

Energy Frontiers Topical Conference  
Room: Mesilla - Session EN+PS-MoM

## Plasmas for Photovoltaics & Energy Applications

Moderator: B. Lane, TEL Technology Center America

8:20am EN+PS-MoM1 **Combinatorial Plasma CVD of Si Thin Films with a Multihollow Discharge Plasma CVD Reactor**, *M. Shiratani, K. Koga, T. Matsunaga, Y. Kawashima, W. Nakamura, G. Uchida, N. Itagaki*, Kyushu University, Japan

A-Si and micro-crystalline thin films for solar cells are widely deposited by plasma CVD in industry. To realize combinatorial plasma CVD of such Si thin films, we have developed a multi-hollow discharge plasma CVD method, by which fluxes of H and SiH<sub>3</sub> as well as their flux ratio on the substrate placed perpendicular to the electrodes depend on the distance from the discharges [1-4]. Thus, we can simultaneously deposit Si thin films with various structures and properties. For 60 MHz discharges of H<sub>2</sub>+SiH<sub>4</sub> (0.3%), no films were deposited just near the discharge regions due to Si etching by H, micro-crystalline films were deposited in a rather narrow area around the no film regions, and a-Si:H films were obtained in the rest wide area far from the discharges. The spatial distribution of film structures indicate that the density ratio of H to SiH<sub>3</sub> decreases sharply with increasing the distance from the discharges and the surface reaction probability of H is much higher than that of SiH<sub>3</sub>, being consistent with the reported surface reaction probabilities [5, 6]. For 2-6 Torr, the micro-crystalline film structure such as crystalline volume fraction and grain size varies sharply not only along the direction perpendicular to the electrodes but also along the direction parallel to the electrodes. These results suggest that the micro-crystalline film structure is highly sensitive to spatial and temporal uniformity of fluxes of H and SiH<sub>3</sub> as well as their flux ratio.

- [1] K. Koga, et al., *Jpn. J. Appl. Phys.* **44**, L1430 (2005).
- [2] W. M. Nakamura, et al., *IEEE Trans. Plasma Sci.* **36**, 888 (2008).
- [3] W. M. Nakamura, et al., *J. Phys.: Conf. Series* **100**, 082018 (2008).
- [4] H. Sato, et al., *J. Plasma Fusion Res. SERIES*, **8**, 1435 (2009).
- [5] A. Matsuda, et al., *Surface Sci.* **227**, 50 (1990).
- [6] J. Perrin, et al., *J. Vac. Sci. Technol. A*, **16**, 278 (1998).

8:40am EN+PS-MoM2 **Infrared Solar Cells Using Plasma-Processed Carbon Nanotubes**, *T. Kaneko, S. Kodama, Y. Li, R. Hatakeyama*, Tohoku University, Japan

Since the conventional silicon solar-cell conversion is limited to a certain window of solar cell photon energies over 1 eV, a full use of the solar spectrum is one of the crucial issues in order to greatly increase the solar cell efficiency. In this sense, carbon nanotubes (CNTs) are attracting much interest for photovoltaic energy conversion because of their broad absorption bands including the infrared range (0.2 ~ 1.3 eV) as well as other advantages such as large surface areas, high mobility of charge carrier, high mechanical strength, chemical stability, and so on. In this connection, we have developed a plasma-ion irradiation method, which enables pristine single-walled carbon nanotubes (SWNTs) to selectively encapsulate various kinds of atoms and molecules, such as metals and fullerenes, serving as electrons donors or acceptors inside their cavities. Then these enhanced p-type, n-type, and pn-junction housed semiconductor-SWNTs are applied toward the realization of high-efficient photovoltaic devices, which is composed of thin films of p- and n-types semiconductor SWNTs or an individual SWNT with p-n junction inside. Here, as a first step, electrical properties of p-n junctions fabricated using a combination of the thin films of pristine (empty) SWNT or C<sub>60</sub>-encapsulated SWNT (C<sub>60</sub>@SWNT), and n-doped Si (n-Si) are investigated.

The electrical properties of these SWNT film/n-Si devices show an obvious rectifying characteristic, and a short-circuit current  $I_{sc}$  and an open-circuit voltage  $V_{oc}$  through a downward shift of  $I$ - $V$  curves are observed under illumination of light with wavelength of 1550 nm which corresponds to the photon energy of 0.8 eV. Moreover, it is found that the device fabricated with the C<sub>60</sub>@SWNT film has a larger  $V_{oc}$  caused possibly by a large diffusion voltage in the interface of p-n junction compared with the device fabricated with the pristine SWNT film, due to the enhanced p-type behavior of SWNTs after C<sub>60</sub> encapsulation. To investigate undesirable photovoltaic effects of n-Si, we fabricate a schottky barrier solar cell consisting of silver (Ag) and n-Si in the absence of SWNTs. It is confirmed that the Ag/n-Si schottky barrier solar cell generates photo currents in the visible range (1.5 ~ 3 eV), while there is almost no difference between with

and without light in the infrared range (0.8 eV) because the light with photon energy less than 1 eV cannot be absorbed by Si.

Based on these results, high performance solar cells which work in the infrared region are for the first time demonstrated to be formed using SWNTs, especially p-type enhanced C<sub>60</sub>@SWNT.

9:00am EN+PS-MoM3 **A Novel Method of Controlling Plasma Uniformity in a Large Area VHF Plasma Source for Solar Applications**, *T. Tanaka, J. Kudela, E. Hammond, C. Boitnott, Z. Chen, J.A. Kenney, S. Rauf*, Applied Materials Inc. **INVITED**

Processing a large area substrate in a capacitively coupled plasma (CCP) reactor is becoming increasingly more difficult as the driving frequency required by the process is becoming higher and the size of the substrates is becoming larger. At the VHF (very high frequency) range the wave length of the driving signal is approaching the size of the substrate, and the resulting standing wave causes a severely non-uniform process. In this presentation, we will present a novel approach using magnetic boundary conditions in conjunction with phase modulation between multiple power feed points to improve process uniformity for a CCP reactor operating in the VHF range. The substrate size we consider is Gen 8.5 (2.2 m × 2.6 m substrate) and the VHF power applied to generate the plasma is 40 and 60 MHz. At 60 MHz, with the vacuum wavelength of 5 m, the size of the substrate is approximately 1/2 of the vacuum wavelength. An electromagnetic simulation with a pseudo vacuum showed that, when 60 MHz is applied in a conventional manner, i.e. it is fed from the center of the back of one of the electrodes, it generates a dome shape electromagnetic field profile, which falls off sharply to almost zero at the voltage node before rising again towards the edges. A similar field pattern was also generated even when the VHF was fed from two feed points located at the opposing edges. The plasma distribution pattern measured with a 4 × 8 grid of optical emission spectroscopic (OES) probes revealed that the plasma was localized in the center when VHF the signal applied to the feed points were in phase. To modify the wave propagation pattern to change the shape of the standing wave in the central area, we placed ferrite material along two of the edges (edges that are away from the feed points) of the powered electrode. In this case, the peak in the central area was significantly stretched towards the ferrite-lined edges. We also found that the stretched "bar" of plasma could be moved over the substrate area by dynamically modifying the relative phase between the feed points in a manner similar to the technique employed by Yamakoshi *et al.* [1], and effectively distribute the processing plasma to much larger area.

- [1] H. Yamakoshi *et al.* *Appl. Phys. Lett.* **88**, 081502 (2006)

9:40am EN+PS-MoM5 **Novel Plasma Processing Routes of Si Nanocrystals for Photovoltaic Applications**, *İ. Doğan, N.J. Kramer, M.A. Verheijen*, Eindhoven University of Technology, Netherlands, *T.H. van der Loop*, University of Amsterdam, Netherlands, *A.H.M. Smets*, Eindhoven University of Technology, Netherlands, *T. Gregorkiewicz*, University of Amsterdam, Netherlands, *M.C.M. van de Sanden*, Eindhoven University of Technology, Netherlands

Photovoltaic applications have been developed mostly on silicon technology in order to generate electricity from solar energy by efficient conversion of solar spectrum. In this work, we have focused on the novel processing routes of Si nanocrystals (Si-NCs) in a remote expanding thermal plasma (ETP). Si-NCs were formed inside a SiH<sub>4</sub>-Ar plasma by excessive heating of SiH<sub>x</sub> clusters via electron and ion collisions. Formation routes of nanoparticles were investigated under different conditions by changing SiH<sub>4</sub> and Ar flow rates, deposition pressures and arc currents. The morphologies of the deposits were powder-like, consisting of densely packed crystalline particles and inter-space of amorphous Si. Due to the variations in plasma regions from center to side walls, the powder color and properties were different on the different parts of the deposited samples. The formation of nanoparticles on these parts was investigated by a number of diagnostic techniques. As a first exploration, transmission electron microscopy (TEM) and Raman spectroscopy (RS) measurements have been carried out. It was confirmed by both TEM and RS that the particle size and morphology was varying throughout the film. For most of the samples, nanoparticles seemed to be mixed in size but the general tendency is to have smaller size distributions from central part to the outer part of the films. Formation of crystalline structures was confirmed by X-Ray diffraction (XRD) with Si(111) peaks. It was also shown by photoluminescence spectroscopy (PL) that the optical emission was in the visible range and shifts with respect to size difference of Si-NCs. Size distribution as a function of PL emission energy has been demonstrated for particles less than 8nm. TEM was employed to investigate the size distribution of the larger particles which was around 50nm. The responsible mechanism in the plasma leading to a systematic change on the particle size was discussed by

means of electron and ion density, and particle residence time. Getting a good control on the plasma conditions and particle size makes it possible for manipulating Si-NCs to higher packing densities in thin films which makes them suitable for photovoltaic devices such as down converters based on multi-exciton-generation (MEG).

**10:00am EN+PS-MoM6 Characterisation of Thin Film CdTe Multilayer Photovoltaic Devices Deposited by Closed Field Magnetron Sputtering**, J.K. Bowers, S. Moh, A. Abbas, P.N. Rowley, H.M. Upadhyaya, J.M. Walls, Loughborough University, UK

A new magnetron sputtering strategy is introduced that utilises high plasma densities ( $\sim 5\text{mA}\cdot\text{cm}^{-2}$ ) to avoid or reduce high temperature processing. The technique uses magnetrons of opposing magnetic polarity to create a "closed field" in which the plasma density is enhanced without the need for high applied voltages. A batch system has been used which employs a rotating vertical drum as the substrate carrier and a symmetrical array of four linear magnetrons. The magnetrons are fitted with target materials for each of the thin films required in the photovoltaic (PV) stack viz. CdTe absorber layer, CdS buffer layer, metal contact and the back transparent conducting oxide (TCO) contact using the superstrate configuration. The "closed field" sputtering technology allows scale up not only for larger batch system designs but it is also configurable for "in-line" or "roll to roll" formats for large scale production. The morphology of each of the layers is characterised together with the overall device performance.

**10:40am EN+PS-MoM8 Material Properties of Hydrogenated Nanocrystalline Silicon Thin Films by RF-PECVD using He-SiH<sub>4</sub> Mixture**, I.K. Kim, J.H. Lim, K.N. Kim, G.Y. Yeom, Sungkyunkwan University, Republic of Korea

Hydrogenated nanocrystalline silicon (nc-Si:H) and amorphous silicon thin film are expected to be promising

materials for solar cell and thin film transistor. Especially, nc-Si:H thin films have been reported to have

an enhanced stability due to its more rigid structure. These thin films are usually grown with

plasma enhanced chemical vapor deposition (PECVD) using silicon-containing gas mixtures such as SiH<sub>4</sub> and H<sub>2</sub>.

To increase the photovoltaic efficiency and to improve the mobility of TFT devices, it is necessary to produce

nanocrystalline silicon films with higher crystallization percentages. But it is reported that high H<sub>2</sub> dilution leads to

a significantly lower deposition rate.

In this study, we investigated the influence of He mixture with SiH<sub>4</sub> gas instead of H<sub>2</sub> to improve the crystallization

percentage of the deposited silicon without significantly decreasing the deposition rate.

To find out properties of the thin film deposited with He/SiH<sub>4</sub> such as structural properties, crystalline volume fraction (X<sub>c</sub>), active radicals in plasma, Si-H bonding characteristics, and conductivity, Scanning Electron Microscopy

(SEM), Raman spectroscopy, Optical Emission Spectroscopy (OES), Fourier-Transform-Infra-Red (FT-IR), and Keithley

measurement kit, were used respectively. The results showed the increase of crystallization percentage by using

He instead of H<sub>2</sub> as the additive gas and, with the increase of the applied RF power up to 140W, crystalline volume

fraction of about 80% could be observed.

**11:00am EN+PS-MoM9 Surface Composition and Gas-Phase Passivation of Plasma-Synthesized Si Nanoparticles**, B.N. Jarivala\*, Colorado School of Mines, N.J. Kramer, Eindhoven University of Technology, Netherlands, B.G. Lee, P. Stradins, National Renewable Energy Laboratory, M.C.M. van de Sanden, Eindhoven University of Technology, Netherlands, C.V. Ciobanu, S. Agarwal, Colorado School of Mines

Tunable band gap of c-Si nanoparticles (NPs) (<5 nm) along with the possibility of multiple exciton generation has led to an increased interest in this form of Si as a material for 3rd generation photovoltaic (PV) devices. In addition to a high degree of control over the particle size, surface passivation of the NPs is key to their utilization in PV applications. In this presentation, we will primarily focus on understanding the growth of Si NPs in a dusty plasma, determining the surface composition of the NPs, and demonstrating novel techniques for passivation and encapsulation through

the gas-phase. The particles are grown in a SiH<sub>4</sub>/Ar plasma generated in a tubular flow rf discharge. The plasma source is attached to an in-house-built vacuum chamber equipped with *in situ* attenuated total reflection Fourier-transform infrared (ATR-FTIR) spectroscopy and a quadrupole mass spectrometer. Using this technique, we have synthesized Si NPs in the size range of 3-7 nm, which transition from amorphous to crystalline over the rf power range of 5 to 40 W. The *in situ* IR data show that the surface hydride composition of the NPs is related to their crystallinity, which in turn depends on particle heating during synthesis. The as-synthesized NPs surfaces are terminated with Si mono-, di- and tri-hydrides. The higher hydride concentration decreases with increasing particle crystallinity, similar to previous observations on the amorphous Si surfaces, where higher Si hydrides are known to decompose with increasing deposition temperatures. These results also are consistent with the particle heating models proposed for dusty plasmas. In the first surface passivation approach, the as-synthesized H-terminated Si NPs, which oxidize even under high-vacuum conditions, are passivated *in situ* through hydrosilylation using 1-alkenes of different chain lengths. We have used density functional theory calculations to investigate the detailed reaction mechanism for various alkene chain lengths, and to understand the effects of alkene coverage on the oxidation of the surface. The surface reaction kinetics for hydrosilylation is observed *in situ* by monitoring the C-H and Si-H stretching vibrations. The ligand coverage is determined to be roughly 50% of the surface sites, which is sufficient to prevent oxidation for several hours. The quality of surface passivation is further determined through the photoluminescence quantum yield measurements, which show a higher yield for surface passivated NPs. In the second approach, the NPs are passivated with metal oxides using atomic layer deposition that involves the two different oxidation steps with O<sub>3</sub> and H<sub>2</sub>O to achieve deposition at <200 °C.

**11:20am EN+PS-MoM10 Effects of Hole-Array-Electrode on the Characteristics of Radio Frequency Capacitively Coupled Plasma Sources for nc-Si Thin Film PECVD**, H.-J. Lee, S.-S. Wi, Pusan National University, Republic of Korea, D. Kim, D. Hwang, W.S. Chang, LG Electronics, Republic of Korea

In order to improve the productivity of thin film growth in rf capacitively coupled plasma based chemical vapor deposition system, modifications of electrode surface geometry has frequently been used. Array of holes in the shower head electrode is probably the most popular one. In this paper, using self-consistent fluid approximation with collisional sheath model, we have analyzed the effects of the hole array on the plasma characteristics in terms of plasma density, electron temperature, ion current density, sheath voltage and electron heating efficiency. It is shown that electron heating efficiency of the hole array electrode increases more than 10 % compared with that of flat electrodes. DC bias voltage at the substrate side increases with hole depth and pitch due to increase in surface area ratio between powered and substrate electrode. Peak electron density near throat region of the hole structure becomes more than 2 time higher than that of flat parallel electrode at the same voltage driving condition. It was experimentally verified that these variations of plasma properties is beneficial for high rate of Si thin film deposition

**11:40am EN+PS-MoM11 Arc Energy in Large Scale Magnetron Sputtering**, D. Carter, H. Walde, Advanced Energy Industries, Inc.

A detailed analysis of sputtering arcs on a large scale (3400 cm<sup>2</sup>) magnetron source reveals some common trends related to energy absorbed in these events and the progression of current and voltage through their duration. Examination of these trends provides insight into the rapid release of arc energy and some of the practical limitations of the techniques used to minimize their impact on deposition processes. Two very different but equally important materials were studied, metallic aluminum and ceramic, aluminum-doped, zinc oxide. While the characteristics and behaviors of arcs from these two materials are generally similar, subtle distinctions in the evolution of current and voltage explain a significant difference in measured arc energies. These observations present factors for consideration regarding arc suppression and also raise the question of what is the minimum achievable arc energy. In an attempt to answer this fundamental question a stored energy model for a large scale magnetron system is proposed. Using practical assumptions for sheath capacitance and source inductance, minimum arc energy is calculated to serve as the ultimate goal for a next generation arc detection and suppression system.

\* Coburn & Winters Student Award Finalist

## Thin Film

Room: Pecos - Session TF+EN-MoM

### ALD: Energy Applications

Moderator: S.M. George, University of Colorado at Boulder

8:20am **TF+EN-MoM1 ALD Applications in Heterogeneous Catalysis**, *P.C. Stair*, Northwestern University & Argonne National Lab, *J. Lu*, Northwestern University, *H. Feng*, *J.E. Libera*, *J.W. Elam*, *M.J. Pellin*, Argonne National Laboratory, *H.-S. Kim*, Northwestern University  
**INVITED**

Atomic Layer Deposition (ALD) has enormous potential for the synthesis of advanced heterogeneous catalysts with controlled composition and structure at the atomic scale. The ability of ALD to produce conformal oxide coatings on porous, high-surface area materials offers the possibility to provide completely new types of catalyst supports. At the same time ALD can achieve highly uniform catalytically active metal and oxide phases with (sub-) nanometer dimensions.

Vanadium oxide species supported on high surface area oxides are among the most important catalytic materials for the selective, oxidative conversion of hydrocarbons to useful chemicals. In our laboratory ALD has been used to synthesize both the catalytic vanadium oxide and the supporting oxide on both high surface powders and anodic aluminum oxide (AAO) nanoliths. These materials have been characterized by SEM, XRF, ICP, UV-Vis absorption spectroscopy, Raman spectroscopy and evaluated for the oxidative dehydrogenation (ODH) of cyclohexane.

More recently we have studied what we call "ABC-type" ALD in which metal nanoparticles and support materials are grown sequentially in each ALD cycle. This method makes possible metal deposition at lower temperatures than conventional AB-type ALD and exceptionally small particles, ca. 0.5 nm. Using additional ALD support layers at the conclusion of the growth, the metal particles are stabilized against sintering at high temperatures and reaction conditions.

9:00am **TF+EN-MoM3 Process and Materials Optimization for Ru/RuO<sub>2</sub> ALD using a Novel Cyclohexadienyl Precursor**, *K. Gregorczyk*, *L. Henn-Lecordier*, University of Maryland, *J. Gatineau*, *C. Dussarrat*, Air Liquide, *G.W. Rubloff*, University of Maryland  
Ruthenium is of particular interest to the semiconductor industry and others due to its low bulk resistivity ( $7\mu\Omega\text{ cm}$ ) and high work function (4.7eV). In addition, its complementary oxide, RuO<sub>2</sub>, can exhibit high specific capacitance (up to 750 F/g) and conductivity ( $80\text{--}100\mu\Omega\text{ cm}$ ), making it attractive for energy storage applications. We report results for Ru and RuO<sub>2</sub> ALD using a novel Ru cyclohexadienyl precursor and oxygen. This precursor is attractive because it is liquid at room temperature, stable in air and non-reactive with water, while its vapor pressure is similar to that of common ALD Ru precursors RuCp<sub>2</sub> and Ru(EtCp)<sub>2</sub>, i.e., 0.1 Torr at 60°C and 1 Torr at 100°C. ALD Ru deposition was achieved in a wafer scale (100mm), cross-flow ALD reactor. Self-limiting ALD surface chemistry is observed between 250-300°C with a growth rate of  $\sim 0.5\text{Å}/\text{cycle}$  and across-wafer uniformity >98%. Four point probe measurements show a low sheet resistance of  $16\mu\Omega\text{ cm}$ . Ru nucleation is improved compared to RuCp<sub>2</sub> and Ru(EtCp)<sub>2</sub> based processes, with no nucleation delay on SiO<sub>2</sub> or TiO<sub>2</sub>, a slight delay on Si, and a significant delay on Al<sub>2</sub>O<sub>3</sub>. Growth rates are constant with the number of deposition cycles. Conformality studies were conducted using high aspect ratio anodic aluminum oxide (AAO) thin films, using a thin TiO<sub>2</sub> nucleation layer before Ru ALD. This Ru ALD process converts to a RuO<sub>2</sub> ALD process at higher oxygen partial pressure, with an oxide conductivity of  $\sim 80\mu\Omega\text{ cm}$ . Post-process thin film characterization using XRD, XPS and AFM will be also presented.

This work was supported by the US Department of Energy, Office of Basic Energy Sciences as part of an Energy Frontier Research Center.

9:20am **TF+EN-MoM4 Atomic Layer Deposition Enabled Metal-Insulator-Metal Tunnel Diode for Infrared Energy Rectifying System**, *L.-T. Wu*, University of South Florida, *N. Kislov*, NanoCVD Inc., *J. Wang*, University of South Florida

Amongst present-day renewable energy sources, solar cells have been widely considered as the most viable solution. However, the energy conversion efficiency for the solar cells is limited to 30% or below due to the device physics. Rectifying antenna (rectenna) is an ideal supplement that is able to efficiently capture the abundant infrared (IR) energy from the solar radiation in part due to IR antenna's inherent high efficiency. The rectenna system consists of two key elements: antenna and rectifying diode. The IR antenna captures the solar radiation within the wavelength of

interest to be delivered to the ultrafast diode that rectifies the received signal into usable DC power.

Rectennas operating at microwave frequencies with efficiency up to 85% has been routinely demonstrated. However, the key remaining challenge for the infrared counterparts can be ascribed to the insufficient cutoff frequency of the semiconductor-based diodes owing to their excessive depletion-induced capacitance. In order to obtain the desired response times less than 10-12seconds, metal-insulator-metal (MIM) tunnel diodes with junction area in the range of  $100\text{nm}\times 100\text{nm}$  were implemented herein to enable the coveted terahertz frequencies due to the greatly reduced junction capacitance and ultrafast quantum tunneling.

In this work, MIM tunnel diodes with sub-micron sized junction have been mass produced using CMOS-compatible processes without the need for E-beam lithography or sophisticated chemical etching. Standard photolithography and atomic layer deposition (ALD) were used to allow formation of a micrometer-wide finger in the second metal layer separated from the electrode in the first metal layer by an ALD-deposited sidewall dielectric spacer, thus forming a nm-thick vertical tunnel junction. The nano-scale junction is defined by the width of the finger and the thickness of the electrode, while the junction thickness is controlled by the ALD process.

On par to nano-scale devices, MIM tunnel diodes with micron-scale self-aligned cross-fingers have been successfully developed. Through this process, we have investigated a wide variety of metal and insulator materials such as Au, Cu, Pt, Ni, Al, Al<sub>2</sub>O<sub>3</sub>, HfO<sub>2</sub> to advance the performance of the MIM diode with particular focus on its efficiency. Some preliminary DC and RF characterization have been carried out to study the device characteristics such as responsivity, nonlinearity and asymmetry of I-V, and frequency responses. Ongoing research for modeling of MIM tunneling diode based on measured S-parameter data and further reduction of the device junction area will be detailed in the final manuscripts.

9:40am **TF+EN-MoM5 New Semiconductor-Insulator-Semiconductor Solar Cell Concept based on Wet Chemically Etched Silicon Nanowires: Processing and Electro-Optical Properties**, *B. Hoffmann*, *V.A. Sivakov*, *G. Broenstrup*, *F. Talkenberg*, Institute of Photonic Technology, Germany, *S.H. Christiansen*, Max Planck Institute for the Science of Light, Germany

Silicon nanowire (SiNW) ensembles with vertical geometry have been realized using wet chemical etching of bulk silicon wafers (n-Si(100)) with an etching hard mask of silver nanoparticles that are deposited by wet chemical electroless deposition on silicon surfaces.

The new concept of the solar cell is based on the semiconductor-insulator-semiconductor (SIS) layer sequence produced by Atomic Layer Deposition (ALD). A thin tunnelling oxide (SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>) with a thickness of 5-20 Å and a 300 nm transparent conductive oxide (Al doped ZnO or In doped SnO<sub>2</sub>) around 1D silicon nanostructures have been realized using Plasma Assisted ALD approach (Oxford Plasma, OpAL).

The first prototype reached an open-circuit voltage of 80mV and a short-circuit current density of  $23\text{mA}/\text{cm}^2$ .

The influence of the thickness and chemical nature of the tunnelling oxide will be discussed. Back side contacts of Ti/Al or Ti/Ag were realized using sputtering. From literature it is known that the planar SIS solar cell can reach an energy conversion efficiency of approx 15%. Absorption of visible and infra-red light is significantly enhanced in nanowires compared to planar layers of identical thickness. Thus, wet chemically etched silicon nanowires have the potential for even higher energy conversion efficiencies compared to the planar SIS solar cells. The morphology, crystallographic and surface structure, optical and solar cell properties will be presented and discussed in details.

10:00am **TF+EN-MoM6 Ultrathin Al<sub>2</sub>O<sub>3</sub> for c-Si Solar Cells: Differences in Passivation by Thermal and Plasma ALD-Synthesized Films**, *G. Dingemans*, *N.M. Terlinden*, *M.L.C. Adams*, *H.B. Profijt*, *M.M. Mandoc*, *M.C.M. van de Sanden*, *E.W.M.M. Kessels*, Eindhoven University of Technology, Netherlands

Ultrathin films of Al<sub>2</sub>O<sub>3</sub> synthesized by ALD at low substrate temperatures (200 °C) have recently demonstrated their potential as surface passivation material in c-Si photovoltaics enabling solar cell efficiencies up to 23.4%. So far, the best results were obtained by plasma ALD Al<sub>2</sub>O<sub>3</sub> but recently it was shown that similar excellent results can be obtained by thermal ALD [1]. For both methods, Al<sub>2</sub>O<sub>3</sub> yield excellent lifetimes after annealing (at 400 °C) on both p- and n-type Si wafers with the best results corresponding to ultralow surface recombination velocities < 1 cm/s (for 3.5 Ohm cm n-

type *c*-Si). However, also several striking differences have been observed in terms of the underlying passivation mechanism as will be addressed in this contribution. From capacitance-voltage (C-V) measurements, corona charging experiments and optical second harmonic generation (SHG) it was found that Al<sub>2</sub>O<sub>3</sub> deposited with thermal ALD contains a lower negative fixed charge density ( $\sim 10^{12}$  cm<sup>-2</sup>) than plasma ALD ( $> 5 \cdot 10^{12}$  cm<sup>-2</sup>). This indicates that field-effect passivation (i.e., shielding of one type of charge carriers from the surface) is less important for thermal ALD. On the other hand, it was observed that chemical passivation (i.e., reduction of interface defect states) is very important for both thermal and plasma ALD Al<sub>2</sub>O<sub>3</sub>. Relatively low interface defect densities  $D_{it}$  of  $< 10^{11}$  eV<sup>-1</sup> cm<sup>-2</sup> were found for both methods after anneal. However, for as-deposited Al<sub>2</sub>O<sub>3</sub>, the interface defect density (and correspondingly the surface recombination velocity) is significantly poorer for plasma ALD Al<sub>2</sub>O<sub>3</sub> than for thermal ALD Al<sub>2</sub>O<sub>3</sub>. From vacuum ultraviolet (VUV) emission measurements, it has been found that the high  $D_{it}$  can be attributed to plasma radiation damage by photons with a photon energy of  $\sim 9.5$  eV. Furthermore, it will be shown that the difference in importance of field-effect passivation explains several differences observed in the passivation performance for thermal and plasma ALD Al<sub>2</sub>O<sub>3</sub> (e.g., the minimum thickness required for excellent passivation).

[1] G. Dingemans, M. C. M. van de Sanden, W. M. M. Kessels, *Electrochem. Solid-State Lett.*, 13, H76 (2010).

