study that the dye absorption increases with the increase of PEG concentrations. Incident photon-to-current conversion efficiency is calculated for all the solar cells with different ZnO thin films to evaluate the economic viability of this technique. The variation of photoelectric conversion efficiency of the solar cells, deposited with different $Zn(CH_3COO)_2$ and PEG concentrations are discussed with the analysis of different microstructure of the ZnO thin films and the corresponding dye-incorporations.

11:40am **EN+EM+NS+P+A+T+V-ThM12 Metal / Polymer Interfaces: Ca on Polyfluorenes**, ***J.A. Farmer****, J.H. Baricuatro,* University of Washington*, E. Zillner,* Universitaet Erlangen-Nuernberg, Germany*, J.F. Zhu,* University of Science and Technology of China*, C.T. Campbell*, University of Washington

Conjugated polymers are being investigated for use in organic photovoltaic devices and organic electronics due to favorable cost and ease of processing compared to devices based on inorganic materials. The synthetic tunability of polymer-based devices makes them applicable to many technological applications. The creation of cheap organic photovoltaic devices would significantly improve our ability to harness solar energy and curb the use of fossil fuels. The development of organic LED and organic electronics may give rise to flexible computer displays and hardware that could revolutionize human interaction with computing devices. Crucial to the performance optimization of these devices is understanding the interaction between the metal electrodes and the polymer. The structure and energetics of the interface between Ca and two polyfluorenes, poly(9,9-di-n-hexylfluorenyl-2,7-diyl) (PDHF) and poly(9,9-di-n-hexylfluorenyl-2,7-vinylene) (PDHFV), were studied in ultrahigh vacuum using adsorption microcalorimetry, and low-energy ion scattering spectroscopy. The initial sticking probabilities of Ca on pristine PDHF and PDHFV at 300 K were 0.40 and 0.53, respectively. The sticking probability of Ca on PDHFV began decreasing after ~0.06 ML, and then increased toward unity after ~0.24 ML. Because no similar behavior was seen on PDHF, this decrease in the Ca sticking probability on PDHFV is tentatively ascribed to the presence of the vinyl group. At submonolayer coverages on both polymers, the integrated Ca ISS peak area increased slowly below 1 ML, with a value less than 1 % of a saturated Ca surface at 300 K. These results indicated that most of the Ca at low coverages were below the surface, and not visible to ISS. Beyond 1 ML the Ca peak area increased, and ultimately a continuous Ca film formed at ~50 ML. Based on the variation of Ca peak area with coverage, Ca grows as 3D islands on these polymer surfaces. The heat of adsorption of Ca on PDHF at 300 K was initially 240 kJ/mol and 315 kJ/mol on PDHFV. The heat of adsorption of Ca on PDHF decreased to the heat of sublimation of Ca in ~0.25 ML; the heat of sublimation was reached by ~0.50 ML for PDHFV. The interesting thermodynamic and sticking behavior below 0.50 ML, where Ca is interacting strongly with specific adsorption sites on the polymer will be discussed, and related to the use of these polyfluorenes in device applications.

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