10:40am **TF+EN-MoM8 Cathodoluminescent and Photoluminescent Properties of Pulsed Laser Deposited Thin Phosphor Films**, *O.M. Ntwaaborwa\**, *P.D. Nsimama, J.J. Dolo*, University of the Free State, South Africa, *M.S. Dhlamini*, University of the Free State and CSIR, South Africa, *E. Coetsee, J.J. Terblans, H.C. Swart*, University of the Free State, South Africa

**INVITED**

Phosphors have many uses today, such as information display, medical imaging, and theft prevention. The phosphors are often used as powders, even though thin films offer higher resolution and better chemical stability. We have investigated the cathodoluminescent (CL) and photoluminescent (PL) properties of thin films of several phosphors (e.g. SrAl<sub>2</sub>O<sub>4</sub>:Eu<sup>2+</sup>, Dy<sup>3+</sup>; SiO<sub>2</sub>:PbS; Gd<sub>2</sub>O<sub>2</sub>S:Tb<sup>3+</sup>; SiO<sub>2</sub>:Ce<sup>3+</sup>, Tb<sup>3+</sup> and Y<sub>2</sub>SiO<sub>5</sub>:Ce<sup>3+</sup>) that were ablation deposited onto Si (100) substrates using either conventional pulsed laser deposition (PLD) or pulsed reactive crossed beam laser ablation (PRCLA). Several deposition parameters were varied, including vacuum versus partial pressure of gas (O<sub>2</sub> or Ar), type of laser pulse, and substrate temperature using either a 307 nm XeCl or 248 nm KrF excimer laser. The CL spectrum and intensity were measured in vacuum from films irradiated with 2 keV electrons for a prolonged period of time, while PL data were collected in air under excitation by either a 325 nm HeCd laser or a monochromatized xenon lamp. Both the CL and PL intensities were strongly dependent on the deposition conditions and post-deposition annealing. Data from scanning electron microscopy (SEM) and atomic force microscopy (AFM) show that the major influence of the deposition conditions on the CL/PL intensity was through changes in the morphology and topography of the films, which affects light scattering and out-coupling. Finally, the CL intensity from the films decreased significantly during prolonged electron beam irradiation. The degraded CL intensity resulted from the formation of non-luminescent oxide layers on the film surfaces. The chemical composition and electronic states of the 'dead' layers were analyzed using x-ray photoelectron spectroscopy (XPS). The influence of the various deposition conditions on the luminescent intensities will be discussed. The mechanism leading to lower CL intensities will be concluded to be electron stimulated surface chemical reactions.

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\* Paul Holloway Award Winner

# Monday Afternoon, October 18, 2010

## Energy Frontiers Topical Conference

Room: Mesilla - Session EN-MoA

### Excitonic and Third Generation Solar Cells

Moderator: J.B. Baxter, Drexel University

2:00pm EN-MoA1 **Beyond the Adiabatic Limit: Charge Separation in Organic Photovoltaic Materials**, R.D. Pensack, J.B. Asbury, Penn State University **INVITED**

The dynamics of charge separation in photovoltaic polymer blends following photoinduced electron transfer from the conjugated polymer, CN-MEH-PPV, to the electron accepting functionalized fullerene, PCBM, are observed with ultrafast vibrational spectroscopy. The investigators take advantage of a solvatochromic shift of the vibrational frequency of the carbonyl (C=O) stretch of PCBM to directly measure the rate of escape of electrons from their Coulombically bound charge transfer (CT) excitons at donor/acceptor interfaces on ultrafast time scales. The data reveal that the rate of dissociation of CT excitons is temperature independent from 200 to 350 K indicating that excess energy in hot CT excitons plays an important role in mediating charge separation. These observations suggest that conceptual and theoretical descriptions properly taking into account the strong coupling of electronic and nuclear degrees of freedom in organic semiconductors are essential to understand the mechanism of charge separation in organic photovoltaic materials. From a practical stand-point, efforts to develop new low band-gap polymers for organic solar cells should target electron donor and acceptor pairs capable of advantageously redistributing excess energy in hot CT excitons to enable efficient charge separation with minimal donor-acceptor energy level offsets.

2:40pm EN-MoA3 **Third Generation Photovoltaics: Multiple Exciton Generation in Colloidal Quantum Dots, Quantum Dot Arrays, and Quantum Dot Solar Cells**, A.J. Nozik, National Renewable Energy Lab and Univ. of Colorado, Boulder, M.C. Beard, J.M. Luther, National Renewable Energy Lab, A.G. Midgett, O.E. Semonin, Univ. of Colorado, Boulder, J.C. Johnson, National Renewable Energy Lab **INVITED**

One potential, long-term approach to more efficient future generation solar cells is to utilize the unique properties of quantum dot (QD) nanostructures to control the relaxation pathways of excited QD states to produce enhanced conversion efficiency through efficient multiple exciton generation (MEG) in QDs.

We have observed efficient multiple exciton generation (MEG) in PbSe, PbS, PbTe, and Si QDs at threshold photon energies of 2-3 times the HOMO-LUMO transition. We have studied MEG in close-packed QD arrays where the QDs are electronically coupled in the films and thus exhibit good carrier mobility. We have developed simple, all-inorganic QD solar cells that produce large short-circuit photocurrents via both nanocrystalline Schottky junctions and nanocrystalline p-n junctions without the need for QD sintering, superlattice order or separate phases for electron and hole transport. The latter shows an NREL-Certified conversion efficiency of 3%. We have demonstrated that the MEG efficiency in conductive Pb chalcogenide QD films after certain chemical treatments can be comparable to isolated QDs in colloids, but the QY varies greatly depending upon the specific chemical treatment, and subsequent QD surface chemistry.

Selected aspects of this work will be summarized and recent advances will be discussed. Various possible configurations for novel QD solar cells that could produce very high conversion efficiencies will be presented, along with progress in developing such new types of solar cells. Recent controversy about MEG and its application to photovoltaic cells will also be addressed.

3:40pm EN-MoA6 **Solar Cells Based on Semiconductor Quantum Dots and Nanowires**, K.S. Leschkes, University of Minnesota **INVITED**

Solar cells based on colloidal semiconductor nanocrystals, or quantum dots (QDs) may have the potential to achieve high power conversion efficiencies at low cost. Quantum confinement of electrons and holes in these nanometer-size crystals endows them with properties that may be advantageous for efficient solar-to-electric energy conversion. For example, varying the QD size changes the electronic energy levels and optical absorption in QDs. This allows the optimization of their optical absorption for maximum overlap with the solar spectrum. In addition, QDs can be prepared in large quantities as stable colloidal solutions under mild conditions and deposited as thin films using inexpensive, high-throughput coating processes to form solar cells.

After a brief review of the literature on QD solar cells, I will focus on a new type of QD solar cell based on heterojunctions between PbSe QDs and thin ZnO films designed to improve on the current state-of-the-art. These QD solar cells were fabricated by depositing thin films of ZnO and PbSe QDs onto a glass substrate coated with conductive indium-tin-oxide (ITO), which forms the bottom contact of the device. Absorption of light produces electron-hole pairs in the QDs that dissociate, either at a QD-electrode interface or within the QD film and generate photocurrent. Specifically, electrons lower their energy by transferring into the ZnO film, which forms a type-II heterojunction with the PbSe QDs. These electrons move across the ZnO film and are collected at the ITO contact while the positive charges are transported to and collected at a top gold electrode.

Under simulated sunlight, the QD solar cells exhibit short-circuit currents as high as 15 mA/cm<sup>2</sup> and open-circuit voltages up to 0.45 V. The solar cell open-circuit voltage depends on the QD size and increases linearly with the QD effective band gap energy. Charge collection in these devices can be increased further by using nanostructured interfaces between PbSe QDs and ZnO. Specifically, the ZnO film can be replaced with a vertical array of ZnO nanowires, and infiltrating this array with colloidal PbSe QDs. These nanowire-quantum-dot solar cells exhibited power conversion efficiencies of 2%, nearly three times higher than that achieved with thin-film ZnO devices constructed with the same amount of QDs. Supporting experiments using field-effect transistors made from these QDs also show that the QDs' electrical properties are strongly influenced by the presence of nitrogen and oxygen atmospheric gases. Such results have important implications with respect to the assembly, characterization, and exposure of QD-based solar cells to an ambient environment.

4:20pm EN-MoA8 **PbSe and PbS Nanocrystal Solar Cells**, J.J. Choi, J. Luria, B.-R. Hyun, A.C. Bartnik, L. Sun, Y.-F. Lim, J.A. Marohn, F.W. Wise, T. Hanrath, Cornell University **INVITED**

Rational progress towards nanocrystal based solar cells demands an improved understanding of electronic and optical interactions of proximate nanocrystals in functional assemblies. We combined transient photoluminescence spectroscopy and electric force microscopy to probe photogenerated exciton dissociation in PbS nanocrystal assemblies. We show that excitons dissociate via charge tunneling between neighboring nanocrystals. Implications in the context of nanocrystal photovoltaic devices will be discussed. We also present the design, fabrication and characterization of excitonic solar cells based on PbSe and PbS nanocrystal active layers. The best performing device shows a 1-sun power conversion efficiency of 4%.

5:00pm EN-MoA10 **Solid-State Quantum Dot Sensitized Solar Cells: Atomic Layer Deposition versus Successive Ionic Layer Adsorption and Reaction**, P. Ardalan, T.P. Brennan, J.R. Bakke, S.F. Bent, Stanford University

Narrow band gap nanostructures such as cadmium sulfide quantum dots (QDs) are known to show size quantization effects. In quantum dot sensitized solar cells (QDSSCs), these QDs can be engineered to transfer an electron to a wide band gap semiconductor such as titanium dioxide (TiO<sub>2</sub>). However, performance in such devices is reduced by charge recombination at the TiO<sub>2</sub> surface and hence use of organic linkers such as self-assembled monolayers (SAMs) on these devices could provide a means of eliminating recombination sites and lead to increased efficiency. In this study, we investigated the effects of different aliphatic and aromatic SAMs with phosphonic acid headgroups and varied tailgroups on the bonding and performance of cadmium sulfide (CdS) solid-state QDSSCs. TiO<sub>2</sub> was deposited on piranha-cleaned Si or microscope glass via atomic layer deposition (ALD) and the resulting surfaces were characterized by ultraviolet photoelectron spectroscopy (UPS), X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), scanning electron microscopy (SEM), and atomic force microscopy (AFM). Next, different SAMs were attached from solution to either ALD-deposited (planar) or doctor-bladed (nanoporous) TiO<sub>2</sub> substrates, and the effects of chain length, aromaticity, and tailgroup on the quality of the SAMs were investigated. CdS QDs were then grown on the SAM-passivated TiO<sub>2</sub> surfaces by either successive ionic layer adsorption and reaction (SILAR) from solution or by atomic layer deposition (ALD) from the gas phase, and the bonding and performance of the resulting materials were evaluated by UV-visible and other spectroscopic techniques. Our results show that CdS QDs with particle sizes in the range of 2 to 6 nm are grown by SILAR on TiO<sub>2</sub> both with and without SAMs, but more CdS can be deposited on samples with SAMs with the exception of the long-chain methyl-terminated monolayer. Furthermore, it is determined that the SAM chain length affects the SILAR CdS deposition at the TiO<sub>2</sub> surfaces more significantly than does the identity of the tailgroup. ALD also is effective for depositing CdS QDs, but

less CdS is deposited by ALD than by SILAR at TiO<sub>2</sub> surfaces for the same number of cycles. QDSSC devices have been made using both SILAR and ALD, and we will present results on the dependence of solid-state QDSSC performance and efficiency on the deposition technique employed to grow the CdS QDs, as well as on the properties of the SAM. Overall, we observed higher efficiencies in devices with SAMs and we propose that this result can be attributed to the presence of a charge recombination barrier.

5:20pm **EN-MoA11 Synthesis and Application of Branched Titania Nanotubes in Dye-Sensitized Solar Cells**, *G. Butail, P. Gopal, M. Raddiar, R. Teki, N. Ravishankar, G. Ramanath*, Rensselaer Polytechnic Institute

Titania is a promising photocatalyst used in a variety of photovoltaic, optoelectronic and biofiltering applications. There is great interest in synthesizing high surface area titania nanostructures by inexpensive means for low-cost power generation, among which titania nanotubes offer higher efficiencies because of unidirectional charge transport and low scattering losses. Here we demonstrate, for the first time, the formation of branched titania nanotubes using potentiostatic anodization of titanium thin films. The realization of branched titania nanotubes provides a means to tune the electronic properties of titania and to functionalize them with multi-sized quantum dots and other metallic/semiconducting nanostructures.

Experimental analysis show anodization diameter to be a linear function of applied voltage. We exploit the relationship between the anodization voltage and nanotube diameter to obtain and control the extent of branching and tune branch diameters between 30 to 110 nm. Branching achieved through single step voltage induced anodization offers the added advantage of control of point of branching depending on rate of anodization at each voltage. We also evaluate the morphology and the optical properties of branched titania nanotubes and compare their light-harvesting efficiency with unbranched nanotubes in dye-sensitized solar cells. We specifically compare branched titania nanotubes formed by ramping down the voltage from 60 to 33 V and compare the them with titania nanotubes formed at 60 V and 33 V. Preliminary results show a 33% increase in active surface area of branched titania nanotubes as compared to unbranched nanotubes formed at 60 V which is further confirmed through BET analysis.

Application of straight (unbranched) titania nanotubes for fabrication of dye-sensitized solar cells using a ruthenium based dye (N719) results in an efficiency of 0.58±0.2% with short circuit current density of 6.3±1.0 mA/cm<sup>2</sup> and fill factor of 22.4±0.2. Use of branched titania nanotubes of same thickness under same conditions reports an efficiency of 1.04±0.1% with increase in short circuit current density to 9.1±0.8 mA/cm<sup>2</sup> and a fill factor of 23.7±0.1%. A two-fold enhancement of photovoltaic efficiency of branched samples as compared to straight nanotubes correlates well to the difference in surface area and optical properties of the two structures.

## Energy Frontiers Topical Conference

Room: Mesilla - Session EN-TuM

### Flexible Solar Cells

Moderator: C.A. Wolden, Colorado School of Mines

8:40am **EN-TuM3 Control of the Structural, Electrical and Mechanical Bending Properties of Highly Transparent Conductive Ga-doped ZnO Films Deposited on Polyester Substrates.** *K. Nagamoto, Y. Matubayashi, T. Kondo*, LINTEC Corporation, Japan, *Y. Sato, H. Makino, N. Yamamoto, T. Yamamoto*, Kochi University of Technology, Japan

In this work, we report the structural, electrical and mechanical bending properties of highly transparent conductive Ga-doped ZnO (GZO) films deposited on flexible substrates for use in electrodes for flexible devices. GZO films were deposited on polyester substrates covered with under-coat layers by ion plating deposition with direct-current arc discharge at a temperature of less than 100 degree Celsius (The glass transition temperature ( $T_g$ ) of polyester substrates are approximately 120 degree Celsius). Polycrystalline GZO films with high (0002) orientation perpendicular to the substrate have obtained. The resistivity of GZO films of a 100 nm thickness on polyester substrates was  $5.0 \times 10^{-4}$  ohm-cm and the average transmittance of more than 80 % in the visible wavelength region.

The mechanical bending properties of GZO films were investigated by bend test: sheet resistance of GZO films as a function of bending diameter before and after bending was determined by Hall-effect measurement. When the substrate is bent by an external force, the outer side surface experiences tensile stress and inner side surface experiences compressive stress. The analysis of data obtained by the bend test shows that sheet resistance for GZO films at 12 mm bending diameter were 150 ohm/sq. (before bending test : 50 ohm/sq.) for compressive stress direction whereas sheet resistance was 1770 ohm/sq. for tensile stress direction. In addition, the bend test was carried out for GZO films deposited at different process temperature. GZO films deposited at lower substrates temperature exhibit improved bending performance. GZO films deposited on polymer substrates have residual stress including intrinsic stress and thermal stress caused by the difference in thermal expansion coefficient between GZO films and the substrates. The bending property of GZO films can be improved by controlling the residual stress affected by process temperature.

We developed multiple depositions to reduce polymer substrates temperature and obtained the relationship between bending properties of GZO films and process temperature.

The financial support from the Japan Science and Technology Agency is gratefully acknowledged.

9:00am **EN-TuM4 Low-Temperature Deposition of Transparent Conducting Oxides on Plastic Substrates.** *E. Ritz*, University of Illinois at Urbana-Champaign, *T. Dockstader*, Kurt J. Lesker Company, *L. Meng, M.J. Neumann, D.N. Ruzic*, University of Illinois at Urbana-Champaign

The future of electronic devices such as touchscreen phones and large flat panel displays is bright, with their usage only becoming more prevalent in our daily lives. Such devices are dependent on transparent conducting oxides (TCOs) and their continued growth necessitates a manufacturing process that is able to deposit an inexpensive coating with high transparency and high conductivity. Operating using a dual unbalanced DC magnetron system with a secondary RF antenna running at 13.56MHz, a process has been developed that can deposit TCO films such as Indium Tin Oxide (ITO) and Aluminum-doped Zinc Oxide (AZO) without significantly heating the substrate while maintaining high transmission and electrical properties. The system utilizes two 75mm-diameter circular magnetrons with a 2-loop immersed inductive RF antenna between them in order to provide increased ionization. By adjusting RF power from 0W to 300W, ionization fraction can be increased from 20% to over 80% for unbalanced configuration as measured by a gridded energy analyzer. In addition, plasma density is increased with RF enhancement from  $10^{10}$  cm<sup>-3</sup> to  $10^{11}$  cm<sup>-3</sup>. This RF enhancement allows for substrate temperatures to remain below 100°C while still achieving film resistivity on the order of  $10^{-3}$ - $10^{-4}$  Ohm-cm (measured by four-point probe method) and transparency of greater than 90% in the visible wavelengths (measured by spectrophotometry.) Low-temperature deposition expands the possibilities for substrate choice to include plastics, such as polyethylene terephthalate (PET), resulting in flexible TCO films. Adjusting process gas oxygen content (from 0-5%) and RF power allows for a means to tune the film properties to the desired transparency and conductivity. Experiments performed using ITO and 2%-doped AZO with glass and PET substrates. Plasma monitoring

accomplished through use of Langmuir probe and optical emission spectroscopy. Additional film quality analysis by means of x-ray diffraction (XRD) and x-ray photoelectron spectroscopy (XPS).

9:20am **EN-TuM5 Flexible Solar Cells Based On Monocrystalline Silicon and GaAs.** *J.A. Rogers*, University of Illinois at Urbana-Champaign **INVITED**

Solar modules that involve large collections of small, ultrathin photovoltaic cells on thin plastic or rubber substrates offer mechanical properties (e.g. stretchability) and other features (e.g. curvilinear shapes; lightweight designs) that cannot be achieved with conventional approaches. This talk describes the use of inorganic micro/nanomaterials in systems that provide the performance of state-of-the-art, wafer-based technologies but with the mechanical properties of a rubber band. We explain the materials science and mechanics of these approaches in the context of monocrystalline silicon and gallium arsenide solar cells, and key mechanics aspects of their use in flexible and stretchable modules.

10:40am **EN-TuM9 Thin Film Photovoltaics from Nanocrystal Inks.** *M. Law*, University of California, Irvine **INVITED**

Colloidal semiconductor nanocrystals (NCs) are metastable objects prone to thermal and oxidative degradation driven by their large surface-to-volume ratios. The fabrication of practical electronic devices based on NC solids hinges on developing methods to prevent oxidation, diffusion, sintering and other undesirable physical and chemical changes to which these materials are susceptible. In this talk, I first describe systematic measurements of the room-temperature electron and hole field-effect mobilities of alkanedithiol-treated PbSe NC films as a function of NC size and the length of the alkane chain. These results establish a baseline for mobility trends in PbSe NC solids and have implications for fabricating high-mobility NC-based optoelectronic devices. Optical, electrical and photoelectron spectroscopy measurements are combined to monitor the room-temperature oxidation of films of PbSe NCs that are treated in solutions of short-chain thiols or carboxylic acids to produce electronically-coupled NC solids. I show that surface oxidation can be prevented by infilling NC films with thin (10-20 nm) Al<sub>2</sub>O<sub>3</sub> layers deposited by low-temperature atomic layer deposition (ALD). ALD treatment of complete PbSe NC field-effect transistors yields high-performance devices that operate indefinitely in air. ALD infilling is a promising route to the preparation of stable, all-inorganic NC solids with tunable electrical properties, and may prove an important breakthrough in the fabrication of robust, high-efficiency quantum dot solar cells.

11:20am **EN-TuM11 Architectures for Enhanced Exciton Harvesting in Organic Photovoltaic Cells.** *R.J. Holmes*, University of Minnesota **INVITED**

Organic semiconductors are attractive for application in photovoltaic cells due to their compatibility with lightweight, flexible substrates, and high-throughput processing techniques. Optical absorption in these materials leads to the creation of tightly-bound, mobile excitons. In order to generate photocurrent in an organic photovoltaic cell (OPV), excitons must diffuse to a dissociating, electron donor-acceptor (D-A) interface. Most organic semiconductors are characterized by exciton diffusion lengths that are considerably smaller than the optical absorption length. This trade-off between diffusion and absorption often necessitates the use of thin active layers to maximize exciton harvesting. Among the approaches that have been demonstrated to mitigate the short exciton diffusion length, the use of a D-A bulk heterojunction has been widely studied. In these structures, the D-A materials are blended to realize a large interface area for exciton dissociation. The film morphology is typically optimized by thermal annealing, which results in the formation of pathways for charge carrier collection. This talk will explore two alternate OPV architectures designed to overcome the exciton diffusion bottleneck. The first involves the use of composite donor layers that contain both a fluorescent host and a phosphorescent guest sensitizer. The inclusion of the phosphor sensitizer in the donor layer enables the population of the long-lived triplet exciton state of the fluorescent host. Diffusion via the host triplet leads to a near-doubling in the exciton diffusion length and an increase in device efficiency. The second architecture relies on the use of OPVs containing a continuously graded D-A film composition as a means to simultaneously optimize the exciton diffusion and charge collection efficiencies. In these graded heterojunction OPVs, the power conversion efficiency is observed to exceed that of comparable devices containing either planar or uniformly mixed heterojunctions. In both of these approaches, improved performance is realized by utilizing architectures that enable an increased level of control over the exciton diffusion and charge collection efficiencies.





# Tuesday Afternoon, October 19, 2010

## Energy Frontiers Topical Conference

Room: Mesilla - Session EN+EM-TuA

### Electronic Materials for Energy Conversion & Storage

Moderator: G.W. Rubloff, University of Maryland

2:00pm **EN+EM-TuA1 High-capacity and High-rate Metal Oxide Anodes for Li-ion Batteries**, *A.C. Dillon, C. Ban*, National Renewable Energy Laboratory, *L.A. Riley, A.S. Cavanagh, S.M. George*, University of Colorado, *Y.S. Jung, Z. Wu, Y. Yan*, National Renewable Energy Laboratory, *S.-H. Lee*, University of Colorado

**INVITED**  
Significant advances in both energy density and rate capability for Li-ion batteries will be necessary for implementation in next generation electric vehicles. By employing metal oxide nanostructures, it is possible to achieve Li-ion anodes that have significantly higher capacity than the state-of-the-art graphite technology. For example we have demonstrated that thin film MoO<sub>3</sub> nanoparticle electrodes (~2 μm thick) have a stable reversible capacity of ~630 mAh/g when tested at C/2.<sup>1</sup> By fabricating more conventional electrodes (~35 μm) with a conductive additive and binder, an improved reversible capacity of ~1000 mAh/g is achieved.<sup>2</sup> The increased capacity for the MoO<sub>3</sub> coin cell electrode compared to the thin film electrode may be attributed to improved electronic/ionic mobility with the conductive additive and more complete access to the nanostructures. We have also demonstrated that by applying a thin atomic layer deposition coating of Al<sub>2</sub>O<sub>3</sub>, improved rate capability for the high volume expansion MoO<sub>3</sub> is achieved for thick more conventional electrodes.<sup>3</sup>

More recently we have focused our work on iron oxide nanostructures, as iron is an inexpensive, abundant and a non-toxic material. Furthermore, we have synthesized binder-free, high-rate capability electrodes. The electrodes contain Fe<sub>3</sub>O<sub>4</sub> nanorods as the active lithium storage material and carbon single-wall nanotubes (SWNTs) as the conductive additive. The highest reversible capacity is obtained using 5 wt.% SWNTs, reaching 1000 mAh/g (~2000 mAh/cm<sup>2</sup>) at C rate when coupled with a lithium metal electrode, and this high capacity is sustained over 100 cycles. Furthermore, the electrodes exhibit high-rate capability and stable capacities of 800 mAh/g at 5C and ~600 mAh/g at 10C. Scanning electron microscopy indicates that this high-rate capability is achieved because Fe<sub>3</sub>O<sub>4</sub> nanorods are uniformly suspended in a conductive matrix of SWNTs. Raman spectroscopy is employed to understand how the SWNTs function as a highly flexible conductive additive. We expect that this method can be used to achieve other binder-free anodes as well as cathodes with similar high-rate capability.<sup>4</sup>

(1) Lee, S.-H.; Kim, Y.-H.; Deshpande, R.; Parilla, P. A.; Whitney, E.; Gillaspie, D. T.; Jones, K. M.; Mahan, A. H.; Zhang, S. B.; Dillon, A. C. *Adv. Mat.* 2008, 20, 3627-3632.

(2) Riley, L. A.; Lee, S.-H.; Gedvilas, L.; Dillon, A. C. *Journal of Power Sources* 2010, 195, 588-592.

(3) Riley, L. A.; Cavanagh, A. S.; George, S. M.; Jung, Y.-S.; Yan, Y.; Lee, S.-H.; Dillon, A. C. *ChemPhysChem* 2010, *in press*.

(4) Ban, C.; Wu, Z.; Gillaspie, D. T.; Chen, L.; Yan, Y.; Blackburn, J. L.; Dillon, A. C. *Advanced Materials* 2010, *in press*.

2:40pm **EN+EM-TuA3 Engineering Li<sub>x</sub>Al<sub>y</sub>Si<sub>z</sub>O Thin Films as a Solid Electrolyte for 3D Microbatteries**, *Y.-C. Perng, J. Cho, D. Membreno, B. Dunn, J.P. Chang*, UCLA

The development of secondary lithium-ion batteries has been directed primarily at portable electronics applications. However, these batteries also have the potential to function as a power source for micro-systems through engineering of electrodes into 3D architectures based on high aspect ratio pillars. In order to utilize this potential, an ultra-thin and highly conformal solid electrolyte layer is required to coat the 3D electrode array. The solid electrolyte lithium aluminosilicate (LiAlSiO<sub>4</sub>), is a promising candidate for this application due to high ionic conductivity along its c-axis resulting from channels formed by the alternating tetrahedra of aluminum-oxygen (Al-O) and silicon-oxygen (Si-O). The length of c-axis of lithium aluminosilicate can be adjusted by changing the crystallization temperature for desired conductivity characteristics.

Atomic layer deposition (ALD) was employed in this work to synthesize thin film lithium aluminosilicate. The self-limiting characteristic of ALD allows for precise control of thickness and composition of complex oxides and results in a highly conformal and pinhole-free coating suitable in 3D micro-battery applications. The metal precursors used in this work are tetraethyl orthosilicate (TEOS), trimethylaluminum (TMA) and lithium t-butoxide (LTB). We also investigated the use of tri-t-butoxy-

hydroaluminat (LTBA) but found that the metal composition was difficult to control and high carbon contents. Using the three precursors mentioned above with water vapor as the oxidant, we deposited SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and Li<sub>2</sub>O, at deposition rates in the range of 0.8~2Å/cycle. The overall deposition rate of stoichiometric LiAlSiO<sub>4</sub> was ~5Å/cycle using a chamber base pressure of 10<sup>-2</sup> Torr and substrate temperature of 300°C. The concentration of each metal element in Li<sub>x</sub>Al<sub>y</sub>Si<sub>z</sub>O thin films is found to correlate closely to ALD cycles and the associated incubation times. The crystalline structures as well as the local environment of the Li-conducting channels are also affected by the ALD cycles and sequences, as indicated by ultraviolet photoelectron spectroscopy (UPS), transmission electron microscopy (TEM) imaging and nuclear magnetic resonance (NMR) analyses. The Li-ion conductivities of ALD Li<sub>x</sub>Al<sub>y</sub>Si<sub>z</sub>O thin films were determined by impedance measurements using a four-point probe setup with contacts made to the film surface. The films have high ion conductivity and low electronic conductivity, the values of which are strongly influenced by the lithium content and distribution in the synthesized thin films.

3:00pm **EN+EM-TuA4 Laser-Deposition and Characterization of Amorphous Thermoelectric Films**, *G.B. Wilks*, Air Force Research Laboratory, *P.T. Murray*, University of Dayton, *S.B. Fairchild, N.W. Gothard, J.E. Spowart*, Air Force Research Laboratory

From the Efficient Cluster Packing model describing the topology of metallic glasses, it is understood that certain compositions are favored for glass-formability based on the ratio of atomic sizes between constituents. In this regard, the half-Heusler composition Zr<sub>0.5</sub>Hf<sub>0.5</sub>NiSn is nearly ideal. Although the crystallized form of this material has been widely studied because of its high thermoelectric power factor, it has been suggested that partial vitrification may enhance the thermoelectric figure of merit by preserving the favorable aspects of electronic structure while significantly disrupting thermal transport. Capitalizing on the high quench rates possible during pulsed laser deposition, a spectrum of thin films including amorphous and partially-amorphous duplex microstructures has been grown under various conditions. Transport characteristics relevant to the thermoelectric effect are rationalized in light of accompanying microstructure characterization.

4:00pm **EN+EM-TuA7 Probing Charge Transport in Exploratory Nanocrystal-Based Devices**, *P. Nagpal, V.I. Klimov*, Los Alamos National Laboratory

**INVITED**  
Colloidally synthesized semiconductor nanocrystals offer the exciting opportunity to exploit unique physical properties, such as size tunable band gap, in low-cost, solution-processed thin film devices. However, charge transport in as-deposited thin films of colloidal nanocrystals is hindered by organic ligands. At the Center for Advanced Solar Photophysics (CASP), a DOE Energy Frontier Research Center, we are investigating the mechanism of charge transport in nanocrystal films by employing them in a range of simple device architectures, with the goal of optimizing them for photovoltaic application. As an example, I will present recent work in nanocrystal-based optical field effect transistors specifically designed to study electron transport and the dynamics of the photogenerated carriers in these semiconductor thin films. These devices offer invaluable information regarding field dependant mobility, optical gating and changes in the Fermi-level at the nanocrystal film interface. I will then discuss other exploratory device efforts at CASP, and how the information generated will be used collectively for the development of solar cells and other energy-related applications.

4:40pm **EN+EM-TuA9 Investigation of GaTIP for Use in Multijunction Photovoltaics**, *C. Downs, T. Vandervelde*, Tufts University

To achieve the highest possible conversion efficiencies in multijunction photovoltaics, the individual layers of the device must both be lattice-matched and have optimal band-gap spacing. Lattice-matched or strain-compensated epitaxy is required for the growth of junctions thick enough to elicit high quantum efficiency. Ideally, for spectral matching, one would have an infinite number of junctions that are current-matched; however, fabrication of a large number of junctions is neither easy nor desirable because of problems that arise from series resistance. In the end, it becomes a balancing act where the optimal number of junctions for a high efficiency concentrator cell is 3-6 junctions, with the conversion efficiency directly linked to how well spacing of the band gaps of the cell are optimized for absorption of the solar spectrum. Unfortunately, many of the optimal lower band-gaps for these multijunction cells do not occur in the dominant materials system (i.e. Ge and mixtures of In, Ga, Al, As, and P). As such, of late there has been a strong push to characterize new materials in hopes of providing more design options for photovoltaic cells. GaTIP is one such material, theorized to be useful as one of the lower junctions of 3+-junction

cells while still being lattice-matched to GaAs and Ge. In this research, the change in lattice constant and band gap of GaTIP with varying compositions are investigated first by computational simulation and then with physical devices. New efficiency records should be achievable by incorporating these new optimal junction materials into the design for multijunction cells. This development will help solar concentrator cells achieve grid parity, thereby becoming a viable renewable energy choice.

5:00pm **EN+EM-TuA10 Photo Induced Ferroelectric Properties of  $\text{Pb}_{0.95}\text{La}_{0.05}\text{Zr}_{0.54}\text{Ti}_{0.46}$  Thin Films**, *H.V. Nampoori, S. Kotru*, University of Alabama

Thin films of lanthanum doped lead zirconate titanate (PLZT) have gained attention due to the large photostrictive response, and their possible use for contact less actuators and sensors. Variation in composition and doping are known to influence the photostrictive responses as well as ferroelectric behavior of these materials. PLZT is also a potential material for photovoltaic devices due to its high electro-optic coefficient and optical transparency.

In this work, thin films of  $\text{Pb}_{0.95}\text{La}_{0.05}(\text{Zr}_{0.54}\text{Ti}_{0.46})\text{O}_3$  (PLZT) were prepared using Metal-Organic Decomposition technique (MOD). The films are deposited by spin coating. Sputter deposited Pt electrodes serve as top contacts for the films. Thickness of the grown films varied from 70-350 nm and the growth temperature was chosen in the range of 550-700°C. Details of the film growth process including effects of temperature, thickness and annealing, and electrical and optical characterization will be presented. In addition parameters which affect the electrical properties like ferroelectric hysteresis and leakage behavior mechanisms will be discussed. The photo induced effects on the ferroelectric and the leakage properties, giving insight to the photovoltaic properties of ferroelectric thin films would be presented

## Energy Frontiers Topical Conference

Room: Pecos - Session EN+TF-TuA

### Thin Films for Photovoltaics

Moderator: L.W. Rieth, University of Utah

2:00pm **EN+TF-TuA1 Ar/H<sub>2</sub> Plasma Treatment of a-Si:H Thin Films: On the Role of Atomic Hydrogen in  $\mu\text{c-Si:H}$  Thin-Film Deposition**, *A.C. Bronneberg, A.M. Creatore, M.C.M. van de Sanden*, Eindhoven University of Technology, the Netherlands

2:20pm **EN+TF-TuA2 Spectroscopic Analysis of the Role of Hydrogen in Amorphous Silicon**, *P. Schäfer, F. Nobis, O.D. Gordan, H. Kupfer, F. Richter, D.R.T. Zahn*, Chemnitz University of Technology, Germany  
Amorphous hydrogenated silicon (a-Si:H) is widely used in photovoltaic applications. The high absorption renders a-Si:H technically relevant especially for thin film solar cells. Despite lower efficiency, an amorphous silicon solar panel possesses the advantage of higher absorption rate and easier processing at lower production cost.

Here the focus lies on highly (p and n) doped amorphous silicon films. The samples are prepared using d.c.-pulsed magnetron sputtering of crystalline silicon targets. A controlled hydrogen flow is added to the sputtering plasma. Hydrogen in amorphous silicon is known to saturate dangling bonds and improves the short range atomic order [1]. To probe the influence of hydrogen in the sputtering process various spectroscopic techniques were applied for sample characterisation.

Raman spectroscopy is a technique sensitive to the morphological aspects of the film. The relaxation of quasi-momentum conservation in amorphous films results in drastically different spectra of amorphous and crystalline silicon. A broad band at  $\sim 485\text{ cm}^{-1}$  appears instead of the sharp crystalline phonon feature at  $520\text{ cm}^{-1}$ . Its shape and asymmetry unveils further information on the short range order like the average dispersion angle from tetrahedral conformation. With the help of Fourier transformed transmission infrared spectroscopy the concentration of hydrogen in the sample is studied. Vibrational hydrogen-silicon stretching modes in the region around  $2000\text{ cm}^{-1}$  are therefore assessed by a modified [2] Brodsky-Cardona-Cuomo approach [3]. Access to the optical constants  $n$  and  $k$  and therefore the complex dielectric function  $\epsilon$  of the sputtered material is granted by variable angle spectroscopic ellipsometry. Thereby important parameters like the Tauc-Lorentz band gap which is mainly determined by interband gap defects are revealed. The combination of these spectroscopic techniques provides a detailed picture of morphological, electrical, and optical parameters of the system. An in depth discussion of the degree of structural improvement, the decrease of interband gap defects, the saturation of

hydrogen content, and evolution of optical properties in correlation with the hydrogen flow will be presented.

[1] R. A. Street, "Hydrogenated Amorphous Silicon", chapter 2.3, Cambridge University Press.

[2] A. A. Langford, M. L. Fleet, B. P. Nelson, W. A. Lanford, N. Maley: Phys. Rev. B **45** (1992) 13367.

[3] M. H. Brodsky, M. Cardona, J. J. Cuomo: Phys. Rev. B **16** (1977) 3556.

2:40pm **EN+TF-TuA3 Improved Efficiency and Air Stability of Hybrid Thin Film Solar Cells with a ZnO Nanoparticle Layer**, *P.H. Holloway, L. Qian, J. Yang, R. Zhou, A. Tang, Y. Zheng, J. Xue*, University of Florida

INVITED

Hybrid solar cells with active and transport layers based on conjugated polymers and/or inorganic semiconductor nanoparticles are an alternative to all-organic or all-inorganic solar cells. In hybrid cells, inorganic nanoparticles complement the absorption of the organic phase and provide better charge transport properties due to higher carrier mobility, while still maintaining the ability to solution-process. These properties will be illustrated first in hybrid solar cells with a mixed active layer based on poly(3-hexyl thiophene) (P3HT) and colloidal CdSe nanospheres, and with a ZnO nanoparticle buffer layer. The CdSe and ZnO nanoparticles were synthesized using a micelle and a sol-gel method, respectively. Both the active and buffer layers were spin-coated from solution onto a poly(3,4-ethylene dioxythiophene) doped with polystyrenesulfonic acid (PEDOT:PSS) layer on an ITO/glass substrate, and finished by deposition of the Al cathode. Compared to control devices without the ZnO layer, devices with the layer showed only slight changes in open-circuit voltage and fill factor, but showed 40-70% higher short-circuit current density, depending on the size of the CdSe nanospheres. ZnO-containing devices showed a maximum power conversion efficiency of 2.5-2.8%, compared to approximately 1.6-1.9% for the best P3HT/CdSe nanosphere devices without the ZnO layer. Using a ZnO layer and a low-gap poly[2,6-(4,4-bis-(2-ethylhexyl)-4H-cyclopenta[2,1-b;3,4-b']-dithiophene)-alt-4,7-(2,1,3-benzothiadiazole)] (PCPDTBT) to better harvest near-infrared photons, we have achieved a maximum power conversion efficiency of 3.3-3.5%. In addition to the efficiency enhancement, the ZnO layer also drastically improved the air stability of both types of hybrid solar cells. While devices without the ZnO layer degraded completely after one to three days of air exposure, devices with the ZnO layer exhibited only a modest 35% efficiency decrease after >70 days of storage in laboratory air. The mechanisms leading to higher efficiencies and reduced degradation will be discussed.

4:00pm **EN+TF-TuA7 Energy Band Alignments and Influence of Doping on Ga-doped ZnO, CuO and Si**, *S.Y. Chiam, S.J. Wang, J.S. Pan, L.M. Wong*, Institute of Materials Research & Engineering, Singapore, *W.K. Chim*, National University of Singapore

It is important to investigate new materials for thin film solar cells for 2<sup>nd</sup> generation devices. Materials extraction cost and annual electricity production considerations highlighted several potential new materials including cuprous oxide ( $\text{Cu}_2\text{O}$ ). In this work, we report on the growth of  $\text{Cu}_2\text{O}$  and highlighted the importance of the oxygen partial pressure during growth. Namely, the partial pressure of oxygen determines the transition of  $\text{Cu}_2\text{O}$  to CuO with increasing partial pressure. This is accomplished at a fixed total pressure as this may influence  $\text{Cu}_2\text{O}$  formation. We then discuss about the interface energy alignments, first between between  $\text{Cu}_2\text{O}/\text{ZnO}$  and then  $\text{ZnO}/\text{Si}$ . The former is of importance as inorganic thin film p-n junction that is suitable for 2<sup>nd</sup> generation solar cell devices. For the latter case, we fabricated device structure on differently doped Si, to investigate influence on doping on the transport characteristics of the hetero- pn junction. It is found that forward bias characteristics for a heterojunction, is not critically dependant on the band offsets, but rather the build-in-field at the heterojunction. If the physics is considered from the point of view of quasi-fermi level separation during light illumination, this build-in-field will also determine the  $V_{oc}$ . In this sense, band offset measurements can only give an indication of the maximum limit of the  $V_{oc}$  for differently doped semiconductors (non-degenerate) heterojunction solar cells. In addition, we show that under illumination, the current conduction for the  $\text{ZnO}/\text{Si}$  at zero-bias is a "forward bias" current, unlike all homojunction devices. This can be understood with a detail examination of the energy band diagrams. This work shows the importance of using measured band offsets to aid in understanding the relative Fermi-level alignment instead of using bulk electron affinity values. The work also demonstrates a whole array of playground possible for thin film heterojunction of different materials to engineer an ideal junction for solar cell devices.

4:20pm **EN+TF-TuA8 Growing Low-Dislocation-Density Ge on Si through Nanometer Sized Voids in Chemical Oxide and Subsequent Integration of III-V Films for Multijunction Solar Cells.** *D. Leonhardt, J.J. Sheng*, University of New Mexico, *J.G. Cederberg, M.S. Carroll*, Sandia National Laboratories, *M.J. Romero*, National Renewable Energy Laboratory, *S.M. Han*, University of New Mexico

In an effort to reduce the manufacturing cost of multijunction solar cells, which currently utilize Ge substrates, we have scaled up a process to produce low-defect-density Ge films on 2-inch-diameter Si substrates. This process begins with the nucleation of over  $1 \times 10^{11}/\text{cm}^2$  Ge islands on Si through 3-to-7 nanometer diameter voids in chemical  $\text{SiO}_2$ . It is shown that upon Ge island coalescence, the Ge film primarily contains stacking faults as opposed to threading dislocations. We have found that annealing the Ge islands at an early stage of island growth removes the stacking faults, but results in the formation of  $5 \times 10^7/\text{cm}^2$  threading dislocations upon further growth. Herein, we report on a detailed investigation using transmission electron microscopy (TEM) to clarify the mechanism of the stacking fault formation in the Ge. We will also discuss the effect of annealing both on the Ge island morphology and in eliminating the stacking faults. Additionally, the origin of the threading dislocations obtained after annealing is revealed through the TEM study. Lastly, we report characterization results of GaAs-based double heterostructures integrated on the annealed Ge films, whose photoluminescence intensity over the entire 2-inch wafer is comparable to the same structures grown on commercially available GaAs and Ge substrates.

4:40pm **EN+TF-TuA9 Optimizing Heterojunctions of ZnTe/ZnSe Solar Cells: Effect of Surface Treatment and Growth Conditions.** *F. Fang, B. McCandless, R. Opila*, University of Delaware

II-VI direct band gap semiconductors are attractive for thin film solar cell (TFSC) applications owing to their potential flexibility in tunable optoelectronic properties and possible application in tandem cells for being band gap materials ( $E_G > 2$  eV). For the *n*-ZnSe/*p*-ZnTe heterojunction solar cell, the defect states and electronic band alignment at the ZnSe/ZnTe interface are crucial for device performance. We have employed Al-K $\alpha$  X-ray photoelectron spectroscopy as well as synchrotron source ultra-violet photoelectron spectroscopy to study the surface chemical composition and electronic structures at heterojunction interface. Scanning electron microscopy (SEM) was used to study observe the film microstructure morphology of the interface.

We used two different deposition techniques: Close Space Sublimation (CSS), a low-cost deposition method already demonstrated for high efficiency and commercial CdTe TFSC, and conventional thermal evaporation. Our preliminary results indicated that surface oxides on CSS-grown ZnSe film formed once open to air, and a significant valence band offset induced by this oxide is observed which acts like additional energy barrier for carrier transport, resulting in low open circuit voltage. Also, during sequential CSS deposition of the two stacking films, the covering ZnTe thin film layer growth damage the microstructure of the underlying ZnSe film, i.e., enlarged pores are observed in ZnSe films in the locations where partially covering ZnTe film was deposited. A degraded device performance is expected and low short circuit currents and fill factors of the cells are detected. By analogy to CdS/CdTe TFSC, we are aiming for close-packed column polycrystalline of ZnSe/ZnTe film growth. Therefore, we are exploring etching processes, annealing temperatures and ambient settings to optimize the growth conditions. Evaporation is under investigation, since we have the option of dual-sources in the self-designed chamber, sequential growth of ZnSe and ZnTe films without vacuum break is feasible. Film morphology as well as energy band alignment at the heterojunctions using evaporation growth is being studied.

5:00pm **EN+TF-TuA10**, *M.A. Wolak, S. Gutmann, M.M. Beerbom, C.S. Ferekides, R. Schlaf*, University of South Florida

The layered semi-metal NbSe<sub>2</sub> combines a chemically inert van der Waals surface with a high work function of about 5.8 eV. This motivated an investigation of NbSe<sub>2</sub> as Ohmic hole injection contact for CdTe solar cells. Current back contacts made from Cu suffer from interdiffusion issues leading to cell degradation. In the discussed experiments, the interface between NbSe<sub>2</sub> and CdTe was investigated using x-ray and ultraviolet photoemission spectroscopy (XPS, UPS). In these experiments CdTe and NbSe<sub>2</sub> thin films were grown in-situ in a vacuum chamber attached to the photoemission system. This enabled the investigation of the CdTe/NbSe<sub>2</sub> interface without interference by ambient contamination. After growth of a CdTe thin film, the NbSe<sub>2</sub> film was prepared in several steps. Photoemission spectroscopic characterization between each of the deposition steps allowed the observation of the formation of the band line-up at the interface. The results of the experiments indicate that an intermixed layer forms at the interface. This layer causes the formation of an interface dipole, preventing the formation of an Ohmic contact. A Schottky-type band line-up formed instead.

5:20pm **EN+TF-TuA11 In-Rich InGa<sub>1-x</sub>N Films for Efficient Photovoltaic Devices Grown by ENABLE.** *T.L. Williamson, M.A. Hoffbauer*, Los Alamos National Laboratory, *K.M. Yu, L.A. Reichertz, W. Walukiewicz*, Lawrence Berkeley National Laboratory

The wide band gap tunability of In<sub>x</sub>Ga<sub>1-x</sub>N thin films (0.7 eV to 3.4 eV,  $1 > x > 0$ ) makes them ideal for efficient photovoltaic (PV) devices. However, growing high-quality In-rich In<sub>x</sub>Ga<sub>1-x</sub>N films with strong photoluminescence in the green-to-red portions of the visible spectrum has faced considerable challenges due to indium phase segregation and other materials issues. These challenges have precluded the growth of both In-rich InGa<sub>1-x</sub>N and compositionally graded InGa<sub>1-x</sub>N materials, and make it difficult to grow higher bandgap Ga-rich materials on top of lower bandgap In-rich materials. Overcoming these difficulties using conventional epitaxial techniques is challenging due to the low decomposition temperatures of In-rich materials (e.g. InN~550°C) and the relatively high growth temperatures for Ga-rich materials (e.g. GaN >800°C).

Energetic neutral atom beam lithography & epitaxy (ENABLE) is a low-temperature thin film growth technology recently developed at LANL that utilizes a collimated beam of energetic neutral N atoms (kinetic energies 0.5 to 5.0 eV) to react with evaporated Ga and In metals to grow InGa<sub>1-x</sub>N. ENABLE is similar to MBE, but provides a much larger N atom flux and correspondingly high film growth rate. The high kinetic energy of the reactive N atoms substantially reduces the need for high substrate temperatures, making isothermal growth over the entire InGa<sub>1-x</sub>N alloy composition range possible at rates of >3 microns/hr with no toxic precursors or waste products.

Data on film photoluminescence, crystallinity, electrical properties, doping, and electro-luminescence of In<sub>x</sub>Ga<sub>1-x</sub>N, graded In<sub>x</sub>Ga<sub>1-x</sub>N, and GaN films grown using ENABLE over the full composition range will be presented. ENABLE-grown In<sub>x</sub>Ga<sub>1-x</sub>N films show strong photo- and electro-luminescence spanning the entire visible region of the spectrum, with reasonable carrier mobilities background carrier concentrations typically in the low  $10^{17}$  range. Evidence for p-type doping of In-rich InGa<sub>1-x</sub>N films and characterization of p/n junctions will be discussed along with the prospects for using ENABLE to fabricate efficient PV devices.

5:40pm **EN+TF-TuA12 Copper Oxide Thin Films: Preparation and Modulation of Semiconducting Properties by Electrochemical Methods.** *F. Caballero-Briones*, CICATA-IPN/Universitat de Barcelona, Spain, *A. Palacios-Padrós*, Instituto de Bioingenieria de Catalunya, Spain, *F. Sanz*, Instituto de Bioingenieria de Catalunya/CIBER-BBN, Spain

Copper oxide is a p-type semiconductor with a direct band gap of 2 eV, suitable for photovoltaic applications. In this work we present an electrochemical method to prepare p-type semiconducting Cu<sub>2</sub>O films around 100 nm thick with noticeable photocurrent response. The film properties were modulated by varying different conditions such as the time at a dissolution potential and the film doping with alkaline ions. The modification of the time of exposure to the dissolution potential allows the tailoring of the crystallinity, the band gap energy and the disorder parameter  $E_0$  and also provided elements to outline the growth mechanism of the Cu<sub>2</sub>O films that involve surface reaction, diffusion of oxygen species that react in the solid state accordingly to the point defect model, and heterogeneous deposition of Cu<sub>2</sub>O from the Cu<sup>+</sup> ions dissolved in a chemical bath-like fashion. On the other side, the study of the behavior of different alkaline metal ions (A: Li, Na, K, Cs) present in the electrolyte used to prepare the Cu<sub>2</sub>O films lead to important results. It was observed that important amounts of the alkaline ion (around 1%) can be incorporated to the film and that are indeed electrically active impurities that modify the band gap energy probably by introducing states within the band gap in the case of Cs or by getting incorporated to the crystalline lattice for Na or Li. Changes in the optical absorption, thickness, density of carriers and in defects are related with the size of the employed ion. To complete the study, an electronic diagram of the Cu|Cu<sub>2</sub>O|Electrolyte interface was prepared by using a combination of techniques including Electrochemical Impedance and Electrochemical Tunneling Spectroscopy/Microscopy.

# Wednesday Morning, October 20, 2010

**Energy Frontiers Topical Conference**  
**Room: Mesilla - Session EN+NS-WeM**

## Organic Photovoltaics

**Moderator:** R.J. Holmes, University of Minnesota

8:00am **EN+NS-WeM1 Interface Properties between Organic Blend Films and Metallic Substrates for Solar Cell Applications.** *L. Lozzi, S. Santucci*, University of L'Aquila, Italy

In the last years a strong effort has been devoted to develop new solar cells based on organic compounds. These organic compounds can be mixed with other molecules, as, for example fullerene or its derivatives, forming a blend film to increase the charge separation efficiency. An important issue to evaluate the properties of these devices is to investigate the interface properties between these films and the metallic substrates generally used to realize the contacts.

In this work we have analysed, by using the photoemission spectroscopy (X-ray, Soft X-ray and Ultraviolet photons) the core levels and the valence band structures, in particular the HOMO states, of copper phthalocyanine (CuPc) and fullerene (C<sub>60</sub>) blend films, composed by different CuPc:C<sub>60</sub> concentrations, deposited onto several metallic substrates (Au, oxidized Al and ITO), generally used as metallic contacts.

The molecular levels show, as a function of the blend film thickness and composition, a different behaviour depending on the substrate type. On Au the organic molecular level show, as the blend film thickness increases, a shift towards high binding energy. This shift depends on the organic composition. Depositing the blend film onto oxidized Al, a small shift in the opposite direction, i.e. towards lower binding energy, has been observed. Instead, when ITO substrate have been used, no shift have been observed.

The core levels generally show a different behaviour with respect to the molecular levels suggesting that no strong interaction with the substrates exist but a small redistribution of the molecular levels is present.

8:20am **EN+NS-WeM2 Energy Level Alignment at Conductive Polymer/Metal Interfaces.** *M.M. Beerbom, W. Wang, R. Schlaf*, University of South Florida

The energy level alignment between two prototypical conductive polymers, poly(3-hexylthiophene) (P3HT) and poly[2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylene vinylene] (MEH-PPV) and metals was investigated with ultraviolet and x-ray photoemission spectroscopy (XPS, UPS) dependent on the metal substrate work function. In these experiments thin films of the polymer material were grown in several steps on in-vacuum cleaned metal substrates. In between deposition steps the surface was characterized with UPS and XPS without breaking the vacuum. This was enabled by electrospray polymer thin film deposition directly from solution, which allows the growth of clean macro-molecular films in vacuum. This enabled the measurement of the hole injection barriers and interface dipoles unaffected by environmental contamination artifacts. The presented results demonstrate a systematic dependence of the interface dipole on the substrate work function. This indicates that the charge neutrality level-based "induced density of interface states" (IDIS) model also holds for non-reactive conductive polymer/metal interfaces.

8:40am **EN+NS-WeM3 Electronic Structure of Key Interfaces in Organic Photovoltaic Cells.** *A. Kahn*, Princeton University **INVITED**

This talk reviews recent work on two types of interfaces that are important for organic photovoltaic cells. In the first part, we present the first direct determination via ultra-violet and inverse photoemission spectroscopy (UPS, IPES) of molecular level alignment between donor (D) and acceptor (A) in a bulk heterojunction.[1] We take the example of the interface between poly(3-hexyl thiophene) (P3HT) and [6,6]-phenyl C<sub>61</sub>-butyric acid methyl ester (PCBM). The P3HT/PCBM blend is a standard, prototypical system for bulk heterojunction organic photovoltaic (OPV) cells. In question here is the relative position of the molecular levels of the donor (D) and acceptor (A) materials in the blend, given that LUMO(D) - LUMO(A) is linked to the charge separation process, and LUMO(A) - HOMO(D) is linked to the open circuit voltage (V<sub>oc</sub>) of the OPV cell. A precise measurement of these molecular level offsets provides a firm basis for the accurate modeling of V<sub>oc</sub> produced by these cells. The second part of the talk looks at the electronic structure of transition metal oxide films, such as MoO<sub>3</sub> or WO<sub>3</sub>, and their role as hole-collecting electrode or central element of a charge recombination layer (CRL) in a tandem solar cell. Recent work has shown that these compounds exhibit exceptionally large electron affinity and work function.[2,3] N-doped by oxygen vacancies,

they can act as efficient high work function hole-extractor (via electron injection through their conduction band) on the anode side of the solar cell. Similarly, combined with a low work function interlayer electrode, they form the central element of a CRL in a tandem cell.

[1] Z. Guan, J. Kim, Y.-L. Loo, and A. Kahn, *Org. Electr.* (submitted)

[2] M. Kröger, S. Hamwi, J. Meyer, T. Riedl, W. Kowalsky, and A. Kahn, *Appl. Phys. Lett.* **95**, 123301 (2009)

[3] J. Meyer, M. Kröger, S. Hamwi, T. Riedl, W. Kowalsky and A. Kahn, *Appl. Phys. Lett.* (in press, 2010)

9:20am **EN+NS-WeM5 Photocarrier Generation and Transport Characteristics in Organic Heterojunction Solar Cells.** *J.D. Myers, W.T. Hammond, J.P. Mudrick, J. Xue*, University of Florida

There have been many recent advances in improving the efficiency of organic photovoltaics (OPVs) by using new organic active materials and/or employing improved device architectures. However, our understanding of fundamental OPV device operation principles is still incomplete. A new measurement technique for OPVs, synchronous photocurrent measurement, can give insight into the generation and transport characteristics of photogenerated charge carriers. In synchronous photocurrent measurements, a device is illuminated with chopped monochromatic light in addition to a constant white light bias with an intensity close to 1 sun. With the device biased at any given voltage, the current of the OPV is fed into a lock-in amplifier, which extracts the relevant photocurrent response to the monochromatic light with a varying wavelength.

With this technique, we have shown the bias dependence of the photocurrent for various small-molecule device structures. In planar (or bilayer) and planar-mixed organic heterojunctions (HJs), the photocurrent under forward bias is negative (flowing from the cathode to the anode, opposite to the direction of the dark current), up to high forward biases (~1 V), well in excess of the built-in potential. This reveals the surprisingly dominant nature of the diffusion photocurrent in these architectures. However, for mixed HJ cells, the photocurrent reverses direction at a certain forward bias with the reversal of directions for the electric field and the drift current inside the active layer. There exists a strong correlation between the zero-photocurrent voltage and charge generation profile in mixed HJ OPVs.

This technique can also determine the relative contributions of field-induced exciton dissociation and donor-acceptor interface exciton dissociation in planar HJ cells. Traditionally, exciton dissociation in planar HJ cells is assumed to occur almost exclusively at the donor-acceptor interface; field-induced dissociation is taken as a negligible contributor to the photocurrent in these devices. However, as the thickness of an active layer (either donor or acceptor) increases, field-induced dissociation becomes more important. The field-induced contribution increases as the average location of exciton generation moves greater than one exciton diffusion length away from the interface, as demonstrated by using optical field simulations.

We have further used photocurrent measurements as an instrument in analyzing the recombination behavior in planar organic HJs utilizing different materials. Synchronous photocurrent measurement is a useful technique in determining the photocarrier behavior in organic HJ solar cells.

9:40am **EN+NS-WeM6 Interface Engineering for Improved Organic Photovoltaic Performance.** *C.K. Chan, D.S. Germack, P. Haney, L.J. Richter, D.M. DeLongchamp, D.J. Gundlach*, National Institute of Standards and Technology

Organic photovoltaic (OPV) cells are attractive for flexible, low-cost, large-area, and lightweight solar conversion applications. Despite this demand, robust and efficient devices have been limited by the quality of organic semiconductor materials and by the poor understanding and control of their interfaces. Interface modification using self-assembled monolayers or conducting polymers can be leveraged to tune the composition and phase segregation in binary bulk heterojunction photovoltaic cells. In this work, the interface composition of a 1:1 mixture of poly(3-hexylthiophene):[6,6]-phenyl-C<sub>61</sub>-butyric-acid-methyl-ester (P3HT:PCBM) was characterized using near-edge x-ray absorption fine structure (NEXAFS) spectroscopy as a function of surface energy. The substrates consisted of a low surface energy Nafion-based copolymer, 4-phenylbutyltrichlorosilane or octyltrichlorosilane self-assembled monolayers on SiO<sub>2</sub>, or high surface energy native SiO<sub>2</sub>. It was observed that while the free surface of the film was always P3HT-rich (7:3 P3HT:PCBM), the bottom interfacial composition varied from P3HT-rich (4:1 P3HT:PCBM) to PCBM-rich (1:4 P3HT:PCBM) as the surface energy of the substrate increased from 20 mN/m<sup>2</sup> to 80 mN/m<sup>2</sup>. These observations were further supported by electrical characterization of bulk heterojunction films deposited on thin-film transistor structures where the surface energy of the gate dielectric was

modified with self-assembled monolayers. The transistor performance exhibited higher hole mobility at P3HT enriched organic-dielectric interfaces (low surface energy substrates), while ambipolar transport was observed in devices with a PCBM enriched interface (high surface energy substrates). These observations of surface energy dependant interfacial composition should have clear implications for optimizing photovoltaic cell design in regards to "conventional" and "inverted" device architectures. However, P3HT:PCBM bulk heterojunction solar cells constructed on low and high surface energy substrates in conventional and inverted device structures exhibit nominally identical performance. Early efforts at modelling the effect of compositional gradients on photovoltaic performance suggest that this is expected given that current densities increase in constricted percolation pathways to maintain constant overall current. Although this may have little impact on initial device performance, the effects of higher current densities in the constricted interfacial regions on device lifetime are currently being investigated.

10:40am **EN+NS-WeM9 Experimental and Theoretical Investigation of Excitonic Energy Transfer in Organic Photovoltaic Cells, W.A. Luhman, R.J. Holmes, University of Minnesota**

This work demonstrates a novel approach for measuring the Förster radius of energy transfer between electron donating and accepting materials commonly used in organic photovoltaic cells (OPVs). Typically an exciton must diffuse to an electron donor-acceptor interface in order to be dissociated and contribute to photocurrent. Alternatively, if an exciton in the donor layer is instead able to undergo long-range energy transfer to the acceptor layer, diffusion is no longer required, and dissociation occurs from the acceptor layer. While such processes are surprisingly common in OPVs, they are often incorrectly ignored in measurements of the exciton diffusion length and in models of device performance. In this work, the efficiency of energy transfer between an emissive donor and an absorptive acceptor is investigated using complementary experimental and theoretical techniques. This is accomplished by spatially separating the donor and acceptor materials using a wide energy gap spacer layer to suppress charge transfer, and tracking the donor photoluminescence as a function of spacer layer thickness. Fitting experimental data obtained for a variety of small molecule and polymer donor materials allows for the extraction of Förster radii that correlate very well with predicted values. The effect of energy transfer on device performance and on measurements of the exciton diffusion length is also investigated using the archetypical small molecule donor material boron subphthalocyanine chloride (SubPc). An exciton diffusion length of  $(7.5 \pm 0.4)$  nm is extracted from photoluminescence quenching experiments that carefully account for the role of energy transfer. These results will ultimately provide insight into the fundamental processes of exciton diffusion and dissociation in OPVs.

11:00am **EN+NS-WeM10 Molecular Architecture and Charge Separation at Abrupt Donor-Acceptor Interfaces, G.J. Dutton, NIST, W. Jin, University of California at San Diego, D.B. Dougherty, North Carolina State University, W.G. Cullen, University of Maryland, S.W. Robey, NIST, J.E. Reutt-Robey, University of Maryland**

Photocurrent production in organic photovoltaic structures differs fundamentally from current generation in inorganic semiconductor solar cells. Dissociation of excitons formed by optical absorption in organic materials requires heterointerfaces between electron donor and acceptor components. The extent to which molecular architecture, particularly along the donor-acceptor interface, impacts electronic level alignment and charge separation is of fundamental interest. In this work, we prepare well-defined molecular interfaces by the physical vapor deposition of select donor (MPc, Pn) and acceptor ( $C_{60}$ ) components under UHV conditions. We determine the detailed structure of the donor-acceptor interface with Scanning Tunneling Microscopy and establish a correlation with electron band alignment (PES) and exciton dynamics (2PPES).

For technologically relevant interfaces between  $C_{60}$  and donors such as pentacene (Pn) or phthalocyanines (Pc), distinct structures/molecular orientations can be selectively engineered by organic MBE through deposition sequence and flux. For the case of  $C_{60}$  and Pn, "co-facial"  $C_{60}$ -Pn interfaces are formed by  $C_{60}$  deposition on crystalline Pn bilayer films supported by Ag(111), whereas "edge-on"  $C_{60}$ -Pn interfaces result from Pn deposition on hexagonal close-packed  $C_{60}$  monolayers supported by Ag(111). Such "edge-on" interfaces expand into large dendritic islands, as per reported "thin-film" phases, and support  $C_{60}$  cluster formation under subsequent  $C_{60}$  deposition. We show how electronic level alignments critical to  $V_{oc}$  and charge separation efficiency are impacted by these structural changes, and extend this information to other small-molecule cases, ZnPc: $C_{60}$  and perfluorinated ZnPc, as time permits.

Finally, for interfaces between CuPc and  $C_{60}$ , we will present the first studies of charge separation at well-characterized organic donor-acceptor interfaces using TR-2PPE. By pumping the CuPc Q-band at 1.65eV, a time-delayed UV pulse then probes the excited state population. We identify

dominant relaxation processes on timescales from 100fs to >100ps. By varying the CuPc film thickness, we observe significantly enhanced charge transfer of the singlet exciton at the interface with  $C_{60}$ . Following the population dynamics as a function of energy also provides evidence for recombination from charge transfer states back to the low-lying CuPc triplet.

This work has been supported in part by the NSF under the UMD MRSEC (DMR0520471) and the Surface & Analytical Chemistry Program (CHE0750203).

11:20am **EN+NS-WeM11 Hybrid Organic/Inorganic Solar Cells Based on Silicon Nanowires, M. Pietsch, Max Planck Institute for the Science of Light, Germany, V.A. Sivakov, B. Hoffmann, G. Broenstrup, F. Talkenberg, Institute of Photonic Technology, Germany, T. Seyller, Friedrich-Alexander Universität Erlangen-Nürnberg, Germany, T. Fritz, B. Schroeter, Friedrich-Schiller University Jena, Germany, S.H. Christiansen, Max Planck Institute for the Science of Light, Germany**

Organic polymer solar cells have received a lot of attention as a promising approach to future photovoltaic energy sources due to their mechanical flexibility and their potential for low cost mass production, high open-circuit voltage values. From another side the hybrid organic/inorganic solar cells containing nanocrystals/nanowires of inorganic semiconductors (e.g. silicon) are promising for several reasons: (i) inorganic semiconductors have a much broader absorption spectrum than organic semiconductors; (ii) nanostructures can be doped to a specific *n*- or *p*-type doping level; (iii) nanostructures provide a large interface to the organic counter part due to their high surface to volume ratio.

The main topic of our research is focused on the formation of the hybrid organic/inorganic solar cells based on the silicon 1D nanostructures. The hybrid solar cells (presented here) are based on silicon nanowires (SiNWs) performed by two different approaches. A Vapor-Liquid-Solid (VLS) mechanism in a conventional chemical vapor deposition (CVD) chamber or electroless wet-chemical etching procedure was applied for the SiNWs realization. As-grown SiNWs are single crystalline and have a smooth (VLS SiNWs) or rough (etched SiNWs) surface covered with a thin oxide layer. Both types of SiNWs show enhanced absorption compared to bulk silicon in the visible spectrum and best results were achieved with etched arrays exhibiting absorption of 90 % over a broad spectral range (300-2000 nm). In a further step the huge nanowire surface was functionalized into a charge separation interface for solar cells by the depositing of semiconducting polymers upon them. To get a detailed picture of charge carrier separation at the organic/inorganic interface XPS/UPS measurements were performed to estimate band alignment between SiNWs and different polymers like PEDOT:PSS or P3HT. The Al:ZnO transparent conductive oxide (TCO) as a contact to the polymer coated SiNWs was realized by applying atomic layer deposition (ALD) technique which allowed us to cover SiNWs with precisely uniform Al:ZnO thin layer. For all device concepts based on SiNWs, the crystal structure, geometry (alignment of SiNW with respect to the substrate), interfacial properties between the SiNW and polymers are a key of importance for functioning of the PV devices. For this reason, the microstructure and optoelectronic properties (optical, microstructure) of the organic/inorganic solar cell will be presented and discussed in details during our presentation.

11:40am **EN+NS-WeM12 Influence of UV Radiation on Charge Injection Barriers in Dye-Sensitized Solar Cells, S. Gutmann, M.A. Wolak, M.M. Beerbom, R. Schlaf, University of South Florida**

The electronic structure of the interfaces in dye-sensitized solar cell structures was investigated using x-ray and ultraviolet photoemission spectroscopy (XPS, UPS). Electro spray thin film deposition in high vacuum was used to build the interfaces of interest directly in vacuum without exposure to the ambient. Electro spray enables the fabrication of clean, essentially uncontaminated thin films of organic molecules and nanoparticles directly in vacuum.

The experiments focused on the investigation of the indium tin oxide (ITO)/nanocrystalline  $TiO_2$  interface, as well as the characterization of the  $TiO_2/RuL_2(NCS)_2$  [cis-bis(4,4'-dicarboxy-2,2'-bipyridine)-bis(isothiocyanato)-ruthenium(II)] ("N3", a prototypical dye used in many currently pursued device structures)-dye interface. Both  $TiO_2$  and N3 films were built up in several steps. After each step, characterization by XPS and UPS was performed. The resulting sequence of spectra allowed the determination of charge injection barriers and interface dipoles at the ITO/ $TiO_2$  and  $TiO_2/N3$  interfaces. Our experiments revealed a strong influence of the UV radiation during UPS measurements on the band line-up at these interfaces. This was revealed though low intensity x-ray photoemission spectroscopy (LIXPS) measurements, which allow the measurement of the work function prior to UV exposure. These results suggest that even low-level UV radiation, such as encountered in an encapsulated solar cell, may lead to cell degradation

over time due to a re-alignment of the electronic structure with detrimental effect on charge transport.

## Energy Frontiers Topical Conference Room: Pecos - Session EN+TF-WeM

### CIGS, CZTS and Chalcopyrite Films & Solar Cells

**Moderator:** E.S. Aydil, University of Minnesota

8:00am EN+TF-WeM1 CIGS and CZTS Nanocrystal-Ink Solar Cells, H.W. Hillhouse, R. Agrawal, Q. Guo, G.M. Ford, Purdue University  
**INVITED**

The development of suitable colloidal nanocrystal inks are a key step in the development of low-cost solar cells since they enable the use of fast and inexpensive coating processes such as spray coating and roll coating to form a thin film photoabsorbing layer. Chalcopyrite structure copper indium gallium diselenide (CIGSe) and stannite or kesterite copper zinc tin sulfides (CZTS) are key photoabsorbing materials for thin film solar cells due to their near ideal band gap and their serendipitous defect chemistry (CIGSe) and Earth abundance (CZTS). Although several methods have been reported that describe the synthesis of CIGSe and related nanocrystals, precise control of the composition for these ternary and quaternary compounds has been problematic [1]. We have reported the solution-phase synthesis of stoichiometric chalcopyrite structured CuInSe<sub>2</sub> nanocrystals [2], Cu(In,Ga)S<sub>2</sub> [3], and the very first synthesis of Cu<sub>2</sub>ZnSnS<sub>4</sub> nanocrystals [4]. The syntheses proceed rapidly from elemental and halide reagents via a simple batch reaction without "hot injection" in a single component coordinating solvent. We have demonstrated the use of these nanocrystals for low-cost solar cells by fabricating devices without using any oxygen-free techniques (after NC synthesis) and employing a scalable roll coating method. The nanocrystal inks are first coated on a back contact (Mo coated sodalime glass in this case). The nanocrystal layer is then easily consolidated into large crystalline domains by a brief thermal treatment in a selenium rich atmosphere to prevent selenium loss or to replace sulfur with selenium. The fabricated cells are robust and increase in efficiency with time, exhibiting similar serendipitous defect chemistry as layers formed by vacuum co-evaporation. We have fabricated solar cells by roll coating CIGS or CZTS nanocrystal-inks over large areas. CIGS devices fabricated by roll coating over large areas with a device architecture of Mo/CIGSSe/CdS/i-ZnO/ITO/Ni/Al are (at the time of the abstract submission) 12.0% efficient under standard AM1.5G illumination. The presentation will focus on the key aspects of the nanocrystal synthesis, ink coating, nanocrystal consolidation, and device fabrication and characterization for both CIGS and CZTS solar cells.

[1] Hillhouse H.W. & Beard M.C., Current Opinion in Colloid & Interface Science, 14, 245 (2009).

[2] Guo, Q.J., Kim, S.J., Kar, M., Shafarman, W.N., Birkmire, R.W., Stach, E.A., Agrawal, R., Hillhouse, H.W., Nano Letters 8, 9, 2982 (2008).

[3] Guo, Q.J., Ford, G.M., Hillhouse, H.W., Agrawal, R., Nano Lett. 9, 8 3060 (2009).

[4] Guo, Q.J., Hillhouse, H.W., Agrawal, R., J. Am. Chem. Soc. 131, 11672 (2009).

8:40am EN+TF-WeM3 Compositional (non)Uniformity and its Effect on CIGS Solar Cell Performance, W. Li, S.R. Cohen, K. Gartsman, P. von Huth, R. Popovitch-Biro, Weizmann Institute of Science, Israel, Th. Rissom, Helmholtz Zentrum Berlin, Germany, D. Cahen, Weizmann Institute of Science, Israel

CIGS is a promising material for solar cell applications. Uniformity of the polycrystalline composition and structure is an important factor in the solar cell performance. This work is an attempt to study CIGS (non)uniformity systematically as a function of depth, employing independent, complementary high resolution techniques which also reveal inter- and intra-grain compositional, structural, and electronic nonuniformities. In particular, thin cross-sections, prepared by field ion beam (FIB), were studied using TEM-based techniques to achieve higher spatial resolution of the composition than is normally possible. It was found that the Ga/In ratio in the devices drops initially with depth, then rises sharply again near the Mo contact. Furthermore, large variations of this ratio are observed from grain to grain. This variation is even observed within individual single crystal grains along their growth direction. Our measurements confirm the formation of a MoSe<sub>2</sub> phase at the Mo - CIGS interface. The lattice constant, measured by selected area diffraction (SAD), varies with the Ga composition, in agreement with Vegard's law. The extent of compositional variation was found to vary inversely with the temperature of sample

preparation. Additionally, our measurements confirm the formation of a MoSe<sub>2</sub> phase at the Mo - CIGS interface.

A series of scanning probe (SPM)-based techniques, including scanning capacitance microscopy (SCM) and conducting probe atomic force microscopy (CP-AFM) were applied to correlate local device performance and doping concentration with the compositional (non)uniformity revealed in these TEM results and will be presented here.

This compositional non-uniformity may well be of relevance for the properties and performance of solar cells made with such films, and this issue will be addressed in the talk.

9:00am EN+TF-WeM4 Combinatorial Cd<sub>1-x</sub>Zn<sub>x</sub>S Thin Films Deposited with a Continuous Flow Microreactor, K.M. McPeak, Drexel University, H.P. Bui, T.P. Beebe, University of Delaware, J.B. Baxter, Drexel University

Chemical bath deposited CdS thin films are commonly used as buffer layers in CdTe and CIGS photovoltaics because they form a high quality *p-n* junction with the absorber. However, light absorption by the CdS reduces solar cell efficiency. Cd<sub>1-x</sub>Zn<sub>x</sub>S has a wider band gap than CdS, offering the potential to reduce deleterious absorption of light in the 300-550 nm range and improve current densities by over 2 mA/cm<sup>2</sup>. To maximize energy conversion efficiency, the Cd<sub>1-x</sub>Zn<sub>x</sub>S should be a single-phase ternary alloy and the stoichiometry should be optimized to ideally position the conduction band edge for increased transmissivity while retaining good junction properties.

We report on chemical bath deposition of combinatorial Cd<sub>1-x</sub>Zn<sub>x</sub>S thin films using a continuous flow microreactor. The microreactor uses a sub-millimeter reaction channel, with the substrate acting as one reactor wall. The microreactor behaves like a plug flow reactor whereby the bath composition changes as flowing material is deposited on the substrate. While the bath composition changes with respect to position down the reaction channel, the composition at any position is time-invariant. The graded bath composition results in deposition of graded thin films whose stoichiometry and optoelectronic properties change significantly over length scales of millimeters to centimeters. Spatially resolved characterization of the substrate enables rapid and direct correlation of material properties to growth conditions, which is not possible with a batch reactor where bath composition changes with time.

Graded Cd<sub>1-x</sub>Zn<sub>x</sub>S films grown with 1:200 Cd:Zn bath composition at the inlet had composition that varied from x=0.0 to x=0.17 over a distance of 12 mm on a single substrate. Film stoichiometry was determined by x-ray photoelectron spectroscopy (XPS) mapping. Stoichiometry changes because of differences in speciation and reaction kinetics of the cation species as they flow down the channel. XPS and XRD confirm that CdZnS is a single phase material. Deep level emission in photoluminescence and XPS indicate that O and OH is also incorporated into the film and is bound to Zn, with amount increasing further down the reaction channel. The graded stoichiometry causes the absorption edge to blue-shift by over 80 nm, as determined by UV-vis transmission and reflectance measurements. Blue-shifting band edge and changes in defect density are also seen by photoluminescence. The continuous flow microreactor offers new potential for deposition of graded thin films that act as combinatorial libraries for high throughput screening and accelerated materials discovery.

9:20am EN+TF-WeM5 A Chemical Bath Process for Depositing Cu<sub>2</sub>ZnSnS<sub>4</sub> Photovoltaic Absorbers, A. Wangperawong, J.S. King, S.M. Herron, B.P. Tran, K. Pangan-Okimoto, S.F. Bent, Stanford University

Inorganic thin film photovoltaics are an attractive technology for achieving large-scale deployment of inexpensive, stable, and efficient solar cells. However, current leading thin-film materials, such as CdTe and CIGS, face production limitations at a global scale as they contain both non-abundant and toxic elements. A material that has gained significant attention is Cu<sub>2</sub>ZnSnS<sub>4</sub> (CZTS), which is not constrained by the drawbacks of CdTe and CIGS and has an ideal bandgap for a single junction photovoltaic device of 1.4-1.5 eV. Several groups have studied the fabrication of CZTS solar cells using a variety of methods ranging from sol-gel processing to sputter deposition, with a record efficiency of 9.6% recently reported. In the present work, we report an alternative water-based method for large area deposition of CZTS thin films that does not require expensive or complex equipment. Specifically, thin films of CZTS were fabricated on silicon, glass and molybdenum-coated substrates through a combination of chemical bath deposition, ion exchange and sulfurization heat treatment. The film composition could be controlled through a combination of number and length of chemical bath steps and ion exchange time. The resulting samples were analyzed by scanning electron microscopy (SEM), Auger electron spectroscopy (AES), X-ray diffraction (XRD), Raman spectroscopy, inductively-coupled plasma optical emission spectroscopy (ICP-OES), and diffuse reflectance absorption spectroscopy. XRD, Raman, and UV-Vis optical spectra are consistent with the formation of CZTS. The

results show that the process produces thin films of CZTS exhibiting uniform composition, well-defined crystal structure, and good optical properties with a bandgap of 1.45 eV. Complete solar cell devices made with chemical bath-deposited CZTS were fabricated. Measurements on these devices exhibit photovoltaic and rectifying behavior, and the results will be discussed.

9:40am **EN+TF-WeM6 Synthesis Routes for  $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$  Thin Film Absorbers**, R. Krishnan, T.B. Song, V.U. Chaudhari, University of Florida, E.A. Payzant, Oak Ridge National Laboratory, R. Noufi, National Renewable Energy Laboratory, T.J. Anderson, University of Florida

Chalcopyrite  $\text{Cu}(\text{In,Ga})\text{Se}_2$  is one of the most promising absorber materials for high efficiency thin film solar cells with reported conversion efficiency exceeding 20%. The National Solar Technology Roadmap for CIGS PV specifically calls for deposition rates of “30–40  $\mu\text{m}/\text{h}$  and  $<1 \mu\text{m}$  CIGS absorber thickness” by 2015. This is compared to the current estimate in the Roadmap of “5  $\mu\text{m}/\text{h}$  and 1.25–3  $\mu\text{m}$  CIGS absorber thickness.” The comparison translates into a reduction of the absorber synthesis time from ~15 to 36 min to ~1.5 to 2 min. The challenge is to get high throughput and yield with columnar grain growth while retaining the high efficiency. In this work *in-situ* high temperature X-ray diffraction with and without selenium overpressure is used to determine absorber synthesis mechanisms for various precursors structures. Qualitative analysis of the data gives information on the reaction pathway and quantitative analysis of the data yields rate constants.

This presentation summarizes studies on the selenization of elemental stacked layers of copper, indium, gallium and selenium in two different configurations. In the first configuration (sample A), copper was first deposited on glass/Mo substrates, followed by gallium, indium and selenium. In the other configuration (sample B), gallium was first deposited followed by indium, copper and selenium. ICP results showed that both the samples were copper poor. Reaction pathways were followed with and without selenium overpressure and isothermal soaking experiments were performed to obtain the kinetic parameters using the Avrami growth model to reduce the data. The reaction pathways were similar for both the configurations, showing formation In,  $\text{Cu}_9\text{Ga}_4$ , and  $\text{Cu}_2\text{Se}$  initially, followed by Se crystallization and formation of the intermediates  $\text{In}_4\text{Se}_3$ ,  $\text{CuSe}_2$ ,  $\text{CuSe}$  and CIS, and finally yielding product  $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ . The value of x computed from Vegard's law yielded 0.35 for sample A and 0.37 for sample B. The activation energy computed from the Avrami model yielded 88.4( $\pm 12$ ) and 125.1( $\pm 9$ ) kJ/mole for samples A and B, respectively. The decrease in the local Avrami exponents (0.21-0.26) suggests the existence of an inhomogeneous distribution of nuclei during growth or interdiffusion of gallium and indium with simultaneous grain growth. Additional characterization such as SEM and TEM were performed to provide physical and compositional support of the pathway.

10:40am **EN+TF-WeM9 Atmospheric Processing Approaches to Low Cost Scalable Photovoltaics**, M.F.A.M van Hest, A. Miedaner, C.J. Curtis, J. Leisch, P. Hersh, National Renewable Energy Laboratory, K. Steirer, R.M. Pasquarelli, J.A. Nekuda, R.P. O'Hayre, Colorado School of Mines, D.S. Ginley, National Renewable Energy Laboratory **INVITED**

Solar photovoltaics are becoming an increasing part of the energy supply mix, however to have a really significant impact they must become cost competitive with more conventional energy sources. Direct write ink based methods could help toward this significant cost reduction. We are investigating solution precursors and ink based atmospheric deposition approaches to a variety of solar cell materials and processes. The first application we are studying is inkjet printing of contacts for photovoltaics in particular for Si solar cells. We have developed metal organic decomposition inks for silver, nickel, copper and aluminum for example. Conductivities close to that of bulk metals were obtained. The second application is the formation of the absorber layer in  $\text{CuInSe}_2$  (CIS) based photovoltaics. CIS/CIGS is the most efficient thin film photovoltaic technology, but typically employ capital-intensive PVD materials deposition and subsequent selenization steps. Our approach uses liquid based precursors that can be inkjet printed and processed under atmospheric conditions. Various precursors were identified leading to  $\text{In}_2\text{Se}_3$ ,  $\text{Cu}_2\text{Se}$  and  $\text{CuInSe}_2$  films without a selenization step on various substrates. Similar chemistries are applicable to copper zinc tin sulfide (CZTS) materials which are potentially more scalable. Details of film deposition and processing for these systems will be discussed. The third application is in the field of organic photovoltaics. Here inkjet printing is used to deposit the photoactive layer such as a polythiophene, for example P3HT, and the conducting contact layer such as PEDOT/PSS. Details will be shown on how solvents can influence the quality of the printed material. Direct write processing of these materials may be enabling for this technology leading to an all printed photovoltaics.

# Wednesday Afternoon, October 20, 2010

## Energy Frontiers Topical Conference

Room: Mesilla - Session EN+NS-WeA

### Nanostructures for Energy Conversion & Storage I

Moderator: S. Agarwal, Colorado School of Mines

2:00pm EN+NS-WeA1 **Electrochemical Performance of Nanostructured Sn Thin Films as Anodes of Thin film Li-ion Battery.** C.S. Nimisha, G. Venkatesh, T. Dhivya, G. Mohan Rao, N. Munichandraiah, Indian Institute of Science, India

Nanostructured Sn thin films have been prepared by rf sputtering and thermal evaporation on to silicon substrates for evaluating the electrochemical performance to use as anode layer of thin film Li-ion battery. The scanning electron microscopy (SEM) shows different film morphologies for evaporated and sputtered films which directly control the electrochemical performance. Crystallinity of the deposited films were ensured by X-ray diffraction (XRD). Bio-Logic SA potentiostat / Galvanostat (model:VPM3) is used for testing electrochemical performances. Sn thin films prepared by thermal evaporation from Sn granules of 99.99% purity resulted in films with nanograins of ~200nm size homogeneously distributed over the surface. Whereas films made by rf sputtering from Sn target (99.99% purity) with Ar as sputtering gas at a pressure of  $5 \times 10^{-3}$  mbar, resulted in highly porous film surface with 'nanobead' (~50nm size) formation inside the edges.

For electrochemical studies half cells were assembled using lithium as counter and reference electrodes in 1M LiAsF<sub>6</sub> dissolved in ethylene carbonate and dimethyl carbonate electrolyte. Charging was done with a constant current density of  $10 \mu\text{A} / \text{cm}^2$  up to 1.2 V, followed by discharging at  $10 \mu\text{A} / \text{cm}^2$  down to 0.2 V. The capacity obtained from both evaporated and sputtered films clearly shows the three plateau regions of lithiation and delithiation for both evaporated and sputtered films. From the evaporated film, a discharge capacity of  $83.6 \mu\text{Ah}/\text{cm}^2$  is obtained, whereas from sputtered film a much higher capacity of  $886 \mu\text{Ah}/\text{cm}^2$  is obtained.

We speculate that the increased surface area of the rf sputtered Sn film due to the porous nature and the presence of nano beads, resulted in higher capacities than the evaporated Sn films, which have relatively bigger sized grains. Also the presence of more nano sized features in the sputtered film surface reduces the pulverization of Sn films during cycling since the absolute volume change would be minimized. The reduction in diffusion length for Li-ion and increased effective surface area ensures higher discharge capacity from rf sputtered Sn films compared to evaporated films. The higher discharge capacity obtained from rf sputtered Sn thin films makes it ideal candidate for integrating as anode layer of thin film Li-ion battery.

2:20pm EN+NS-WeA2 **Lithographically Defined Porous Carbon Electrodes.** R. Polsky, B. Burckel, X. Xiao, C.M. Washburn, M. Roberts, B. Bunker, Sandia National Laboratories, A. Raub, S. Brueck, University of New Mexico, S. Brozik, D.R. Wheeler, Sandia National Laboratories

Pyrolyzed Photoresist Films (PPF) have electrochemical properties similar to glassy carbon electrodes with the unique feature that they can be lithographically defined to create microstructures and microfeatures. Previously we reported that the near atomically flat surface of PPF results in the deposition of gold nanoparticles (1-3 nm) with narrow size distributions. [1] Herein we describe the fabrication of porous carbon structures using interference lithography (IL) to generate 3-D structures in PPF that contain five patterned layers with microporous hexagonal lattices (~800 nm in diameter). [2] Because IL is a maskless approach porous carbon structures are able to be patterned over large volumetric areas (2.5 X 2.5 cm). We demonstrate the porous carbon structures can be used as a highly adaptable electrode material suitable for the deposition of metal nanoparticles (Au, Ag, and Pt) and conducting polymers with possible applications in such areas as fuel cells, ultracapacitors, and biosensors.

#### References

- [1] R. Polsky, C.M. Washburn, G. Montano, H.Q. Liu, T.L. Edwrads, D.M. Lopez, J.C. Harper, S.M. Brozik, D.R. Wheeler, *Small*, **2009**, 5, 2510-2513.
- [2] D.B. Burckel, C.M. Washburn, A.K. Raub, S.J. Brueck, D.R. Wheeler, S.M. Brozik, R. Polsky, *Small*, **2009**, 5, 2792-2796.

2:40pm EN+NS-WeA3 **Designing Inorganic Nanostructures for Solar Cells and Energy Storage Devices.** Y. Cui, Stanford University INVITED

The capability of synthesizing materials with nanometer size and shape control has enabled exciting opportunities to engineer materials for controlling and understanding electronic, photonic, mechanical and ionic

processes, which are important for applications such as energy conversion and storage devices. In this talk I will show two examples on how we design nanoscale materials towards high performance photovoltaics and energy storage devices. In the first example, nanocone- and nanodome-shaped substrates are designed for efficient photon management and charge carrier separation, which result in significant improvement of solar cell power efficiency compared to the flat film devices. Second, nanowires are exploited to maximize efficiency of simultaneous electron and ionic insertion with facile strain relaxation, which enable novel ultrahigh capacity storage capacity materials towards next generation of high energy density batteries.

4:00pm EN+NS-WeA7 **Synthesis of Rare Earth Ion Co-Doped Core-Shell Nanostructures for Improved Energy Generation Efficiency.** J.A. Dorman, J. Hoang, J.H. Choi, J.P. Chang, University of California, Los Angeles

The development of rare-earth ion (RE) doped phosphors allows for the conversion of photons at various wavelengths to those at energies similar to that of the photovoltaic band gap. Work has been shown that through the incorporation Er<sup>3+</sup> and Yb<sup>3+</sup> into complex metal oxides, specifically yttrium based compounds, both energy upconversion and downconversion can be utilized to convert absorbed photons to a more desirable energy for Si based solar cells. However, both photoluminescence and energy transfer mechanisms are highly susceptible to the local crystal environment, including the overall crystal field and surrounding molecules. The addition of a shell layer increases luminescence by decreasing the effect of surface quenching sites while promoting energy transfer between layers.

This work focuses on the synthesis of core-shell nanostructures while controlling the luminescence spectrum through the spatial distribution within the particle architecture using a combination of wet chemical synthesis and atomic layer deposition (ALD). Y<sub>2</sub>O<sub>3</sub>: Er<sup>3+</sup>, Yb<sup>3+</sup> core nanoparticles (NPs) were synthesized using the molten-salt synthesis. Enhanced luminescence was observed after deposition of a high quality shell of Y<sub>2</sub>O<sub>3</sub>: Yb<sup>3+</sup>, roughly 5-10 nm thick, by radical enhanced ALD. However, the deposited shell layer has a slightly lower density, as shown in TEM imaging. The downconversion and upconversion luminescence spectra was collected for Y<sub>2</sub>O<sub>3</sub>:Er<sup>3+</sup>, Yb<sup>3+</sup> NPs, 1 mol % Er<sup>3+</sup> and the Yb<sup>3+</sup> mol % ranging from 0 to 8 %, with a 980 nm diode excitation. The various NPs cores emitted strongly in the green (532 nm) and red (650 nm) upconversion luminescence and IR (1540 nm) downconversion luminescence, the <sup>2</sup>H<sub>11/2</sub>, <sup>4</sup>S<sub>3/2</sub>→<sup>4</sup>I<sub>15/2</sub>, <sup>4</sup>F<sub>9/2</sub>→<sup>4</sup>I<sub>15/2</sub> and <sup>4</sup>I<sub>13/2</sub>→<sup>4</sup>I<sub>15/2</sub> transitions, respectively. A systematic luminescent red shift, ~2 nm, was observed when comparing the core to core-shell structures for all samples. Visible luminescence occurs via an energy transfer process, requiring two absorbed photons (red) and three absorbed photons (green), between the Yb<sup>3+</sup> <sup>2</sup>F<sub>5/2</sub> and Er<sup>3+</sup> <sup>4</sup>I<sub>11/2</sub> and <sup>4</sup>I<sub>13/2</sub> energy levels. The proposed energy transfer mechanism incorporates the interaction between RE ions at the core-shell interface based on the local binding environment modeled using enhanced x-ray absorption fine structure (EXAFS) spectroscopy. Additionally, the energy transfer coefficients are extracted using the excitation lifetimes and the red-to-green ratio is correlated to key spectroscopic parameters, such as the Judd-Ofelt parameters and branching ratio. These values can be compared to the bulk Y<sub>2</sub>O<sub>3</sub> luminescence and the actual measured lifetimes, 200 ms (green) and 600 ms (red), as the figure of merit.

4:20pm EN+NS-WeA8 **High Figure of Merit Nanostructured Bulk Thermoelectrics from Doped Pnictogen Chalcogenide Nanoplate Crystals.** R.J. Mehta, C. Karthik, B. Singh, Y. Zhang, E. Castillo, T. Borca-Tasciuc, G. Ramanath, Rensselaer Polytechnic Institute

Nanostructured pnictogen chalcogenides are attractive for realizing high thermoelectric figure of merit (ZT) materials for solid-state refrigeration and electrical power harvesting from heat. Here, we report a scalable surfactant-assisted microwave synthesis approach to realize bulk assemblies of sulfur-doped nanostructures with 25% to 250% higher room temperature ZT than the non-nanostructured bulk counterparts of both n- and p-type nanostructured bulk materials with room temperature ZT ~ 1. We synthesized ~5- to 20-nm-thick single-crystal hexagonal sulfur-doped nanoplates of the pnictogen chalcogenides in a microwave oven, followed by compaction and sintering to obtain bulk nanostructured pellets. The n-type material was obtained from single-component nanostructure assemblies of bismuth chalcogenides, while the p-type material was obtained by mixing bismuth telluride and antimony telluride nanostructures. Electron spectroscopy shows that <1% sulfur doping from thioglycolic acid, used as a nanoplate-sculpting and surface-passivating agent, increases the power factor  $\alpha^2\sigma$  to ~5% greater than that of the state of the art alloys. Electron microscopy analyses reveal that measured k values as low as 0.5 – 1.4 W/mK, which are ~50% lower than bulk alloys, are due to 50-100 nm



grains with intragrain structural modulations with characteristic wavelengths between 3-10 nm. Our findings open up completely new possibilities for realizing novel high ZT thermoelectric materials through the assembly of doped single-crystal nanostructures.

4:40pm **EN+NS-WeA9 Core-Shell Nanodielectrics through Hybrid Wet Chemistry/Laser Process for Embedded Energy Storage Capacitors**, **B. Rajesh**, University of Houston, *N. Badi*, University of Houston and Integrated Micro Sensors, Inc., *A. Bensaoula*, *R. Supparesk*, *T.R. Lee*, University of Houston

Extensive interest is being invested into the research of nanodielectrics because of their promising applications in energy storage solutions as both discrete and embedded capacitors. They are useful in integral passive technology for miniaturization, improvement of power distribution and as decoupling capacitors. Their applications include, but are not limited to, high speed computing boards (servers, routers, super computers) and module boards (cell phones, PDA, note book computers). We fabricated high capacitance density dielectrics for flexible electronics by embedding core-shell type gold-silica nanoparticles in a polymer matrix using a coupled sol-gel procedure with laser engineering technique.

We report on fabrication of nanodielectric capacitors based on core-shell nanoparticles embedded in polyvinyl pyrrolidone (PVP) dielectric matrix. We developed a process chain to optimize the use of PVP as dielectric and measured its dielectric constant (K) as 7 at 10 KHz and breakdown field as 130V/ $\mu\text{m}$ . Monodispersed core-shell nanoparticles (NPs) are prepared with two different structures: 1) 35nm gold core – 95nm silica shell and 2) coating 35nm gold NPs with polymer compatible self assembled monolayer (SAM). Pre-processing is performed to uniformly disperse the NPs in a polymer matrix and to selectively form the polymer shell around each of the nanoparticles. Post-processing is carried out to spin coat on substrates and to cure under UV light to make capacitor slabs.

The results from SEM and AFM analysis, thermal and frequency response, breakdown dielectric strength and dielectric loss of the films for different loadings of NPs will be reported in the talk. K value of 20 and breakdown field of 50V/ $\mu\text{m}$  were measured for a dielectric with 10% loading of Au/SiO<sub>2</sub> NPs. Resulting capacitance value of 11.5nF/In<sup>2</sup> is in par with commercially available capacitor devices. It is worth mentioning that currently manufacturers use ceramic based dielectric material which makes it hard to manufacture (reproducibility, stability and cost) and shows limited flexibility (a requirement in modern printed circuit board technologies) due to high ceramic loading. Our fabricated nanodielectrics have the advantage of ease of fabrication and high flexibility due to the low metal loading.

It is forecasted that the effective permittivity of the dielectric and thereby the K value increases with loading of NPs till a percolation threshold is reached and then rapidly decreases with further loading. Future research is aimed at using other inexpensive metal NPs like silver and testing different polymers for best desirable characteristics of the capacitors.

5:00pm **EN+NS-WeA10 Characterization of Vertical InN Nanorods and InN-GaN Core-Shell Structures Grown by Merged Metal Organic Hydride Vapor Phase Epitaxy**, *V.U. Chaudhari*, *D. Wood*, *R. Krishnan*, *T.B. Song*, *T.J. Anderson*, University of Florida

The pseudobinary solid solution Ga<sub>x</sub>In<sub>1-x</sub>N alloys exhibits a direct band gap in the range 3.4 to 0.7 eV and thus suitable for optoelectronic device applications. Recent simulations from our group have also suggested this alloy could produce high efficiency thin film photovoltaic devices on the order of 18% efficiency, similar to CIGS devices. The use of nanorod structures for light emitting and absorbing applications promises relatively high junction area, crystalline quality, and collection efficiencies. In addition, the nanorod assemblies are less rigid, and thus open to flexible substrates. The synthesis of nanorods with specific orientation, however, remains a challenge.

The synthesis of self-assembled, vertical InN nanorods and InN-GaN core shell nanostructures on Si without the need for a catalyst or template is reported. This self-catalyzed approach has made it possible to grow nanorods with uniform yet tunable diameter without any patterning of the substrate. The synthesis is performed in a Merged Metal Organic Hydride Vapor Phase Epitaxial growth system. This system allows growth of Ga<sub>x</sub>In<sub>1-x</sub>N by either metal organic CVD, using trimethylgallium, trimethylindium and NH<sub>3</sub>, or hydride VPE in which the metal organic precursor is reacted with HCl. This presentation summarizes properties of the nanorods grown in the temperature range 560 to 600 °C at atmospheric pressure in N<sub>2</sub>. As revealed by transmission electron spectroscopy, the grown nanorods are defect-free, single crystal showing the wurtzite structure. Scanning electron microscopy and X-ray diffraction results reveal growth in vertical direction with (002) preferred orientation. The InN-GaN core shell structures exhibited a polycrystalline GaN shell with (002) and (101) preferred orientations. This particular behavior of GaN is attributed to the high growth rates used. Annealing studies of these microstructures under

ammonia atmosphere showed the absence of alloy formation with virtually no inter-diffusion of In and Ga.

5:20pm **EN+NS-WeA11 Fabrication of InAs/GaAs Nanocomposites Using Ion Implantation**, *M.V. Warren*, *C. Uher*, *R.S. Goldman*, University of Michigan, Ann Arbor

The controlled formation of semiconductor nanocomposites offers a unique opportunity to tailor functional materials with a variety of novel properties. In particular, nanocomposites consisting of InAs nanostructures embedded in GaAs have been proposed for high efficiency photovoltaics and high figure-of-merit thermoelectrics. A promising approach to nanocomposite synthesis is matrix-seeded growth, which involves ion-beam-amorphization of a semiconductor film, followed by nanoscale re-crystallization via annealing [1]. In earlier studies of In<sup>+</sup> implantation into GaAs, the formation of InGaAs alloys upon annealing was reported [2-4]. Due to the large size difference between In and Ga, it is likely that phase separation occurs, especially for high indium fraction InGaAs alloys. Therefore, we are examining the possibility of selective formation of InAs-rich nanocrystals in a GaAs matrix using high dose In implantation into GaAs. However, Profile Code simulations suggest that the retained In dose in GaAs,  $4.5 \times 10^{20} \text{ cm}^{-3}$ , is limited by sputtering. To increase the concentration of implanted In, we have developed a sputter-mask method, for which a sacrificial layer with sputter yield lower than that of GaAs is used to prevent sputtering of GaAs:In. Using 100kV ions with fluences ranging from  $3.8 \times 10^{15}$  to  $3.8 \times 10^{17} \text{ cm}^{-2}$ , we have implanted In<sup>+</sup> ions into GaAs with 50 nm sputter-masks consisting of AlAs. Following implantation, the films were annealed at 500 to 600°C for 30 to 60 s. We will discuss the influence of In<sup>+</sup> dose and annealing conditions on the nucleation and growth of InAs, as well as the influence of nanostructuring on the temperature dependence of the resistivity and Seebeck coefficient of the implanted structures.

This work is supported in part by the GAANN Fellowship and the US Department of Energy, Office of Basic Energy Sciences as part of an Energy Frontier Research Center

[1] X. Weng, W. Ye, S. Clarke, A. Daniel, V. Rotberg, R. Clarke, and R.S. Goldman, *J. Appl. Phys.* 97, 064301 (2005).

[2] M.V. Ardyshev and V.F. Pichugin, *Russian Physics Journal* 47, 175 (2004).

[3] M. Kulik, F.F. Komarov, and D.D. Maczka, *Vacuum* 63, 755 (2001).

[4] M. Kulik, A.P. Kobzev, D. Jaworska, J. Zuk, and J. Filiks, *Vacuum* 81, 1124 (2007).

## Nanometer-scale Science and Technology

**Room: La Cienega - Session NS+EM+EN-WeA**

### Photonic and Plasmonic Materials and Devices

**Moderator: P. Cheng, Cornell University**

2:00pm **NS+EM+EN-WeA1 Spatially-Resolved Study of Luminescence and Composition in III-Nitride Nanowires**, *G.T. Wang*, *Q. Li*, Sandia National Laboratories

Given the strong interest in III-nitride-based nanowires for optoelectronic and energy applications, a better understanding of their optical properties and structure-composition is required, particularly at nanoscale spatial resolutions, which could shed light into issues such as the nature and distribution of radiative defects and alloy compositional variations. Here, we present a spatially-resolved, correlated study of luminescence and composition in GaN, Al(Ga)N/GaN, and InGaN/GaN core-shell nanowires grown by metal-organic chemical vapor deposition. For GaN nanowires, a surface layer exhibiting strong yellow luminescence (YL) near 566 nm in the nanowires was directly revealed by high resolution, cross-sectional cathodoluminescence (CL) imaging, compared to weak YL in the bulk. In contrast, other defect related luminescence near 428 nm (blue luminescence) and 734 nm (red luminescence), in addition to band-edge luminescence (BEL) at 366 nm, were observed in the bulk of the GaN nanowires but were largely absent at the surface. As the nanowire width approaches a critical dimension, the surface YL layer completely quenches the BEL. The surface YL is attributed to the diffusion and piling up of mobile point defects, likely isolated gallium vacancies, at the surface during growth. AlGaIn/GaN and AlN/GaN core-shell nanowires were observed to exhibit stronger BEL and weaker YL as compared with bare GaN nanowires, which may relate to the passivation of nanowire surface states. InGaIn/GaN core-shell nanowires were also investigated by correlated CL and cross-sectional scanning TEM (STEM). Dislocation-free InGaIn layers with up to ~40% indium incorporation were achieved on GaN nanowires. The indium composition distribution in the InGaIn layers were qualitatively correlated to the strain energy density distribution as calculated by finite

element analysis models. The observed high indium incorporation and high crystalline quality in the heteroepitaxial InGaN layers is attributed to strain-relaxed growth on the nanowires. Sandia National Laboratories is a multi-program laboratory operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin company, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

**2:20pm NS+EM+EN-WeA2 Photonic Crystal Cavities and Vertical Confinement to Increase the Conversion Efficiency of a Thermophotovoltaic Cell, C. Shemelya, T. Vandervelde, Tufts University**

For many years researchers have attempted to efficiently harvest waste heat and transform it into a usable energy via thermophotovoltaics (TPVs). The low quantum efficiency (QE; i.e. the probability that a photon will be absorbed) in most TPV cells is probably the biggest limiting factor in achieving an economically viable device and directly affects the conversion efficiency (CE; i.e. the probability that a photon will be converted into a carrier that is collected). In many cases, top of the line TPV cells might only have a CE of 20%. Recent advances in micro-/nano-fabrication techniques have enabled the creation of novel structures to enhance the absorption and, therefore, the conversion of the incident thermal photons. In particular, photonic crystals (PhC) interface enhancements have been shown to increase the efficiency of photon to current conversions for infrared photodetectors. The addition of a back reflecting layer, or vertical confinement layer can further increase conversion efficiencies. Here, we report on the enhancement of photon conversion by integration of PhC structures and vertical confinement layers into the TPV cells. To this end, photonic crystals consisting of rods of either air or dielectric surface-passivation material are placed into the base semiconductor TPV cells to increase duration of thermal photon absorption, resulting in significantly enhanced QE and CE. The use of photonic crystals and vertical confinement in augmenting the conversion efficiency of TPV cells is applicable for most IR wavelengths, making this a widely useful technology. The ability to harvest waste heat for energy will help make many processes and/or systems more energy efficient, which will be a critical component in ushering in an era of energy independence.

**2:40pm NS+EM+EN-WeA3 Unconventional and Broadband Plasmonics, T.W. Odom, Northwestern University** **INVITED**

Breakthroughs in photonics and optoelectronics demand actively controlled materials that are inexpensive, robust, and scalable. The interaction of light with surface plasmons—collective oscillations of free electrons—in metal nanostructures has resulted in exceptional displays of enhanced optical transmission, collimation of light through a subwavelength aperture, and negative permeability and refraction at visible wavelengths. The structures that display these phenomena typically consist of ordered arrays of particles or holes with sizes of the order 100 nm. Surface plasmons can interact with each other over much longer distances, however, and thus the ability to organize nanoscale materials over multiple length scales could lead to new plasmonic metamaterials with novel optical properties.

This talk will describe how superlattices and low symmetry plasmonic lattices provide an important first step to meet these goals. We will introduce new soft nanolithography tools for creating new plasmonic structures, including PEEL (a procedure combining Phase-shifting photolithography, Etching, Electron-beam deposition, and Lift-off) and solvent assisted nanoscale embossing (SANE). These methods can achieve arrays of 50-nm features simultaneously over 6-in<sup>2</sup> areas without needing electron, ion, or photon-based lithographies. We will then discuss how the optical properties of the plasmonic crystals and the nanoparticle arrays can be engineered and then manipulated by external factors to produce large optical responses.

**4:00pm NS+EM+EN-WeA7 Controlling Plasmon Enhanced Photoconduction in Porphyrin-Gold Nanoparticle Assemblies, D.J. Conklin, S.U. Nanayakkara, T.-H. Park, University of Pennsylvania, J.T. Stecher, M.J. Therien, Duke University, D.A. Bonnell, University of Pennsylvania**

Recently we demonstrate plasmon-induced electronic transport in hybrid metal nanoparticle-molecular devices that realized enhancements of up to a factor of 200. This was realized in a hybrid structure that consists of an array of gold nanoparticles linked by (porphinato)zinc(II) oligomers. Here we examine the role of metal particle size, spacing, molecular length and radiation power on the photoconductive properties. Controlling these parameters allows the relative roles of nano antennae focus increasing effective photon flux and hot electron distribution to the current enhancement to be compared.

This phenomenon offers a pathway to selectively enhance specific optical energies or to design a hybrid structure that can simultaneously enhance a

range of optical wavelengths. Applications in optical devices and a range of photovoltaics could exploit this new phenomenon [ACS Nano, 2010, 4 (2), pp 1019-1025].

**4:20pm NS+EM+EN-WeA8 From Red-Coloured Coatings to Light Trapping in Solar Cells: on the Tunability and Control of the Surface Plasmon Resonance Behaviour, M. Creatore, H. Takeke Beyene, M. Ponomarev, M.C.M. van de Sanden, Eindhoven University of Technology, Netherlands**

The combination of (noble) metal nanoparticles (NPs) with dielectrics is an on-going research subject, due to the generated surface plasmon resonance (SPR) effect, relevant in several technological applications such as color filters, optical switching devices and sensors, to name a few.

In this contribution, we report on the tunability and control of the surface plasmon resonance behaviour through the engineering of metal NP/dielectric interfaces for two applications, i.e. thickness- and viewing angle- independent red- coloured decorative coatings and light trapping enhancement in silicon- based tandem thin film solar cells. Both studies have been carried out by making use of a vacuum chamber where plasma-enhanced chemical vapour deposition for the dielectric layer and magnetron sputtering for the metal NP deposition are combined.

Multilayer structures composed of gold NPs sandwiched between SiO<sub>2</sub> layers represent a valid solution for the independent control of NP size and density: while a constant NP size guarantees a narrow surface plasmon frequency, an increased NP density leads to an enhancement in the absorption [1]. A multi-diagnostic approach consisting of spectroscopic ellipsometry, transmission electron microscopy and Rutherford backscattering analysis has allowed the characterization of the deposited coatings: gold NPs (diameter 10-15 nm) with a surface area coverage of 26% and sandwiched between 40 nm- thick SiO<sub>2</sub> layers, exhibit a red colour, whereas the color intensity (i.e. from cool to warm deep red) increases with the layer number, i.e. NP density.

While in this first application the main mechanism contributing to extinction is *absorption*, for an efficient sun light management/ trapping within a solar cell, *scattering* plays a dominant role. In particular, for amorphous (a-Si:H)/microcrystalline ( $\mu$ c-Si:H) silicon tandem solar cells a promising approach consists in the incorporation of an intermediate layer (e.g. ZnO) sandwiched between the top a-Si:H and the bottom  $\mu$ c-Si:H cell, able to efficiently scatter photons of a specific frequency range back to the top cell or forward to the bottom cell. In this respect, copper NPs (30-150 nm diameter) when coupled to ZnO layers, are responsible for the generation of a plasmon peak at 700 nm, which shifts towards higher wavelengths with an increase in NP size, therefore showing its potential towards low energy photon forward scattering into the bottom  $\mu$ c-Si:H cell.

[1] H. T. Beyene, F.D. Tichelaar, P. Peeters, I. Kolev, M.C.M. van de Sanden, M. Creatore, accepted for publication in Plasma Processes and Polymers (2010).

**4:40pm NS+EM+EN-WeA9 Index-Matching at the Nanometer Scale, G. Broenstrup, C. Leiterer, N. Jahr, B. Hoffmann, F. Talkenberg, Institute of Photonic Technology, Germany, S.H. Christiansen, Max Planck Institute for the Science of Light, Germany**

Silicon nanowires (SiNW) show high potential as future building blocks for photonic devices. They show strong resonant enhancement effects resulting in high absorption efficiencies and even higher scattering efficiencies. Since both effects are based on the same underlying physical principles the resonant enhancement of the absorption as well the resonant enhancement of the scattering of light occurs at the same wavelength. These large scattering efficiencies could result in an increased reflectivity of structures based on these SiNWs.

To overcome the increased scattering efficiencies we show an index matching core-shell approach.

The SiNWs are wrapped with a thin oxide layer with a refractive index smaller than the refractive index of silicon. The thickness of the wrapping layer is formed using atomic layer deposition (ALD), which allows to control the thickness of the layer at the Angstrom scale. The microstructure is analyzed using transmission electron microscopy (TEM).

The scattering behavior of these individual SiNWs with an oxide layer are measured using an optical microscope with a coupled spectrometer. The experimental data is analyzed using an extended Mie theory.

It will be shown, that this method can be used to tune the absorption efficiencies and the scattering separately to different wavelengths.

5:00pm **NS+EM+EN-WeA10 20  $\mu$ s Photocurrent Response from Lithographically Patterned Nanocrystalline Cadmium Selenide Nanowires**, *S.-C. Kung, W.E. van der Veer, F. Yang, K.C. Donovan, R.M. Penner*, University of California, Irvine

Lithographically patterned nanowire electrodeposition (LPNE) provides a method for patterning nanowires composed of nanocrystalline cadmium selenide (*nc*-CdSe) over wafer-scale areas. We assess the properties of (*nc*-CdSe) nanowires for detecting light as photoconductors. Structural characterization of these nanowires by X-ray diffraction and transmission electron microscopy reveals they are composed of stoichiometric, single phase, cubic CdSe with a mean grain diameter of 10 nm. For *nc*-CdSe nanowires with lengths of many millimeters, the width and height dimensions could be varied over the range from 60 to 350 nm (*w*) and 20 to 80 nm (*h*). Optical absorption and photoluminescence spectra for *nc*-CdSe nanowires were both dominated by band-edge transitions. The photoconductivity properties of *nc*-CdSe nanowire arrays containing  $\sim 350$  nanowires were evaluated by electrically isolating 5  $\mu$ m nanowire lengths using evaporated gold electrodes. Photocurrents,  $i_{\text{photo}}$ , of  $10\text{-}100\times (i_{\text{dark}})$  were observed with a spectral response characterized by an onset at 1.75 eV.  $i_{\text{photo}}$  response and recovery times were virtually identical and in the range from 20 to 40  $\mu$ s for  $60 \times 200$  nm nanowires.

5:20pm **NS+EM+EN-WeA11 Efficient, Single Layer Organic Light-Emitting Devices Based on a Graded Composition Emissive Layer**, *N.C. Erickson, R.J. Holmes*, University of Minnesota

We demonstrate efficient electrophosphorescence from devices comprised of a single organic active layer. High efficiency is realized by combining both hole- and electron-transporting host materials (HTM and ETM, respectively) into a single, graded composition emissive layer with the green emitter, *fac*-tris(2-phenylpyridine) iridium (III). The composition of the host-material is continuously graded to realize 100% HTM at the anode, and 100% ETM at the cathode. A peak external quantum efficiency of  $\eta_{\text{EQE}}=(19.3 \pm 0.4) \%$  is realized in the forward-viewing direction at a luminance level of 600  $\text{cd/m}^2$ , corresponding to a power efficiency of  $\eta_p=(66.5 \pm 1.3) \text{ lm/W}$ . This performance is similar to that realized in more conventional and complex, multi-layered structures. The graded composition of the structure balances electron and hole injection and transport leading to efficient exciton formation, permitting high efficiency using a single active layer. The graded composition architecture may be further utilized to realize simple, efficient organic light-emitting devices for use in display and lighting applications.

# Thursday Morning, October 21, 2010

Energy Frontiers Topical Conference

Room: Pecos - Session EN+AS-ThM

## Surface and Interface Analysis of Materials for Energy

Moderator: S.M. Han, University of New Mexico

8:00am EN+AS-ThM1 **Functionalization of Carbon Materials for the Controlled Deposition of Pt Electrocatalysts for Fuel Cell Applications.** *S. Pylypenko*, Colorado School of Mines, National Renewable Energy Lab, *A. Dameron, T. Olson, K.C. Neyerlin, J. Bult, C. Engtrakul*, National Renewable Energy Lab, *A. Queen*, Colorado School of Mines, *K. O'Neill, T. Gennett, H.N. Dinh, B. Pivovar*, National Renewable Energy Lab, *R.P. O'Hayre*, Colorado School of Mines

Catalyst-support interactions are essential in the design of materials for a variety of applications related to renewable energy technologies. In the fuel cell field, improved understanding of these interactions enables controlled improvement in the catalytic activity and durability of carbon-supported fuel cell electrocatalysts. Carbon surface chemistry and structure can be altered to achieve a desired coverage, morphology and composition of the metal nanoparticle. For example, doping a model HOPG surface with argon or nitrogen results in structural and chemical modification of its surface that leads to improved dispersion, decreased nanoparticle phase and, at certain conditions, enhanced stability. In this work, the role of surface defects, oxygen and nitrogen groups introduced during doping and their effect on electrocatalyst deposition and performance is evaluated through a combination of spectroscopic (XPS, Raman, EELS) and microscopic (SEM, TEM) methods. The same methods are used to evaluate the effect of various surface modifications (via Ar plasma, O<sub>2</sub> plasma and their mixture, HNO<sub>3</sub>, TMA functionalization, etc.) on high surface area carbon materials (CNTs, for instance) and their effect on nucleation and growth of Pt in a controlled nanoparticle or continuous coating phase.

8:20am EN+AS-ThM2 **Structural and Morphological Properties of Carbon Supports studied by XPS and SEM: Effect on Catalyst Degradation.** *A. Patel, K. Artyushkova, P. Atanassov*, University of New Mexico, *A. Young, M. Dutta, Z. Ahmad, V. Colbow, S. Wessel*, Ballard Power Systems, Canada

Understanding the chemical structure and morphology of Pt electrocatalysts and their supports, and linking these parameters to electrocatalytic activity, corrosion stability and overall performance of the fuel cell is essential for elucidation of failure mechanisms and optimization of support properties. The strategy presented in this work can be viewed as universal methodology that allows correlation between multiple variables relevant to fuel cell technology.

In this work we have investigated the performance and corrosion stability of Pt electrocatalysts supported on different carbon supports in order to understand the effect of the carbon support on catalyst degradation. Low surface area (LSA), mid-range surface area (MSA), high surface area (HSA) and heat treated (to induce graphitization) high surface area carbons were extensively studied and characterized.

X-ray Photoelectron Spectroscopy (XPS) has been chosen to obtain information on graphiticity and amount of surface oxides on carbon supports. The ability to discriminate between different carbon chemical environments, not just elemental compositions, is one of the primary advantages of XPS in the characterization of carbon corrosion.

Morphological properties such as size of particles, size of particles agglomerates, surface area, roughness and porosity are equally contributive to corrosion process. Digital Image Processing (DIP) can be applied to SEM and TEM images to extract statistical parameters, such as roughness, particle size distributions, shape parameters, texture parameters, which all are related to morphology of carbon blacks.

Performance and durability of Pt electrocatalysts supported on various carbon blacks were evaluated extensively electrochemically to provide activity from rotating disk electrode measurements, capacitance and photon resistance from Electrode Impedance Spectroscopy, voltage degradation rates, effective platinum surface area and kinetic losses.

This multi-analytical approach provides a large set of variables (structural, physical and microscopic properties) which must be related to corrosion and performance behaviour of carbon blacks. Multivariate statistical methods of data analysis (MVA) become, thus, of critical importance in structure-to-property relationship modeling. Principal Component Analysis (PCA) is used as a visualization tool to find samples which are globally correlated or anti-correlated, and to facilitate visualization of the variables responsible for the correlations. Through this methodology, we have determined which set

of structural and morphological parameters are responsible for durable and active electrocatalyst.

8:40am EN+AS-ThM3 **Anchoring of N3, N719 and Z907 Dye Molecules on TiO<sub>2</sub>(110) Surface.** *P. Nachimuthu, A. Pandey, Z.Q. Yu, Z.H. Zhu, K.M. Beck, S. Thevuthasan, M.A. Henderson, D.R. Baer*, Pacific Northwest National Laboratory

In dye-sensitized solar cells, the alignment of the energy levels for the dye and TiO<sub>2</sub> resulting from the electronic coupling between these states determines the photoinduced electron transfer across the dye-TiO<sub>2</sub> interface. The electronic coupling which in turn is strongly modified by the mode of binding of the dye molecules onto TiO<sub>2</sub> surface, its relative orientations and geometrical structures. In order to understand the mode of binding of the dye molecules on TiO<sub>2</sub>(110) surface, the N3, N719 and Z907 dye molecules in the powder form and adsorbed on TiO<sub>2</sub>(110) surface using 0.25-1.0 mg/ml in ethanol were investigated using high-resolution x-ray photoelectron spectroscopy. The S 2p XPS data from N3 dye molecules adsorbed onto TiO<sub>2</sub> surface show two S components in addition to SO<sub>x</sub>, suggesting that the S atoms in the -NCS functional groups exist in two different chemical environments with a binding energy difference of ~1 eV and the intensity ratio of ~1 indicating that in each intact N3 molecule on TiO<sub>2</sub>, one -NCS group is bound to TiO<sub>2</sub>(110) surface and the other is projected away from TiO<sub>2</sub> surface. The O 1s XPS data show components at 531.2 eV and 533.1 eV which are arising from C=O / COO<sup>-</sup> and C-OH bonds from carboxylic acid groups in N3 molecule, respectively, in addition to a peak at 529.7eV from TiO<sub>2</sub>. The relative intensity ratio of the O 1s XPS components at 533.1 eV to 531.2 eV signifies the presence of protonated carboxylic acid groups in N3 molecule and is found to be 0.388 suggesting that only one carboxylic acid group in each N3 molecule is deprotonated and it is most likely bound to TiO<sub>2</sub> surface. In contrast, both the -NCS groups in the N719 and Z907 dye molecules were projected away from the TiO<sub>2</sub> surface and are not involved in binding with TiO<sub>2</sub> surface. One of the carboxylic acid groups in Z907 is deprotonated and it is most likely bound to TiO<sub>2</sub> surface. Furthermore, with decreasing the dye concentration in ethanol results in a gradual dissociation of -NCS groups from Ru in these dye molecules.

9:00am EN+AS-ThM4 **Characterization of Minority Carrier Lifetime in Ge Films Epitaxially Grown on Si by Nanoscale Interfacial Engineering.** *J.J. Sheng, D. Leonhardt*, University of New Mexico, *J.G. Cederberg, M.S. Carroll*, Sandia National Laboratories, *M.J. Romero, S. Johnston*, National Renewable Energy Laboratory, *S.M. Han*, University of New Mexico

High-quality Ge-on-Si (GoS) heterostructures are pursued for many applications, including near infrared (NIR) photodetectors and integration with III-V films for multijunction photovoltaics. However, such integration poses many engineering challenges, ranging from lattice mismatch, to thermal expansion coefficient mismatch, to non-planar morphological evolution. We have previously demonstrated a scale-up of growing low-dislocation-density Ge on Si by manipulating the Ge-Si interface at the nanoscale, using a thin chemical SiO<sub>2</sub> layer and a surface reaction involving Ge and SiO<sub>2</sub>. We have also developed a slurry-free, chemical-mechanical polish step to planarize the GoS surface resulting in a Ge surface with a root mean square (RMS) roughness of less than 1 nm. Herein, we focus on the characterization of carrier lifetime in the Ge epilayers grown on Si by the said nanoscale Ge-Si interfacial engineering. Using photoconductivity decay techniques, minority carrier lifetime is measured in the GoS substrates to extract surface recombination velocity as well as carrier lifetime in bulk Ge. The effective surface recombination velocity, representing both Ge-Si interface decorated with chemical SiO<sub>2</sub> and Ge surface, is approximately 1.26x10<sup>4</sup> cm/sec, largely dominated by recombinations at the oxide. We observe that the extracted lifetimes, which vary with the Ge film thickness, correlate well with the dislocation density that varies as a function of distance from the Ge-Si interface. In this presentation, we will further discuss capacitance-voltage characterization of metal-oxide-semiconductor structures fabricated on our GoS substrates.

9:40am EN+AS-ThM6 **A Multi-technique Approach to the Characterization of New Materials for Energy Production.** *T. Nunney, R.G. White, N. Bulloss, P. Camus, J. Konopka*, ThermoFisher Scientific, UK, *H.M. Meyer III*, Oak Ridge National Laboratory

In order to meet the challenges of more economical and environmentally benign energy production, a new generation of complex materials and devices is being developed, these include thin film solar cells, fuel cells, and batteries. In all stages of development there is a requirement for materials characterization and analysis; from the initial development stages, through to testing of the finished article. Most materials need to be analyzed for

compositional homogeneity across the sample surface and also for layer chemistry, interface chemistry and thickness through the sample. It is rare that a single technique can achieve all of these testing requirements, and therefore a complementary approach involving several techniques is demanded.

In this presentation we will discuss how a multi-technique approach can address a variety of technical problems, illustrated by examples from real applications case studies. We will mainly concentrate on the information supplied from two techniques, XPS and EDS, but we will also consider the additional data that can be obtained from other sources such as Raman spectroscopy.

X-ray photoelectron spectroscopy (XPS) is ideally suited to the quantitative determination of the surface chemistry and the way in which that chemistry changes in the surface, near-surface and interface region of the materials.

Energy Dispersive Spectroscopy (EDS) collects characteristic X-rays generated by rastering an electron beam over a solid sample to generate a full elemental X-ray spectrum at each pixel of the electron image. The latest generation silicon drift detectors for EDS are capable of collecting and storing hundreds of thousands of X-ray counts per second. This large volume of X-ray data, collected across the sample, allows for rapid identification and characterization of surface defects and lateral compositional variations. Software advances now allow rapid, multivariate statistical analysis processing of very limited amounts of X-ray data to determine not only the elemental distribution across the sample but also the chemical phase distribution.

10:40am **EN+AS-ThM9 Novel Visible-Light Photo-Sensitive Zirconium Oxynitride ( $ZrO_xN_y$ ) Thin Films**, *C.V. Ramana, N.E. Esparaza, I. Fernandez*, University of Texas at El Paso, *A.L. Campbell*, Wright Patterson Air Force Base

Zirconium oxide ( $ZrO_2$ ) exhibits excellent optical properties such as high refractive index, large band gap, low optical loss, high transparency in the visible and near-infrared regions, and high dielectric constant. However,  $ZrO_2$  is UV-light sensitive. In addition, interfacial reactions during thin-film growth suppress the effective dielectric constant and degrade the optical performances. The present work was performed on  $ZrO_xN_y$  thin films to effectively alter the electronic structure by the method of nitridation, which well-known to suppress the interfacial reactions.  $ZrO_xN_y$  thin films were produced by magnetron-sputter deposition under the reactive pressure of nitrogen and oxygen. The effect of nitrogen/oxygen flow rate on the structure and optical properties of  $ZrO_xN_y$  thin films was investigated and compared with that of  $ZrO_2$ . The optical measurements of  $ZrO_2$  films show a very high optical transmission with a band gap of 5 eV. The optical absorption measurements on  $ZrO_xN_y$  thin films grown at various reactive nitrogen pressures indicate a progressive shift from insulating to semiconductor behavior. The corresponding changes in the profiles of index of refraction were also remarkably distinct. The results indicate that tailoring the electronic structure and optical constants of  $ZrO_xN_y$  thin films to meet the requirements of visible-light functionality can be achieved by carefully controlling the reactive pressure. The results will be presented and discussed in detail.

11:00am **EN+AS-ThM10 Quantification of Hydrogen and Deuterium in Niobium and Niobium Oxide**, *P. Maheshwari, F.A. Stevie*, North Carolina State University, *G.R. Myneni, G. Ciovati*, Jefferson Lab, *M. Rigsbee, D.P. Griffis*, North Carolina State University

Superconducting Radio Frequency (SRF) cavities provide enhanced efficiency and reduced energy utilization in present day particle accelerators. Niobium (Nb) is the material of choice for these cavities due to its high critical temperature and critical magnetic field. In order to understand why certain treatments, especially a low temperature bake, improve performance, it is important to study Nb surface characteristics and identify elemental contamination that can affect the performance of the cavity. H, C, O, and N are of interest because they are interstitial impurities in Nb. In earlier work, [1] SIMS analysis using a CAMECA IMS-6F with Cs<sup>+</sup> primary beam showed that C and N were probably not significant factors impacting performance and that there was a very high level of H in the Nb. TEM analysis also showed that the surface niobium oxide was a uniform layer with typical thickness about 6nm. Ion implants of C, N, O, and D into Nb provided quantification of C, N, O and indicated that D is very mobile in the Nb. [2]

Analysis of samples before and after heat treatment showed that the H level could be dramatically reduced after certain heat treatments. Removal of the oxide with HF caused the H to return to its former level and the native oxide was again established. SIMS measurement of H in the niobium oxide showed a low H level and, as noted above, the oxide appears to be a very effective H barrier. One possible cause for the removal of H by low temperature heat treatment is the possible formation of openings in the oxide barrier which allows the hydrogen to exit the Nb surface, followed by

the renewal of the oxide after heat treatment which does not allow H to re-enter. Another theory is that the heat treatments drive the H deeply into the Nb.

In order to better understand the role of the niobium oxide, implants have now been made into a specially prepared 120nm thick niobium oxide layer on Nb substrate. H is shown to have an implant shape in the oxide and verify that H is not mobile in the oxide. An implant of D with peak at the oxide/Nb interface showed an implant shape up to the interface and a sharp drop once the Nb was reached. If the H relative sensitivity factor from the oxide is used to quantify the H in a Nb sample without heat treatment, the H concentration is measured as  $2E22$  atoms/cm<sup>3</sup>.

[1] A. D. Batchelor, D. N. Leonard, P. E. Russell, F. A. Stevie, D. P. Griffis, G. R. Myneni, Proceedings of Single Crystal Niobium Technology Workshop, Brazil, AIP Conference Proceedings, Melville, NY (2007) 72-83.

[2] P. Maheshwari, H. Tian, C. Reece, G. Myneni, F. Stevie, M. Rigsbee, A. Batchelor, D. Griffis, Surf. Int. Anal. (in press 2010)

11:20am **EN+AS-ThM11 Study of Thin Film Solar Cell Materials using Variable-Wavelength Electric Force Microscopy**, *J. Luria, J.J. Choi, T. Hanrath, J.A. Marohn*, Cornell University

Organic electronics offer a clear path to large scale, low cost photovoltaics. But efficiency issues such as charge transport, extraction, and device degradation keep these materials from being market-viable. Electric Force Microscopy (EFM) allows us to probe electronic properties of various materials and meso-scale morphologies. By observing the photo-induced response and degradation, we are able to inform synthetic and fabrication processes.

We have developed a general approach to illuminate samples in our custom-built vacuum electric force microscope. We will describe experiments using variable-wavelength light to characterize lead sulfide, PFB/F8BT polymer blend, and other thin film photovoltaic devices.

**Energy Frontiers Topical Conference**  
**Room: Mesilla - Session EN+NS-ThM**

**Nanostructures for Energy Conversion & Storage II**  
**Moderator: K.S. Leschkes, Applied Materials**

8:00am **EN+NS-ThM1 Rare Earth Oxide Nanocavity Upconversion**, *V.D. Jankovic, J. Hoang, J.P. Chang*, UCLA

Rare-earth (RE) oxides represent an important class of photonic materials owing to their nonlinear optical and upconversion (UC) properties which find applications in high power lasers, remote sensing, optical communications and photovoltaics. In the context of solar cells, these materials could increase cell efficiencies by upconverting photons with energies below and near the silicon bandgap (1.1eV) which are poorly absorbed by the indirect band-gap semiconductor to higher energy photons that can be absorbed more efficiently. Unfortunately, up-conversion efficiencies in rare-earth ions are usually low due to non-radiative processes such as concentration quenching. One strategy to address this problem is to couple RE ions with metal nanoparticles. Noble metal nanoparticles exhibit localized surface plasmon resonances which can readily be tuned to a particular spectral range of interest by means of size, shape and local dielectric environment. By coupling metal nanoparticles' plasmon resonances to rare earth ion energy transitions, the absorption cross sections of rare earth ions can be significantly improved.

In this work, we designed and synthesized Au|Yb:Er:Y<sub>2</sub>O<sub>3</sub> core|shell nanorods as a potential route to improve solar cell efficiencies in the near infrared regime. A modified Mie scattering algorithm determined the optimum theoretical Au nanorod aspect ratio to be 9, for a resonance close to the Yb 980-nm energy transition. The Au nanorods were synthesized using a surfactant mediated growth technique, in which cetyltrimethylammoniumbromide micelles were used to direct the growth of Au nanoparticles in the [111] direction while suppressing the growth in [100] and [110] directions. Au nanorods with aspect ratios from 6 to 12 have been synthesized by varying the concentration of the reducing agent, ascorbic acid. Spatially and compositionally controlled Yb:Er Y<sub>2</sub>O<sub>3</sub> shells were deposited using sequential radical enhanced atomic layer deposition process. The plasmon-Er color center and plasmon-Yb sensitizer distance was systematically varied by controlling the thickness of the Y<sub>2</sub>O<sub>3</sub> spacer layer from 1nm to 10nm. The length, aspect ratio, nanorod monodispersity and shell thickness were verified using transmission electron microscopy,

while the shell composition was verified by energy dispersive X-Ray spectroscopy. Photoluminescence and radiative lifetime measurements with 980 nm excitation were used to investigate the distance dependence effects of the noble metal-emitter coupling on the optical properties of the core/shell nanorods. Quantitative measurements of the absorption cross section are underway and will also be presented

8:20am **EN+NS-ThM2 Thermal Transport Property of SiGe Nanowire**, *E.K. Lee*, Samsung Advanced Institute of Technology, Republic of Korea, *J.W. Lee*, Sungkyunkwan University, Republic of Korea, *L. Yin*, Texas A&M University, *B.L. Choi*, *S.J. Lee*, Samsung Advanced Institute of Technology, Republic of Korea, *D.M. Whang*, Sungkyunkwan University, Republic of Korea, *C.H. Yu*, Texas A&M University, *J.M. Kim*, Samsung Advanced Institute of Technology, Republic of Korea

Thermoelectric power conversion of waste heat is one of the promising energy harvesting method in the future.

The developments of bulk thermoelectric material are studied by many researchers, but the results are limitedly progressed. However, when the size of material becomes small enough comparable to the mean free path of phonons, the thermal conductivity is remarkably reduced. The thermal conductivities of some nanowires show a few orders of magnitude lower than those of bulk materials due to enhanced boundary scattering. In this point, SiGe nanowire is one of attractive candidates for thermoelectric energy conversion. Here we report the thermal property of SiGe nanowire grown by vapor-liquid-vapor mechanism and the correlation between thermal conductivity and morphology of nanowires. The thermal conductivity of SiGe nanowires was measured using micro-fabricated devices over temperature range of 60K to 450K.

8:40am **EN+NS-ThM3 Hydrogen Storage in Metal Organic Frameworks (MOFs)**, *N. Nijem*, *J.-F. Veyan*, University of Texas at Dallas, *L. Kong*, *K. Li*, *J. Li*, *D.C. Langreth*, Rutgers University, *Y.J. Chabal*, University of Texas at Dallas

Hydrogen storage is one of the most challenging problems in hydrogen-based energy technologies. 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 molecular 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 and because many options are possible to enhance the interaction of molecular hydrogen with the host.

This work explores the incorporation of hydrogen into various MOFs using infrared (IR) absorption spectroscopy to characterize its interaction. IR spectroscopy can distinguish possible H<sub>2</sub> binding sites based on the perturbation of the internal H<sub>2</sub> stretch mode. IR measurements are performed on saturated metal center MOFs varying the ligand and/or the metal center and on unsaturated metal center MOF-74-M (M=Zn, Mg and Ni). We combine room temperature, high pressure with low temperature (20-100K) measurements and theoretical van der Waals density functional (vdW-DF) calculations to derive quantitative information from IR shifts and dipole moment strengths.

Our results show that, in contrast to the current understanding, IR shifts are independent of binding energies and depend instead on the chemical environment of the molecule, including effects such as H<sub>2</sub>-H<sub>2</sub> interactions. For example, we see little difference in IR shifts between saturated MOFs with low binding energy (~4kJ/mol), and unsaturated MOFs with higher binding energy (~10kJ/mol) sites at room temperature. Furthermore, we show that dipole moments of adsorbed H<sub>2</sub> depends greatly on parameters such as geometry of adsorption site and H<sub>2</sub>-H<sub>2</sub> interactions. Measurements performed at low temperatures on MOF-74 show that IR shifts of H<sub>2</sub> is greatly red shifted (an additional ~30 cm<sup>-1</sup>) due to H<sub>2</sub>-H<sub>2</sub> interactions on close proximity adsorption sites, and that dipole moments of adsorbed H<sub>2</sub> can appreciably vary with loading.

Our analysis indicate that the intensity of H<sub>2</sub> IR band cannot always be a measure of the amount of H<sub>2</sub> adsorbed, therefore methods such as variable temperature IR (VTIR) used to deduce binding energies cannot always be implemented.

9:00am **EN+NS-ThM4 The Influence of Acid Treatment of TiO<sub>2</sub> Film Prepared by FFCVD on the Performance of Dye-Sensitized Solar Cell**, *B.R. Chen*, *Y.J. Chen*, National Dong Hwa University, Taiwan, Republic of China

In this study, we use the acid treatment to enhance the dye-sensitized solar cell (DSSC) efficiency from 4.58% to 5.87%. Comparing with the untreated film, the photocurrent and efficiency both largely increase ~28%. We also found that the use of acetic acid, as well as hydrochloric acid, can easily

enhance the performance of DSSCs. The untreated film was prepared using a one-step method by the flat-flame chemical vapor deposition (FFCVD) system which deposits the nanoporous TiO<sub>2</sub> film directly as working electrode used in the DSSC. The TiO<sub>2</sub> film was grown on ITO substrate at the temperature of 400°C and the pressure of 20 torr. The efficiency of DSSC using as-synthesized TiO<sub>2</sub> electrode approaches 4.58% with the film thickness about 11~13 nm with proper tuning of carrier gas flow rate in the TiO<sub>2</sub> deposition process. We know that the DSSCs with best efficiency about 11% were prepared exclusively by hydrothermal method. The efficiency we have is among the highest for DSSCs prepared through non-hydrothermal process. The influence of acid treatment increase conversion efficiency was largely attributed to the short circuit current increase. In previous studies, some group improved the acid treatment to make the dye absorption increase effectively. However, most of them performed the treatment during hydrothermal process for the powder synthesis, which cannot be incorporated with the direct film preparation process. Therefore, we take the dipping method to treat our nanoporous TiO<sub>2</sub> film, and try to determine if the treatment can enhance the dye absorption as well. The crystalline quality and morphologies of surface modified TiO<sub>2</sub> electrodes were characterized by using XRD and FESEM. FT-IR and XPS were used to perform the surface characterization. The dye absorption of the DSSCs was also characterizes by UV-vis spectrophotometer. The efficiency of DSSCs using these working electrodes were measured under AM 1.5G 100 mW/cm<sup>2</sup> by Keithley 2400 sourcemeeter. The optimized cell efficiency is 5.87% with the short-circuit photocurrent density of 14.50 mA/cm<sup>2</sup> and open-circuit voltage of 0.60 V at 0.1M hydrochloric acid solution and half-an-hour soaking.

9:20am **EN+NS-ThM5 Development of Novel Nanomaterials as the Building Blocks for Next-Generation Solar Cells**, *J.M. Pietryga*, *D.C. Lee*, *I. Robel*, *V.I. Klimov*, Los Alamos National Laboratory **INVITED**

The use of colloiddally synthesized nanomaterials in devices is attractive not only because of the low-cost and scalability of solution-based fabrication methods, but because of the facile control over electronic and optical properties of these materials made possible by structural fine-tuning. As the range of applications-of-interest has become more sophisticated, such tuning has progressed beyond simple control over effective band gap using quantum size effects to include much more fundamental modification of electronic structure and dynamics. Design and synthesis of novel nanomaterials that exploit such effects to create unique materials for use in next-generation solar cells are an important part of the ongoing effort within the Center for Advanced Solar Photophysics, a DOE Energy Frontier Research Center. I will examine a number of specific examples from this work, including germanium nanocrystals with partial direct-gap behavior and unique infrared-active heterostructures with extremely long-lived charge-separated excited states, and how such materials may be incorporated into devices.

10:40am **EN+NS-ThM9 CdSe-Coated ZnO Nanowires for Extremely Thin Absorber Solar Cells**, *H. Majidi*, *J.B. Baxter*, Drexel University

Solar cells can provide an abundant, clean, and sustainable source of electricity, but high costs have limited their implementation. Extremely thin absorber (ETA) cells are robust solid state cells that utilize low cost processing while promising potential efficiencies above 15%. However, the highest reported efficiency of ETA cells is only 2.5%. Improving this efficiency will require fundamental understanding and control of the charge transfer in materials and interfaces within the cell.

We report on materials synthesis and photovoltaic response of ETA cells consisting of a vertical array of *n*-type ZnO nanowires coated with CdSe absorber and with the pores between nanowires filled with *p*-type CuSCN. CdSe absorbs visible light and injects photoexcited electrons into the ZnO nanowires. The architecture of the ETA cell enables use of absorbers with smaller carrier lifetimes than those used in thicker planar films, and elimination of liquid electrolytes renders them more robust than conventional dye sensitized solar cells. However, CdSe deposition must be carefully controlled to obtain highly crystalline, uniform, and conformal coatings with an optimal thickness to achieve maximum light harvesting and charge injection efficiency.

We have deposited CdSe coatings at room temperature using electrodeposition with precise control over morphology and material properties. Detailed information about nucleation, crystal growth, and morphology of the coating on both planar ZnO films and ZnO nanowire arrays was obtained by electrochemical probes and electron microscopy at the early stages of deposition. Under potentiostatic deposition, applied potential of ~ -1.25 V resulted in instantaneous nucleation and high areal density of nuclei and, hence, conformal coatings. Smaller applied potentials ~-1.05 V resulted in sparse and progressive nucleation and non-uniform coatings. However, deposition at potentials larger than -1.6 V resulted in precipitation in electrolyte solution. After annealing, x-ray diffraction and transmission electron microscopy show nanocrystalline CdSe in both

hexagonal and cubic phases. Using the optimal potential range determined from the potentiostatic studies, we investigated galvanostatic deposition of CdSe coatings on ZnO nanowire arrays. The thickness of CdSe coating is precisely controlled by electrodeposition charge density, and the deposition is conformal and uniform, which is ideal for ETA cells. UV-Vis transmission spectroscopy and photoelectrochemical solar cell measurements demonstrate that CdSe coatings effectively sensitize ZnO nanowires to visible light.

11:00am **EN+NS-ThM10 Titanium Dioxide Nanowires for Dye-Sensitized Solar Cells, Lithium Ion Batteries and Photocatalysis, E.S. Aydil, B. Liu, A. Khare, University of Minnesota**

One-dimensional titanium dioxide nanowires find applications ranging from photocatalysis to lithium ion batteries and dye sensitized solar cells. A simple and environmentally benign method was developed for growing oriented single-crystalline TiO<sub>2</sub>-B and/or anatase TiO<sub>2</sub> nanowire arrays on titanium foil over large areas. These nanowire arrays are suitable for use as the anode in lithium-ion-batteries; they exhibit specific capacities ranging from 200-250 mAh/g and retention of these capacities at high charge-discharge rates and over as many as 200 charging-discharging cycles. These promising properties are attributed to both the nanometer size of the nanowires and their oriented alignment. The comparable electrochemical performance to existing technology, improved safety, and the ability to roll titanium foils into compact three-dimensional structures without additional substrates, binders or additives suggest that these TiO<sub>2</sub> nanowires on titanium foil are promising anode materials for large scale energy storage. Another application of these nanowires is in photocatalysis. Ideally, after photogeneration, electrons and holes must be segregated to different parts of the photocatalyst to take part in separate oxidation and reduction reactions. One way to achieve spatial control of electron-hole separation is by building junctions into the catalyst with built-in electric fields that tend to separate the electron and the hole into two different regions of the catalyst. We sought to accomplish this by controllably forming junctions between different phases of TiO<sub>2</sub>. A solution method followed by a subsequent heating process has been developed to prepare core-shell TiO<sub>2</sub> nanowires made of TiO<sub>2</sub>-B core and anatase shell. We control the anatase phase surface coverage on the TiO<sub>2</sub>-B phase and show that the maximum photocatalytic activity is obtained when the solution containing the reactants can contact both the anatase and TiO<sub>2</sub>-B phases. The photocatalytic activity drops both with bare TiO<sub>2</sub>-B nanowires and with completely anatase covered TiO<sub>2</sub>-B nanowires. In contrast, nanowires partially covered with anatase phase gives the highest photocatalytic activity. The improved photocatalytic activity is attributed to the effective electron-hole separation at the junction between the anatase and TiO<sub>2</sub>-B phases, which reduces charge recombination and increases the electron and hole lifetimes. Finally, we have developed a method to grow rutile TiO<sub>2</sub> nanowires on transparent conducting oxide substrates for use in dye-sensitized solar cells (DSSC). A light-to-electricity conversion efficiency of 3% could be achieved by using 4 mm-long TiO<sub>2</sub> nanorod films as the photoanode in a DSSC.

11:20am **EN+NS-ThM11 Device Characteristics of Dye Sensitized Solar Cells Based on Evaporated TiO<sub>2</sub> Nanowire Photoanodes, S.M. Pursel, S.H.A. Lee, T.E. Mallouk, M.W. Horn, The Pennsylvania State University**

11:40am **EN+NS-ThM12 Dye Sensitized Solar Cells with Aerogel-Templated Nanostructured Photoanodes Fabricated using Atomic Layer Deposition, A. Yanguas-Gil, J.W. Elam, Argonne National Laboratory, V.O. Williams, Northwestern University, M. Mushfiq, D.M. Hess, R. Winter, U. Sampathkumaran, Innosense LLC, M.J. Pellin, Argonne National Laboratory, J.T. Hupp, Northwestern University**

The combination of sol/gel processing techniques with Atomic Layer Deposition is a versatile and scalable route to fabricate nanostructured electrodes with different functional materials. By controlling the sol/gel process it is possible to create scaffolds with very different microstructures and pore-size distributions, while ALD allows a layer-by-layer control of the electrode composition. One of the main advantages of this approach is the possibility of creating nanostructured electrodes with multiple functional coatings that lead to a faster transport of the injected electrons to the transparent conducting oxide, [1, 2] thus paving the way for the use of alternative redox shuttles that would allow higher photovoltages and higher efficiencies.

In this work we present results on the influence that the sol/gel process and the ALD steps have on the microstructure and transport properties of the photoanodes, and the optical properties and efficiency of the cells. In particular, we have studied the influence of the aging and drying steps in the aerogel/xerogel growth, and we have compared the performance of TiCl<sub>4</sub> and Ti(OiPr)<sub>4</sub> as precursors during the ALD step. Our results show that aerogel-templated nanostructured electrodes are a promising alternative to

nanoparticle-based photoanodes for dye sensitized solar cells. Our work is funded by the US Department of Energy, Office of Energy Efficiency and Renewable Energy, Industrial Technologies Program.

[1] A. B. F. Martinson, J. W. Elam, M. J. Pellin and J. T. Hupp, *Nano Lett.* **7**, 2183 (2007).

[2] T. W. Hamann, A. B. F. Martinson, J. W. Elam, M. J. Pellin and J. T. Hupp, *J Phys. Chem. C* **112**, 10303 (2008).

# Thursday Afternoon, October 21, 2010

**Energy Frontiers Topical Conference**  
**Room: Mesilla - Session EN+SS+TF-ThA**

## Transparent Conductors

**Moderator:** S. Gupta, University of Alabama

2:00pm **EN+SS+TF-ThA1 Synthesis of ZnO:F by DC Reactive Magnetron Sputtering.** *X. Noirfalise*, University of Mons, Belgium, *T. Godfroid*, Materia Nova, Belgium, *G. Guisbiers*, IEMN Lille, France, *R. Snyders*, University of Mons, Belgium

Nowadays, numerous applications in the electronics and/or optoelectronics field need transparent thin films presenting a good electrical conductivity. The transparent conductive oxides (TCO) which reveal a large band gap and a good electrical conductivity fulfil these requirements. Recently, due to the significant increase of the demand, the prize of the most employed TCO, namely indium tin oxide (ITO) has strongly increased. Therefore, an alternative to this material becomes necessary. Among all the candidates, ZnO:F and Cd<sub>2</sub>SnO<sub>4</sub> present the best performance in term of transparency and electrical conductivity. For obvious environmental reasons the latter cannot be considered. Therefore, ZnO:F is identified as the best candidate to replace ITO in TCO applications.

The most employed techniques for the synthesis of ZnO:F are Chemical Vapor Deposition and Spray Pyrolysis which both require organometallic precursor and high temperature processing. Another drawback of these technologies is the low chemical purity of the synthesized films because of the presence of the precursor decomposition products. At the contrary, reactive magnetron sputtering is an environmentally friendly technology allowing the synthesis of thin films with very fine control of the chemistry. Therefore, the aim of this work is to study the reactive magnetron sputtering of ZnO:F.

Thin films were prepared by DC reactive sputtering using a zinc target in an Ar/O<sub>2</sub>/F<sub>2</sub> mixture. In a first attempts, ZnO films have been synthesized in order to optimize the matrix properties in terms of crystallinity and transparency. The studied parameters were the DC power (P<sub>DC</sub>), the total pressure (P<sub>Tot</sub>) and the O<sub>2</sub> flow (f<sub>O2</sub>). Our data reveal that the ZnO films presenting the best features are prepared for P<sub>DC</sub> = 70 W, P<sub>Tot</sub> = 30 mTorr and f<sub>O2</sub> = 3 sccm.

The second step was to introduce fluorine in this matrix. Therefore, we have studied the crystallographic, chemical, electrical and optical properties of the deposited films as a function of the fluorine content. In our deposition window, all films present a high transmission in the visible (> 80%). Our XRD data reveal decrease of the crystallite size with the increase of the fluorine content. Above a fluorine concentration of 2-3%, the ZnO:F crystallinity decreases. Our XPS and XRD data suggest that F atoms substitute O atoms in the ZnO structure. Finally, the electrical properties have been investigated by Hall effect measurements. For the optimal synthesis conditions (~ 2% of fluorine in the film), a charge carrier density of ~ 10<sup>20</sup> cm<sup>-3</sup>, an electrical resistivity of 10<sup>-2</sup> Ω.cm and charge mobility of about 4 cm<sup>2</sup>/V.sec have been measured.

2:20pm **EN+SS+TF-ThA2 Relationship Between Resistivity Stability and Structure of Transparent Conducting Impurity-doped ZnO Thin Films.** *J.-I. Nomoto*, *T. Hirano*, *T. Miyata*, *O. Ueda*, *T. Minami*, Kanazawa Institute of Technology, Japan

Recently reported results show that the resistivity stability for moisture-resistance and heat-resistance tests in transparent conducting impurity-doped ZnO thin films prepared on low temperature glass substrates is considerably affected by the film thickness as well as the kind and content of doped impurity. In this paper, we discuss the relationship between the obtainable resistivity stability and the structure in Al-, Ga- and B-doped ZnO (AZO, GZO and BZO) thin films prepared with a thickness in the range from 30 to 3000 nm by various deposition methods. Transparent conducting AZO, GZO and BZO thin films were prepared on glass substrates at 200°C by dc or rf magnetron sputtering, vacuum arc plasma evaporation and pulsed laser depositions. The resulting film structures were evaluated using a scanning electron microscope (SEM), an atomic force microscope (AFM) and a transmission electron microscope (TEM). The surface morphology of the impurity-doped ZnO films was found to change significantly after exposure to a highly moist environment (air at 85% relative humidity and 85°C) for 1000 h, as evidenced from AFM and SEM images; although the resistivity stability in these tests tended to improve with increasing impurity-doped ZnO thin film thickness, the effect was considerably dependent on the kind of doped impurity. In contrast, the surface morphology changed only slightly even after exposure to an oxidizing atmosphere (air at a temperature of 200°C) for 1000 h. The

resistivity stability in the heat-resistance tests was found to depend significantly on whether the testing temperature was lower or higher than approximately 300°C. The amount of resistivity increase in the moisture-resistance and heat-resistance tests was found to correlate with the structure of the impurity-doped ZnO thin films, as evidenced from TEM images. The variation exhibited in the resistivity stability in these resistance tests is mainly attributed to micro-structural differences associated with the crystallinity of the deposited impurity-doped ZnO thin films.

2:40pm **EN+SS+TF-ThA3 Bulk and Surface Physics of Indium Oxide Thin Films Grown on Cubic Zirconia by O-plasma Assisted Molecular Beam Epitaxy.** *R.G. Egdell*, University of Oxford, UK **INVITED**

Tin doped indium oxide (In<sub>2</sub>O<sub>3</sub>) aka ITO is one of the most important transparent conducting oxides, yet it is only recently that many fundamental aspects the bulk and surface physics of indium oxide itself and of ITO have been addressed [1-3]. We have an ongoing programme concerned with growth of In<sub>2</sub>O<sub>3</sub> on Y-stabilised ZrO<sub>2</sub> by oxygen plasma assisted molecular beam epitaxy and will review our most recent work in this area. Issues that will be addressed include the following:

The influence of surface energies and strain on the growth of In<sub>2</sub>O<sub>3</sub> on low index zirconia surfaces. Mechanisms for relief of strain, including crystallographic tilting and development of nanostructures during high temperature MBE growth.

The influence of strain on the optical properties of ultrathin In<sub>2</sub>O<sub>3</sub> films.

Surface structure and surface physics of In<sub>2</sub>O<sub>3</sub> and ITO surfaces, including development of electron accumulation layers for material with low bulk doping levels.

### References

- 1 P D C King *et al.*, Physical Review Letters 2008 **101** 116808
- 2 A Walsh *et al.*, Physical Review Letters 2008 **100** 167402/1-4
- 3 K H L Zhang *et al.*, Chemistry of Materials 2009 **21** 4353-4355

3:40pm **EN+SS+TF-ThA6 Recent Developments in Transparent Conducting Oxides for Thin-Film Solar Cells.** *J. Burst*, *M. Scott*, *T. Gessert*, National Renewable Energy Laboratory, *S. Weiss*, *B. Rogers*, Vanderbilt University, *T. Coutts*, Timothy J. Coutts Consulting, Inc

Transparent conducting oxides (TCOs) are utilized in all thin-film solar cells. Their function is to reduce electrical losses associated with collection of photogenerated current. However, they exhibit optical and electrical losses of their own and many researchers have tried to reduce these losses either by adjusting deposition conditions, post-deposition annealing, or by using completely novel materials. In our own work, we have shown that it is important to develop TCOs with high free-carrier mobility rather than high concentrations, which causes increased optical losses. Our latest results suggest significant gains in the performance of thin-film solar cells may be made via relatively minimal changes to the TCOs.

We have shown that the properties of transparent conducting oxides (TCOs) can be improved by doping them with approximately 1 atomic % cations whose oxides exhibit high dielectric permittivity. Our experiments have shown that TCOs doped with "high permittivity" cations have increased permittivity compared to the undoped TCO. Also, for similar carrier concentrations and mobilities, the doped TCOs have free-carrier absorption bands shifted to longer wavelengths (1500 nm doped v. 1300 nm undoped), thereby reducing optical losses compared to the undoped TCO. These observations are consistent with predictions based on the Drude free-electron model. In addition, there is evidence that the increased permittivity helps screen scattering centers, thereby leading to enhanced mobility. We will demonstrate that increasing film permittivity reduces optical losses in several standard TCO materials (ZnO, SnO<sub>2</sub>, and In<sub>2</sub>O<sub>3</sub>). Film resistivity as low as 6x10<sup>-5</sup> Ω.cm (corresponding to a sheet resistance of about 1 Ω/sq for a film 500 nm thick) has been achieved without compromising the high optical transmittance. The study has also indicated that TCO films with additions that alter permittivity appear to be less sensitive to variation in deposition ambient and temperature. Although this insight will clearly assist development of future TCO materials, we believe the results are even more relevant to present TCOs that may embody industrial advantages but remain limited by low mobility. *This abstract is subject to government rights.*

4:00pm **EN+SS+TF-ThA7 The Study of AZO/Au/AZO as a Transparent Electrode for Organic Light Emitting Diodes.** *J.H. Park*, Hanyang University, Republic of Korea

Transparent conducting oxide (TCO) thin films and coatings are an important and integral part of a number of electro optical devices because TCOs play an important role as transparent electrodes for flexible



optoelectronic devices such as liquid crystal displays, solar cell panels, and organic light emitting devices (OLEDs). Typical TCOs are impurity-doped indium oxides, tin oxides and zinc oxides that offer commercially acceptable performance in terms of conductivity transmittance, environmental stability, reproducibility and surface morphology. The Al-doped ZnO (AZO) films show low resistance and high transmittance in the visible range of the spectrum. However, their resistivity is rather high in some cases to adapt as a transparent electrode for advanced applications. Recently, in order to improve properties of TCO, thin metal or metal alloy film was embedded between TCO layers. In this study, we will discuss the effect of Au middle layer thickness on the electrical and optical properties of the multilayer TCOs and OLED applications. The AZO films were deposited on Corning Eagle 2000 glass substrates by atomic layer deposition (ALD). The optimization conditions of AZO films were 1/19 ratio of TMA/DEZ and 180°C. And Au middle layer was deposited by e-beam evaporator. The AZO/Au/AZO films exhibit better electrical properties compared to the AZO films. The carrier concentration was increased from  $1.9 \times 10^{20}$  to  $5.8 \times 10^{20} \text{ Cm}^{-3}$ . The mobility was decreased from 12.6 to 12.4  $\text{Cm}^2/\text{Vs}$ . The resistivity was decreased from  $2.6 \times 10^{-3}$  to  $8.5 \times 10^{-4} \Omega \text{ Cm}$ . However transmittance was decreased from 91 to 76 %, on average. The AZO/Au/AZO films were used as anode electrodes for red emission OLED application. The device showed that a maximum luminance of  $2.4 \times 10^3 \text{ cd/m}^2$  at 11 voltage. More detailed electrical and physical results will be discussed and presented.

4:20pm **EN+SS+TF-ThA8 Origin of the Distribution of Electrical Properties of ITO Sputtered Films on Substrate**, *Y. Hoshi, Y. Yasuda*, Tokyo Polytechnic University, Japan, *H. Shimizu*, Niigata University, Japan  
The ITO films deposited by magnetron sputtering and facing target sputtering at low substrate temperature have quite different distributions of film properties. However, their origin was still not clear. In this paper, we clarify the origin of the different distributions between the sputtering methods, and will propose a sputtering method to deposit the ITO films with good uniformity.

In the deposition of ITO films by a conventional planar magnetron sputtering, the films deposited at the center of the substrate have higher oxygen content than the films deposited at the end of the substrate. It should be noted that the film deposited by a facing target sputtering has much lower oxygen content than the films deposited by conventional planar magnetron sputtering. As a result, the ITO films with poor transparency were always obtained by the sputtering in pure Ar gas, when a Facing Target Sputtering system was used.

These phenomena can be explained by the following model; When sputter-deposition of ITO films was performed at a low temperature, only oxygen atoms produced by the sputter-emission from the target surface promote the oxidation of indium atoms on the film surface. In other words, oxygen molecules cannot oxidize the indium atoms at a low temperature.

In addition, oxygen atoms sputter-emitted from the target have different angular distributions than indium atoms have. That is, the emission ratio of oxygen atoms to indium atoms sputter-emitted from the target surface changes depending on the emission angle and gradually decreases with an increase of the emission angle. This phenomenon mainly causes the distribution of the properties of ITO films on the substrate, although bombardment of high energy negative oxygen ions also affects the distribution of film properties in planar magnetron sputtering.

In order to deposit uniform film on the substrate, compensation of the angular distribution in the emission ratio of oxygen atoms to indium atoms is necessary. Use of two sputtering sources arranged like a facing target sputtering system is one of the solutions to compensate the distribution and obtain the films with more excellent uniformity.

4:40pm **EN+SS+TF-ThA9 Deposition of Al-doped ZnO by Atomic Layer Deposition Using Ozone as the Oxygen Source**, *W.L. Gladfelter, H. Yuan, B. Luo, S.A. Campbell*, University of Minnesota

Transparent conducting oxide (TCO) films are used in many photovoltaic and optoelectronic devices. The need to deposit conformal films at relatively low temperature has raised interest in atomic layer deposition (ALD). Literature reports establish that n-doped zinc oxide has been deposited by ALD using water as the source of oxygen and aluminum or gallium as the dopant. The interest in replacing water with ozone has led to many new ALD routes to metal oxide films, including ZnO. In this presentation we will describe an effective ALD route to Al-doped ZnO. Aluminum-doped ZnO (AZO) films were grown on Si and SiO<sub>2</sub>/Si substrates in the temperature range from 150 - 300°C using diethylzinc as the zinc precursor and ozone as the oxygen source. Trimethylaluminum was used as the aluminum precursor. Two approaches to doping were studied. In one a nanolaminate was formed by interspersing a trimethylaluminum/ozone cycle in between the diethylzinc/ozone cycles. The overall aluminum concentration depended on the number of

diethylzinc/ozone cycles. The second approach involved co-injection of both metal precursors in which their relative concentrations were controlled by adjusting the precursor vessel temperature. The influence of the deposition method on the composition, structural, electrical, and optical properties of the AZO films as a function of doping metal concentration will be reported. X-ray diffraction patterns showed all the samples were polycrystalline and exhibited preferential (0001) orientation. The (0002) reflection for AZO films shifted in opposite directions depending on the deposition method. The carbon content of the films was below the detection limit of Auger electron spectrometry. The lowest resistivity ( $6 \times 10^{-4} \Omega \cdot \text{cm}$ ) of the AZO films was obtained using the co-injection process. The average optical transmission was over 85 % in the range of 400-800 nm and the optical band gap increased with increasing doping in accordance with Burstein-Moss effect. The resistivity of AZO films grown by the co-injection method decreased to  $3 \times 10^{-4} \Omega \cdot \text{cm}$  after rapid thermal annealing (RTA) in an Ar atmosphere.

5:00pm **EN+SS+TF-ThA10 Atomic Layer Deposited (ALD) Al-doped ZnO Films for Transparent Conductor Applications**, *P. Banerjee*, University of Maryland, *W.-J. Lee, G.-Y. Bae*, Dong-Eui University, Republic of Korea, *S.-B. Lee, G.W. Rubloff*, University of Maryland

Among various materials for thin film transparent conductor applications, Al-doped ZnO (AZO) is a particularly attractive material because of its excellent properties, such as higher thermal stability, good resistance against damage by hydrogen plasma and potentially, low cost compared to indium tin oxide (ITO). Of the various available deposition techniques, Atomic layer deposition (ALD) provides superb control at the nanoscale for thickness, uniformity, conformality and Al doping of AZO films. This is particularly attractive for use in nanostructures, as well as in more conventional applications such as liquid crystal displays.

We report here results for structural, optical and electrical properties of ultrathin ALD AZO films as a function of at% Al. AZO films of ~ 100nm thickness were deposited on quartz substrates at 150C using a commercial BENEQ TFS 500 reactor using diethyl zinc (DEZ) and H<sub>2</sub>O as precursors for ZnO, and trimethyl aluminum (TMA) and H<sub>2</sub>O as precursors for Al<sub>2</sub>O<sub>3</sub>. Al-doping was incorporated in a film by introducing a single cycle of TMA-H<sub>2</sub>O after fixed cycles of DEZ-H<sub>2</sub>O pulses. This 'super' cycle was repeated until the desired thickness was achieved. Al-doping was varied from 0.0at% to 24.5at%, on various samples, as determined by EDX. In addition, XRD, AFM, UV-Vis spectroscopy and temperature-dependent (80K-340K) Hall measurements were carried out to understand the structural, optical and electrical properties in these films.

Strong texture effects were observed in the AZO films on the quartz substrates as the films preferentially crystallized along the [100] direction. This texturing effect is different from the [002] normally reported for AZO films deposited using established methods other than ALD. Crystallinity and electrical conductivity peaked at 3at% Al, consistent with previous published work. AFM results show a dramatic drop in surface roughness with Al doping. Optical transmittances of over 80% were obtained for all films in the visible region.

Calculation of lattice parameter constants from XRD data and analysis within the framework of the Burstein-Moss effect, reveal that AZO films act as substitutionally doped films for Al doping less than ~7.3at%. Beyond this value of doping, phase segregation and possible formation of a low conductivity phase cause a reduction in the concentration and mobility of free carriers and hence a degradation of the electrical properties.

5:20pm **EN+SS+TF-ThA11 Silicon-Titanium Oxides as Transparent Conductors for Photovoltaic Applications**, *J. Chivers, T. Vandervelde*, Tufts University

We report on the use of Earth-abundant silicon-dioxide and titanium-dioxide as a transparent conducting oxide (TCO) and antireflective (AR) coating. TCOs are a critical component in modern photovoltaic devices, used as a front-side contact that won't block incident light. At present, many TCOs require rare-Earth materials (e.g. Indium), which is problematic for large-scale manufacturing. The abundant, well characterized materials used here can be integrated into an existing product line quickly and cheaply. The varied band gap and index of refraction conditions inherent in the SiTiO<sub>2</sub> system allow controlled variation of material properties during monolithic growth. Some TCOs may also act as an AR coating, further increasing light absorption. The ideal AR coating would gradually change from the index of refraction of air to that of the underlying semiconductor. Most AR coatings used today make this transition in a small number of steps, which limits their efficacy. In this work, we investigate deposition processes that slowly grade the index of refraction while maintaining conductivity and transparency.

# Thursday Afternoon Poster Sessions

## Energy Frontiers Topical Conference

Room: Southwest Exhibit Hall - Session EN-ThP

### Energy Frontiers Topical Conference Poster Session

**EN-ThP1 N-doped TiO<sub>2</sub> Photocatalytic Thin Films : Synthesis with Controlled Nitrogen Partial Pressure and Study on Their Catalytic Activity, J.-H. Boo, S.-J. Cho, C.-K. Jung, Y.-H. Song,** Sungkyunkwan University, Republic of Korea, S.-S. Kim, Paichai University, Republic of Korea

We have deposited N-doped TiO<sub>x</sub>N<sub>y</sub> thin films on Si(100) substrates at 500°C using PEMOCVD method. Titanium iso-propoxide was used as precursor with different nitrogen flow rate to control oxygen and nitrogen contents in the films. Changes of chemical states of constituent elements in the deposited films were examined by XPS analysis. The data showed that with increasing nitrogen flow rate, the total amounts of nitrogen and titanium were increased while that of oxygen was decreased, resulting in a binding energy shift toward high energy side. The characteristics of film growth orientation and structure as well as morphology change behavior were also analyzed by XRD, TED, TEM, AFM, and SEM. Deposition at higher nitrogen flow rate results in finer clusters with a nano-scale grain size and a slower growth rate.

In order to elevate photocatalytic activity of the as-grown N-doped TiO<sub>x</sub>N<sub>y</sub> films, argon and oxygen plasmas ignited by atmospheric discharge at 300 W were also used within 5 min. at room temperature. Photocatalytic activity was evaluated by the measurements of the contact angle, UV-Visible spectroscopy. In this work, the effect of the plasma on the improvement of hydrophilic property of N-doped TiO<sub>x</sub>N<sub>y</sub> photocatalysts has mainly been investigated. Superhydrophilic property and smooth surface morphology appeared in the UV light irradiation with O<sub>2</sub> plasma treatment.

Keywords : N-doped TiO<sub>x</sub>N<sub>y</sub> Thin Film, Photocatalyst, PEMOCVD, Atmospheric Plasma, Surface Modification

**EN-ThP2 Optical and Electrical Properties of Transparent Conducting B-doped ZnO Thin Films Prepared by Various Deposition Methods, J.-I. Nomoto, S. Hotta, T. Miyata, T. Minami,** Kanazawa Institute of Technology, Japan

Recently, transparent conducting impurity-doped ZnO films with a high transmittance in the near-infrared region have attracted much attention for transparent electrode applications in thin-film solar cells. It is necessary to achieve a reduction of the plasma resonance frequency resulting from a decrease of carrier concentration. However, in order to maintain a low resistivity in impurity-doped ZnO films, any decrease in carrier concentration should be compensated by an appropriate increase of mobility. In this paper, we describe the preparation of transparent conducting B-doped ZnO (BZO) thin films with a lower carrier concentration as well as a higher Hall mobility by various deposition methods. BZO thin films were prepared on low temperature glass substrates by dc or rf magnetron sputtering deposition, pulsed laser deposition (PLD) and vacuum arc plasma evaporation methods. The optical and electrical properties were evaluated in BZO thin films prepared with various thicknesses up to about 3 μm and doped B contents (B/(B+Zn) atomic ratio) up to 5 at.%. In addition, long-term resistivity stability was evaluated with exposure to a highly moist environment (air at 85% relative humidity and 85°C) as well as an oxidizing atmosphere at a high temperature (air at a temperature up to 250°C). In the moisture-resistance tests, the BZO thin films exhibited an increase in resistivity during long-term testing; increasing the thin film thickness tended to lessen this increase in resistance, irrespective of the deposition method. In the heat-resistance tests, the resistivity of thin films thicker than approximately 200 nm was found to be stable for 1000 h at a testing temperature up to 200°C. A Hall mobility of 42 cm<sup>2</sup>/Vs and a carrier concentration of 3.4×10<sup>20</sup> cm<sup>-3</sup> were obtained in a BZO thin film prepared by PLD. Resistivities of 4-6×10<sup>-4</sup> Ωcm were obtained in 500 nm-thick-BZO thin films prepared with a B content of 1 at.%, irrespective of deposition methods. The low-resistivity BZO thin films exhibited an average transmittance in the visible range above 80 %; transmittances were above 80% at a wavelength of 1100 nm and 75% at 1300 nm.

**EN-ThP3 Enhanced Performance of Dye-Sensitized Solar Cell by Inorganic/Organic Core-Shell Formation using Dip-Coating Method, M.J. Shin, J.M. Kim, H.J. Kim, B. Hong,** Sungkyunkwan University, Republic of Korea

Dye-sensitized solar cell (DSSC) is considered as alternative to traditional solar cells due to its environment-friendly energy conversion capability and

low fabrication cost. However, DSSC still suffers from efficiency loss due to a high recombination rate between the injected electrons and the oxidized dye or ions in electrolyte.

In this work, we present a very efficient but simple method is presented to improve the efficiency of DSSC using inorganic/organic core-shell electrode. This core-shell electrode consists of an inner nanoporous TiO<sub>2</sub> matrix covered with an aminopropyltriethoxysilane (APS) monolayer. It is relatively easy to control the shell density by controlling the concentration of APS using the dip-coating method. We confirmed that the efficiency of DSSC with TiO<sub>2</sub>/APS core-shell instead of conventional TiO<sub>2</sub> was significantly dependent on the shell density. Relative change in surface chemistry with APS concentration was investigated by various analysis methods. The power conversion efficiency under AM 1.5 G spectral illumination of 100 mWcm<sup>-2</sup> was improved by 20 % (from 4.37 % to 5.28 %) when APS concentration was optimized. This TiO<sub>2</sub> nanoparticles covered with APS are supposed to increase dye adsorption on TiO<sub>2</sub> surface and to prevent interfacial recombination of charge carriers. For the various analysis, it was used UV-absorbance spectroscopy, FT-IR (Fourier transfer IR), EIS (Electrochemical Impedance spectroscopy), TOF-SIMS (Time-of-Flight Secondary Ion Mass Spectrometry) and HR-TEM (High Resolution-Transmission Electron Microscope).

**EN-ThP4 Characteristics of Undoped ZnO as Window Layer for CIGS Thin Film Solar Cell using Nano-Inks, E.C. Choi, J. Chang, D.Y. Jung, B. Hong,** Sungkyunkwan University, Republic of Korea

ZnO is a very useful material as II-VI compound semiconductor with a wide band gap of 3.3 eV and a property of native n-type semiconductors. It has been studied actively due to its excellent optical, electrical and structural properties suitable for many applications such as transparent conductive oxide (TCO), solar cell window layer and surface acoustic wave (SAW) devices. In particular, n-type and undoped ZnO films are used as the window layer of GIGS solar cell (n-ZnO/-ZnO/CdS/CIGS/Mo/glass).

The surface morphology of CIGS film deposited on Mo/glass substrate by liquefied deposition method using nano-inks is severely uneven and the film has many crevices. Also, the CBD-CdS layer with the thicknesses of about 50 nm does not perfectly cover the surface of the CIGS layer. Consequently, these crevices, which remain before the TCO deposition, lead to the formation of shunt path between TCO and CIGS layers.

Therefore, in this study, we investigate the role of undoped ZnO film with high resistivity to prevent the shunt path between TCO and CIGS layers, and ZnO films are deposited varying the thickness and the plasma power to investigate characteristics of undoped ZnO film for CIGS solar cell. It is confirmed that the efficiency of CIGS solar cell depends on the properties of the undoped ZnO films. The films are deposited using magnetron sputtering system in argon ambient and are analyzed using Hall measurement, UV-visible spectrometer and XRD.

**EN-ThP5 Effect of Hydrogen and Deuterium Gas on the Thermionic Electron Emission from Nitrogen Doped Diamond Films, M. Zumer, V. Nemanic, B. Zajec, Jozef Stefan Institute, Slovenia, R.J. Nemanich, F.A.M. Koec,** Arizona State University

Nitrogen doped, hydrogen terminated diamond films have shown a work function of less than 1.5 eV and thermionic electron emission has been detected at temperatures as low as 300 °C. This report explores the influence of hydrogen and deuterium gas on the electron emission using a triode setup with an applied electric field that ranges from low values to 4 MV/m. The extracting grid and phosphor screen were set to the same potential. The hydrogen terminated, nitrogen doped diamond films were deposited on 25 mm diameter molybdenum substrates by microwave plasma assisted chemical vapour deposition. The process involves a nucleation layer, nitrogen doped layer and surface termination which were all optimized to enhance the emission. The thermionic electron emission from 300 to 500 °C was quite intense. A typical average emission current density at 500 °C was of the order of 2E-6A/cm<sup>2</sup> at a base pressure of the order of 10<sup>-7</sup> mbar. The emission was relatively stable exhibiting only a weak tendency to decrease with time. The emission was relatively uniform across the surface as opposed to the intense emission sites often observed in field emission. When hydrogen was leaked into the chamber, the emission current density increased by greater than an order of magnitude as the pressure was increased from UHV to 10<sup>-5</sup> mbar. Results indicated that atomic hydrogen generated by a nearby Bayard-Alpert ionization gauge induced the effect. An identical leak rate of deuterium causes a similar but less intense increase of the emission current. At both cases, the initial UHV of the thermionic emission was restored by establishing again the UHV. The question of whether the hydrogen (deuterium) improves the surface through bonding and forming a NEA or whether it assists in the charge

transfer process is assessed. These results should guide the development of an efficient thermionic cell for direct conversion of heat to electricity.

**EN-ThP6 Hot Electron Transfer from Semiconductor Nanocrystals.** *W. Tisdale*, University of Minnesota, *K. Williams*, University of Texas at Austin, *B. Timp*, *D. Norris*, *E.S. Aydil*, University of Minnesota, *X.-Y. Zhu*, University of Texas at Austin

In typical semiconductor solar cells, photons with energies above the semiconductor bandgap generate hot charge carriers that quickly cool before all of their energy can be captured, a process that limits device efficiency. Although fabricating the semiconductor in nanocrystalline morphology can slow this cooling, the transfer of hot carriers to electron/hole acceptors has not yet been thoroughly demonstrated. We use time-resolved optical second harmonic generation to observe hot electron transfer from colloidal lead selenide nanocrystals (PbSe NCs) to a titanium dioxide electron acceptor (TiO<sub>2</sub>). With appropriate chemical treatment of the nanocrystal surface, this transfer occurs much faster than expected. Moreover, the electric field resulting from sub-50 femtosecond charge separation across the PbSe-TiO<sub>2</sub> interface impulsively excites coherent vibrations of the TiO<sub>2</sub> surface atoms, whose motions can be followed in real time.

**EN-ThP7 Synthesis and Characterization of Free-Standing Si Nanocrystals using PECVD.** *R. Chaukulkar*, *B.N. Jariwala*, *S. Weeks*, Colorado School of Mines, *N.J. Kramer*, Eindhoven University of Technology, Netherlands, *S. Agarwal*, Colorado School of Mines

Si nanocrystals (NCs) (size <5nm) are generating an increased interest as a material to be used in third generation photovoltaics (PVs) owing to their size-dependent band gap, visible photoluminescence and multiple exciton generation (MEG). Synthesis of both liquid and gas phase NCs have been reported in the literature. We synthesize the Si NCs using a capacitively-coupled SiH<sub>4</sub>/Ar plasma generated using radio-frequency power. The Si NCs are characterized using *in situ* attenuated total reflection Fourier-transform infrared spectroscopy (ATR-FTIR) and *ex situ* techniques such as transmission electron microscopy (TEM), energy-dispersive X-ray spectroscopy, infrared spectroscopy, photoluminescence spectroscopy, Raman spectroscopy and X-ray diffraction. The size of the NCs can be controlled by varying the residence time in the plasma volume. The residence time is adjusted to attain a particle size of 5nm collected on a grid. The crystallinity of the NCs depends on the amount of rf power put in the plasma. By varying the input rf power we were successful in demonstrating the transition from amorphous to crystalline nanoparticles using X-ray diffraction and TEM.

**EN-ThP8 Physical Properties of Zinc Oxide Thin Films for Hybrid Solar Cell Application.** *S.-H. Nam*, *M.-H. Kim*, Sungkyunkwan University, Republic of Korea, *S. Kim*, Paichai University, Republic of Korea, *B. Hong*, *J.-H. Boo*, Sungkyunkwan University, Republic of Korea

Zinc oxide (ZnO) films have been investigated in recent years as transparent conducting oxide layers, because of their good electrical and optical properties in combination with large band gap, abundance in nature, and absence of toxicity. Zinc oxide thin films were prepared at deposition thickness in the range of 50 nm to 150 nm by RF magnetron sputtering on glass substrates with pure zinc oxide target. The crystallinity nanostructure and surface morphology of zinc oxide thin films were investigated by X-ray diffraction (XRD), scanning electron microscopy (SEM). As the thickness of the films increased, the grain size and surface roughness increased. Also, we studied the optical-electrical properties of the zinc oxide thin films such as carrier concentration, mobility, and resistivity by hall measurement. As changed by thickness of zinc oxide thin films, concentration become increasing. But mobility and resistivity become decreasing.

**EN-ThP9 Al and N co-doped ZnO:(Al,N) Thin Films for Solar Driven Hydrogen Production.** *S. Shet*, National Renewable Energy Laboratory

ZnO thin films with significantly reduced bandgaps were synthesized by doping N and co-doping Al and N at 100°C. All the films were synthesized by radio-frequency magnetron sputtering on F-doped tin-oxide-coated glass. We found that co-doped ZnO:(Al,N) thin films exhibited significantly enhanced crystallinity as compared to ZnO doped solely with N, ZnO:N, at the same growth conditions. Furthermore, annealed ZnO:(Al,N) thin films exhibited enhanced N incorporation over ZnO:N films. As a result, ZnO:(Al,N) films exhibited improved photocurrents than ZnO:N films grown with pure N doping, suggesting that charge-compensated donor-acceptor co-doping could be a potential method for bandgap reduction of wide-bandgap oxide materials to improve their photoelectrochemical performance.

**EN-ThP10 Optical and Thermal Studies on CdSe Quantum Dots and Rods.** *H. Awad*, *S. Abdallah*, Ain Shams University, Egypt, *K. Easawib*, *S. Negm*, Benha University, Egypt, *H. Talaat*, Ain Shams University, Egypt

**EN-ThP11 Study of Optical and Thermal Properties Of CdTe Quantum Dots Using Photoacoustic Spectroscopy.** *A. Badawi*, *N. Al-Hosiny*, Taif University, Saudi Arabia, *S. Abdallah*, Taif University, Saudi Arabia and Ain Shams University, Egypt, *S. Negm*, *H. Talaat*, Ain Shams University, Egypt

Semiconductor nanoparticles are currently of great interest for their industrial applications in a variety of optoelectronic devices specially solar cells. Recently, CdTe semiconductor quantum dots (QDs) have become one of the promising materials for high efficiency photovoltaic solar cell. Therefore, massive attention has been devoted to investigate their optical and thermal properties in order to improve the performance of the solar cell. In this work, CdTe QDs were fabricated by the chemical solution deposition (CD) technique [1]. Four samples of increasing time of growth leading to different sizes labeled (a-d) were obtained. The sizes of these samples were estimated using transmission electron microscope (TEM); as an sample (d) is shown in Fig. (1)

NOTE: WE ARE UNABLE TO INCLUDE FIGURES

Photoacoustic spectroscopy (PA) was employed to study both the optical and thermal properties of the samples at room temperature and modulation frequency  $f = 15\text{Hz}$ . Fig ( 2) show the PA spectra for the four different particle sizes samples (a-d) in the wavelength range 400–700 nm. The absorption edges shift towards lower energy region with increasing size , from (a) at 540 nm to (d) at 595 nm. The PA spectra give typical results with those obtained by regular UV-Vis absorption, though the samples were in colloidal form for UV-Vis and in powder form for the PA. The sizes of the CdTe nanocrystals were calculated using the effective mass approximation (EMA) model [2].

NOTE: WE ARE UNABLE TO INCLUDE FORMULAS

where  $m^*$  is the reduced electron-hole mass,  $E_g$  is the bulk crystal band gap,  $R$  is the average radius of the nanocrystal,  $E_{g(\text{nano})}$  is the lowest energy for electronic transition and  $h$  is the Planck's constant. The calculated average diameters of CdTe nanocrystal show an increase from 2.13 nm for (a) to 2.43 nm for (d), in agreement with the values determined by TEM.

NOTE: WE ARE UNABLE TO INCLUDE FIGURES

The PA technique was also employed to investigate the thermal properties of the CdTe QDs which are of great importance to solar energy conversion. The powder of each sample size was compressed into a disk. The PA signal amplitude was recorded at various chopping frequencies for each sample (depth profile analysis) using the Argon laser at wavelength 514 nm. The plot of  $\ln$  PA amplitude versus the  $\ln f$ . (Fig. 3) shows a distinct change in slope, at the characteristic frequency ( $f_c$ ) where the sample changes from being thermally thick to thermally thin. The thermal diffusivity ( $D$ ), was then calculated using the relation [4].

NOTE: WE ARE UNABLE TO INCLUDE FORMULAS

where  $L$  is the thickness of the sample. The calculated diffusivity varies from 0.65 cm<sup>2</sup>/s for (a) to 0.38 cm<sup>2</sup>/s for (d). These values of the thermal diffusivity are at least one order of magnitude larger than the bulk value (0.05 cm<sup>2</sup>/s) [4]. Our results are in agreement with the results of other authors [4,5], where the decrease in thermal diffusivity with increasing the particle size is attributed to the decrease in the population of phonons.

[1] Guo-Yu Lan, Zusing Yang, Yang-Wei Lin, Zong-Hong Lin, Hao-Ying Liao and

Huan-Tsung Chang, J. Mater. Chem., 2009, 19, 2349–2355

[2] Y.-S. Yuang, Y.-F. Chen, Y.-Y. Lee, L.-C. Liu, J. Appl. Phys. 76, 3041 (1994)

[ 3.] A.L. Efros, A.L. Efros, Sov. Phys. Semicond. 16, 772 (1982)

[ 4] P. Raji, C. Sanjeeviraja, K. Ramachandran, Cryst. Res. Technol. 39, 617 (2004) [5] T. El- Brolossy, S. Abdallah., S. Negm and H. Talaat Eur. Phys. J. 153, 361–

364 (2008)

**EN-ThP12 CdTe Quantum Dots Sensitized TiO<sub>2</sub> Electrodes for Photovoltaic Cells.** *A. Badawi*, *N. Al-Hosiny*, *S. Abdallah*, Taif University, Saudi Arabia, *S. Negm*, *H. Talaat*, Ain Shams University, Egypt

Semiconductors quantum dots (QDs) has been paid much attention in QDs sensitized solar cell because of their high potential in light harvesting under visible region along with particle size tuning properties. CdTe semiconductor quantum dots (QDs) have become one of the promising materials for high efficiency photovoltaic solar cell [1]. It has a high extinction coefficient ( $4.4 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ ) at 370 nm and valence band, conduction band, and band gap energies of -3.9, -5.5, and +1.6 eV, respectively, would behave as sensitizers capable of effectively injecting

electrons into TiO<sub>2</sub> NPs (band gap:3.4 eV)[2]. CdTe QDs were fabricated by the chemical solution deposition (CD) technique [3]. In this article we describe the preparation and photovoltaic characterization of CdTe quantum dot-sensitized solar cells (QDSSCs). We coated Fluorine doped Tin Oxide (FTO) substrates with 20 nm-diameter TiO<sub>2</sub> nanoparticles (NPs) by the doctor blade method. Then, the as prepared CdTe quantum dots of different sizes were deposited on the TiO<sub>2</sub>-coated substrates by the chemical bath deposition (CBD) technique for various periods of dipping times under ambient conditions. Other FTO substrates were coated with platinum to form the counter electrode, while the electrolyte containing I<sup>-</sup>/I<sub>3</sub><sup>-</sup> redox species was sandwiched between the two electrodes. The I-V characteristic curve of the QDSSCs was measured under AM1.5-simulated sunlight at 100 mW/cm<sup>2</sup>. As a result, the open-circuit photovoltage V<sub>oc</sub> and the short circuit photocurrent density J<sub>sc</sub> were about 0.48 volts and 300 μA/cm<sup>2</sup> respectively. The fill factor FF and efficiency for energy conversion η of the photovoltaic cell were calculated to be about 0.48 and 0.113 %, respectively. Our results are comparable with that obtained by Guo-YuLan et-al [2].

#### References

- [1] Y.Shen. J.Bao.N.Dai, J.Wu.F.Cu, J.C.Tao.J.C.Zhang. Appl.Surf. Sci. 255 (2009).
- [2] Guo-Yu Lan, Zusing Yang, Yang-Wei Lin, Zong-Hong Lin, Hao-Ying Liao and Huan-Tsung Chang . J. Matt. Chemistry (19),2349 (2009).
- [3] Dmitri V. Talapin, Stephan Haubold, Andrey L. Rogach, Andreas Kornowski, Markus Haase, and Horst Weller , J. Phys. Chem. B 2001, 105, 2260-2263

# Friday Morning, October 22, 2010

## Energy Frontiers Topical Conference

Room: Mesilla - Session EN+SS-FrM

### Photocatalysis and Solar Fuels

Moderator: S.-H. Lee, University of Colorado

8:20am EN+SS-FrM1 **Hybrid Metal-Semiconductor Nanomaterials for Electrochemical Hydrogen Generation**, *M.R. Dirmyer, E.P. Luther, A.K. Burrell, B.C. Tappan, A.H. Mueller*, Los Alamos National Laboratory

8:40am EN+SS-FrM2 **Surface Electronic Properties of Tantalum Oxynitride Perovskites**, *S. Balaz, S. Porter, P.M. Woodward, L.J. Brillson*, The Ohio State University

We used a complement of X-ray photoemission spectroscopy (XPS), depth-resolved cathodoluminescence spectroscopy (DRCLS), Kelvin Probe Force Microscopy (KPFM), and Atomic Force Microscopy (AFM) to measure the surface electronic properties of the tantalum oxynitride series  $\text{ATaO}_2\text{N}$  ( $A = \text{Ca, Sr, Ba}$ ) and  $\text{RTaON}_2$  ( $R = \text{La, Pr}$ ), promising candidates for photocatalytic splitting of water under illumination by visible light. Besides creating perovskites with band gaps that straddle the redox potentials of water closely, a major challenge to conversion efficiency is the recombination of free carriers by trap states formed by lattice defects. We used DRCLS to measure the energies and densities of these recombination centers with respect to the bulk oxynitride energy bands and Fermi levels. Previously reported UV-VIS diffuse reflectance measurements indicate band gap absorption onsets at 2.4, 2.1, 1.8 [1], 2.0, and 2.0 eV [2] for  $\text{CaTaO}_2\text{N}$ ,  $\text{SrTaO}_2\text{N}$ ,  $\text{BaTaO}_2\text{N}$ ,  $\text{LaTaON}_2$  and  $\text{PrTaON}_2$ , respectively. DRCL spectra reveal both broad band-to-band transitions in the 2-5 eV range as well as intense and narrow sub-band gap peak features at 1.95, 1.70, 1.70, 1.70 and  $1.79 \pm 0.01$  eV for the same oxynitride sequence. The relatively constant DRCLS gap state energies indicate similar defects derived from the oxygen and nitrogen 2p orbitals comprising the valence band for all five compounds. By varying the incident beam energy, we probed the surface to the bulk with DRCLS, showing these peak energies nearly unchanged as a function of depth. However 0.1-0.2 eV shifts within the outer 10 nm suggest surface interactions that modify these localized states. The higher energy CL features reflect the slowly rising conduction band densities of states plus more pronounced O 2p-Ta 5d transitions calculated by density functional theory [1]. XPS valence band spectra show Fermi levels 0.5-2 eV above the valence bands, while KPFM work functions vary in the range 4.7 – 4.9 eV, indicating valence band maxima comparable to the 5.67 eV oxidation potential of water. Charging and potentials that vary laterally with nanoscale thickness can affect the XPS and KPFM values significantly but not DRCLS. The appearance of strong defect emissions at energies well within the band gap is indicative of strong recombination that can limit optical conversion efficiencies. Hence, these studies reveal the importance of O- and N-derived native point defects in limiting the efficiency of oxynitride photocatalysts.

[1] Y.-I. Kim, P. M. Woodward, K.Z. Baba-Kishi, and C.W. Tai *Chem. Mater.* 2004, 16, 1267.

[2] S. Porter, Y.-I. Kim, P. Woodward, Am. Phys. Soc. March Meeting, March 15-19, 2010, abstract X27.00003.

9:00am EN+SS-FrM3 **Zinc-Gallium Oxynitrides as Visible-Light Photocatalysts: Band Gaps and Formation Energies**, *H. Schmidt, D.J. Doren, V.B.R. Boppana, R.F. Lobo*, University of Delaware

Solid solutions of GaN and ZnO have been shown to be a promising class of photocatalysts, capable of splitting water under visible-light irradiation. The structural and electronic properties of  $\text{Ga}_{1-x}\text{Zn}_x\text{N}_{1-x}\text{O}_x$  have been studied using density-functional theory with the Linear Augmented Plane Wave (LAPW) method at varying values of  $x$ . A GGA+U approach is used to better describe the semicore 3d states of Ga and Zn. These calculations show that there exists a p-d coupling between the N 2p and Zn 3d states, leading to a decreased band gap. The band gaps in the mixed metal oxynitrides are lower than either ZnO or GaN, thus allowing excitation by visible light. The trend in band gaps over the range of Zn concentrations ( $x$ ) is consistent with experimental results. The expected band gap minimum is at a composition that is difficult to synthesize. Formation energies have been calculated to understand the limitations on synthesis of these materials. Several starting materials and synthesis environments have been studied in the formation energy calculations to determine how the thermodynamically preferred products depend on experimental conditions and whether high concentrations of zinc can be obtained in these materials.

9:20am EN+SS-FrM4 **Electronic Structure Analysis and Photocatalytic Properties of Novel Spinel Zinc Gallium Oxy-Nitride Semiconductors**, *B. Boppana, H. Schmidt, D.J. Doren, R.F. Lobo*, University of Delaware

A sol-gel precursor was used to synthesize zinc gallium oxy-nitrides with visible light band gaps. At low temperatures, novel spinel oxynitrides were produced with band gaps of 2.5 to 2.7eV, surface areas of 16 to 36  $\text{m}^2/\text{g}$ , and nitrogen content less than 1.5%. As the temperature was raised, these spinels get consumed to form wurzitic oxy-nitrides also with band gaps less than 3 eV but with surface areas of 4 to 6  $\text{m}^2/\text{g}$ . The reduction in the band gap for the spinel oxy-nitrides is associated with the incorporation of N2p orbitals in the valence band with corresponding changes in the anion position parameter. We established that the presence of a small fraction of gallium tetrahedral centers and anion vacancies might affect its unique electronic properties. The changes associated with the gallium coordination environment as the spinel zinc gallate precursor transforms to a spinel oxynitride at 550°C and further changes into a wurzite oxynitride at 850°C are studied through x-ray diffraction, ultraviolet-visible diffuse reflectance spectroscopy, neutron powder diffraction, x-ray absorption spectroscopy and other techniques. Electronic structure and formation energies of the spinel and wurzite oxy-nitrides were studied using density-functional theory (DFT) with the Linear Augmented Plane Wave (LAPW) method at varying dopant concentrations. Furthermore, these novel spinel photocatalysts were found to be active in degrading methylene blue in visible light and oxygen production from silver nitrate. The protocol developed opens a different avenue for the synthesis of semiconductors possessing the spinel crystal structure and with band gaps engineered to the visible region with potential applications for both opto-electronics and photocatalytic applications.

9:40am EN+SS-FrM5 **Synthesis and Surface Characterization of Nano-Scaled Structures for Energy Conversion Devices**, *W. Patterson, M. Robson, K. Artyushkova, P. Atanassov*, University of New Mexico

Using a microemulsion-based synthesis approach to create silica particles with internal porosity characterized by a nano-scale, bi-modal pore size distribution, we have developed functional templates for non-Platinum catalysts for fuel cell technologies. This material is derived from novel silica particles synthesized through oil/water/surfactant microemulsion templating under controlled conditions to have two distinct pore size regimes (~5 nm and ~40 nm). The larger pores, determined by the volume of microemulsion droplets, allow for more facile infiltration of precursors as compared to fumed silica previously used as the templating material. The smaller pores are determined by micellar dimensions and allow sites for creation of active site centers.

After formation of the silica, a subsequent carbon/active-site precursor co-impregnation process is followed by pyrolysis and etching. This leads to formation of open-frame structures of synthetic carbon supports decorated with the nano-phase metallic catalyst of choice. The resulting high surface area material is a bi-porous, carbonaceous matrix decorated with a low loading of non-precious metal. Last year, this effort resulted in demonstrating Pt/C catalysts for oxygen reduction. We have since focused efforts towards non-Pt precursors for pyrolytic formation of a nitrogen-containing carbon backbone structure in combination with transition metals, Co and Fe.

Synthesis conditions, such as the amount of precursor, pyrolysis temperature, and etching conditions play an important role in formation of the porous structure of the resulting electrocatalyst. Well designed nanoporous structures can effectively minimize transport limitations, thus increasing the accessibility of the active sites by gas and electrolyte phases in the fuel cell active layer.

Thorough characterization including SEM, TEM, XRD, and XPS was performed. Detailed physisorption was performed to characterize the pore structure and surface area of the materials. A thorough analysis of the surface composition and structure as a function of pyrolysis temperature for the pyrolyzed Co-N precursor with sucrose was performed and high-resolution XPS spectra were acquired.

Using methodology previously developed for correlation of material structure to properties, we provide an enhanced characterization of composition and structure, identification of active sites, and some insight into the mechanism of reduction/oxidation reactions.

10:00am EN+SS-FrM6 **Enhancement of Visible-Light Photocatalytic Efficiency of TiO<sub>2</sub> Nanopowder by Anatase/Rutile Interface Formation.**  
*Y.J. Chen, C.S. Lin*, National Dong Hwa University, Taiwan, Republic of China

In this article we report that the presence of anatase/rutile interface is essential on realization of visible-light photocatalytic ability of TiO<sub>2</sub> produced by the novel flat-flame chemical vapor condensation (FFCVC) method. Previous study shows that when nitrogen is replaced by argon as precursor carrier gas as well as quench gas in the FFCVC process, the synthesized TiO<sub>2</sub> nanopowder changes from anatase/rutile dual phases to anatase single phase. The UV-vis absorption spectra suggest that the synthesized TiO<sub>2</sub> with single anatase phase may still possess visible light absorption capability when the process parameters are carefully chosen. However, the photocatalytic efficiency drops to minimal value for the single-phase TiO<sub>2</sub> compared with that for dual-phase TiO<sub>2</sub>. To confirm that the photocatalytic efficiency difference is caused by the formation of anatase/rutile interface, we synthesize the TiO<sub>2</sub> nanopowder using argon as carrier gas while using either nitrogen or argon as quench gas for comparison. Results show that when using nitrogen as quench gas, the TiO<sub>2</sub> powder is mostly anatase phase with minor rutile content, while when using argon as quench gas, the TiO<sub>2</sub> powder is almost anatase phase with hardly any rutile content. From the x-ray diffraction analysis, the grain size of anatase from both processes is similar, indicating that the choice of quench gas does not influence significantly on the nucleation process of the TiO<sub>2</sub> nanopowder. On the other hand, the use of nitrogen as quench gas does promote the formation of rutile phase, even though the rutile content is still minimal. This observation indicates that the nitrogen as quench gas does have some effect, although weak, on TiO<sub>2</sub> nanopowder during its final coalescence and growth stage. The visible-light photocatalytic experiment shows that even two powder samples are similar, the photocatalytic efficiency of TiO<sub>2</sub> with minor rutile content is significant while that of TiO<sub>2</sub> with single anatase phase is insignificant. Since the anatase from both processes is considered the same, the photocatalytic efficiency difference must be due to that minor rutile formation. Since the photocatalytic reaction occurs mostly on the anatase surface, the enhancement of photocatalytic efficiency by the formation of rutile phase leads to the conclusion that the anatase/rutile interface is the major cause for the efficiency enhancement. We will show the XPS, EPR, and XRD characterization of powders and discuss the materials science behind the phenomenon.

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 Membreno, D.: EN+EM-TuA3, 9  
 Meng, L.: EN-TuM4, 7  
 Meyer III, H.M.: EN+AS-ThM6, 20  
 Midgett, A.G.: EN-MoA3, 5  
 Miedaner, A.: EN+TF-WeM9, 15  
 Minami, T.: EN+SS+TF-ThA2, 24; EN-ThP2, 26  
 Miyata, T.: EN+SS+TF-ThA2, 24; EN-ThP2, 26

Moh, S.: EN+PS-MoM6, 2  
 Mohan Rao, G.: EN+NS-WeA1, 16  
 Mudrick, J.P.: EN+NS-WeM5, 12  
 Mueller, A.H.: EN+SS-FrM1, 29  
 Munichandraiah, N.: EN+NS-WeA1, 16  
 Murray, P.T.: EN+EM-TuA4, 9  
 Mushfiq, M.: EN+NS-ThM12, 23  
 Myers, J.D.: EN+NS-WeM5, 12  
 Myneni, G.R.: EN+AS-ThM10, 21

— **N** —

Nachimuthu, P.: EN+AS-ThM3, 20  
 Nagamoto, K.: EN-TuM3, 7  
 Nagpal, P.: EN+EM-TuA7, 9  
 Nakamura, W.: EN+PS-MoM1, 1  
 Nam, S.-H.: EN-ThP8, 27  
 Nampoori, H.V.: EN+EM-TuA10, 10  
 Nanayakkara, S.U.: NS+EM+EN-WeA7, 18  
 Negm, S.: EN-ThP10, 27; EN-ThP11, 27; EN-ThP12, 27  
 Nekuda, J.A.: EN+TF-WeM9, 15  
 Nemanic, V.: EN-ThP5, 26  
 Nemanich, R.J.: EN-ThP5, 26  
 Neumann, M.J.: EN-TuM4, 7  
 Neyerlin, K.C.: EN+AS-ThM1, 20  
 Nijem, N.: EN+NS-ThM3, 22  
 Nimisha, C.S.: EN+NS-WeA1, 16  
 Nobis, F.: EN+TF-TuA2, 10  
 Noirfalise, X.: EN+SS+TF-ThA1, 24  
 Nomoto, J.-I.: EN+SS+TF-ThA2, 24; EN-ThP2, 26  
 Norris, D.: EN-ThP6, 27  
 Noufi, R.: EN+TF-WeM6, 15  
 Nozik, A.J.: EN-MoA3, 5  
 Nsimama, P.D.: TF+EN-MoM8, 4  
 Ntwaeaborwa, O.M.: TF+EN-MoM8, 4  
 Nunney, T.: EN+AS-ThM6, 20

— **O** —

Odom, T.W.: NS+EM+EN-WeA3, 18  
 O'Hayre, R.P.: EN+AS-ThM1, 20; EN+TF-WeM9, 15  
 Olson, T.: EN+AS-ThM1, 20  
 O'Neill, K.: EN+AS-ThM1, 20  
 Opila, R.: EN+TF-TuA9, 11

— **P** —

Palacios-Padrós, A.: EN+TF-TuA12, 11  
 Pan, J.S.: EN+TF-TuA7, 10  
 Pandey, A.: EN+AS-ThM3, 20  
 Pangan-Okimoto, K.: EN+TF-WeM5, 14  
 Park, J.H.: EN+SS+TF-ThA7, 24  
 Park, T.-H.: NS+EM+EN-WeA7, 18  
 Pasquarelli, R.M.: EN+TF-WeM9, 15  
 Patel, A.: EN+AS-ThM2, 20  
 Patterson, W.: EN+SS-FrM5, 29  
 Payzant, E.A.: EN+TF-WeM6, 15  
 Pellin, M.J.: EN+NS-ThM12, 23; TF+EN-MoM1, 3  
 Penner, R.M.: NS+EM+EN-WeA10, 19  
 Pensack, R.D.: EN-MoA1, 5  
 Perng, Y.-C.: EN+EM-TuA3, 9  
 Pietryga, J.M.: EN+NS-ThM5, 22  
 Pietsch, M.: EN+NS-WeM11, 13  
 Pivovar, B.: EN+AS-ThM1, 20  
 Polsky, R.: EN+NS-WeA2, 16  
 Ponomarev, M.: NS+EM+EN-WeA8, 18  
 Popovitch-Biro, R.: EN+TF-WeM3, 14  
 Porter, S.: EN+SS-FrM2, 29  
 Profijt, H.B.: TF+EN-MoM6, 3  
 Pursel, S.M.: EN+NS-ThM11, 23  
 Pylypenko, S.: EN+AS-ThM1, 20

— **Q** —

Qian, L.: EN+TF-TuA3, 10  
 Queen, A.: EN+AS-ThM1, 20

— **R** —

Raddiar, M.: EN-MoA11, 6  
 Rajesh, B.: EN+NS-WeA9, 17  
 Ramana, C.V.: EN+AS-ThM9, 21  
 Ramanath, G.: EN+NS-WeA8, 16; EN-MoA11, 6  
 Raub, A.: EN+NS-WeA2, 16

Rauf, S.: EN+PS-MoM3, 1  
 Ravishankar, N.: EN-MoA11, 6  
 Reichertz, L.A.: EN+TF-TuA11, 11  
 Reutt-Robey, J.E.: EN+NS-WeM10, 13  
 Richter, F.: EN+TF-TuA2, 10  
 Richter, L.J.: EN+NS-WeM6, 12  
 Rigsbee, M.: EN+AS-ThM10, 21  
 Riley, L.A.: EN+EM-TuA1, 9  
 Rissom, Th.: EN+TF-WeM3, 14  
 Ritz, E.: EN-TuM4, 7  
 Robel, I.: EN+NS-ThM5, 22  
 Roberts, M.: EN+NS-WeA2, 16  
 Robey, S.W.: EN+NS-WeM10, 13  
 Robson, M.: EN+SS-FrM5, 29  
 Rogers, B.: EN+SS+TF-ThA6, 24  
 Rogers, J.A.: EN-TuM5, 7  
 Romero, M.J.: EN+AS-ThM4, 20; EN+TF-TuA8, 11  
 Rowley, P.N.: EN+PS-MoM6, 2  
 Rubloff, G.W.: EN+SS+TF-ThA10, 25; TF+EN-MoM3, 3  
 Ruzic, D.N.: EN-TuM4, 7

— **S** —

Sampathkumaran, U.: EN+NS-ThM12, 23  
 Santucci, S.: EN+NS-WeM1, 12  
 Sanz, F.: EN+TF-TuA12, 11  
 Sato, Y.: EN-TuM3, 7  
 Schäfer, P.: EN+TF-TuA2, 10  
 Schlaf, R.: EN+NS-WeM12, 13; EN+NS-WeM2, 12; EN+TF-TuA10, 11  
 Schmidt, H.: EN+SS-FrM3, 29; EN+SS-FrM4, 29  
 Schroeter, B.: EN+NS-WeM11, 13  
 Scott, M.: EN+SS+TF-ThA6, 24  
 Semonin, O.E.: EN-MoA3, 5  
 Seyller, T.: EN+NS-WeM11, 13  
 Shemelya, C.: NS+EM+EN-WeA2, 18  
 Sheng, J.J.: EN+AS-ThM4, 20; EN+TF-TuA8, 11  
 Shet, S.: EN-ThP9, 27  
 Shimizu, H.: EN+SS+TF-ThA8, 25  
 Shin, M.J.: EN-ThP3, 26  
 Shiratani, M.: EN+PS-MoM1, 1  
 Singh, B.: EN+NS-WeA8, 16  
 Sivakov, V.A.: EN+NS-WeM11, 13; TF+EN-MoM5, 3  
 Smets, A.H.M.: EN+PS-MoM5, 1  
 Snyders, R.: EN+SS+TF-ThA1, 24  
 Song, T.B.: EN+NS-WeA10, 17; EN+TF-WeM6, 15  
 Song, Y.-H.: EN-ThP1, 26  
 Spowart, J.E.: EN+EM-TuA4, 9  
 Stair, P.C.: TF+EN-MoM1, 3  
 Stecher, J.T.: NS+EM+EN-WeA7, 18  
 Steirer, K.: EN+TF-WeM9, 15  
 Stevie, F.A.: EN+AS-ThM10, 21  
 Stradins, P.: EN+PS-MoM9, 2  
 Sun, L.: EN-MoA8, 5  
 Supparesk, R.: EN+NS-WeA9, 17  
 Swart, H.C.: TF+EN-MoM8, 4

— **T** —

Takeke Beyene, H.: NS+EM+EN-WeA8, 18  
 Talaat, H.: EN-ThP10, 27; EN-ThP11, 27; EN-ThP12, 27  
 Talkenberg, F.: EN+NS-WeM11, 13; NS+EM+EN-WeA9, 18; TF+EN-MoM5, 3  
 Tanaka, T.: EN+PS-MoM3, 1  
 Tang, A.: EN+TF-TuA3, 10  
 Tappan, B.C.: EN+SS-FrM1, 29  
 Teki, R.: EN-MoA11, 6  
 Terblans, J.J.: TF+EN-MoM8, 4  
 Terlinden, N.M.: TF+EN-MoM6, 3  
 Therien, M.J.: NS+EM+EN-WeA7, 18  
 Thevuthasan, S.: EN+AS-ThM3, 20  
 Timp, B.: EN-ThP6, 27  
 Tisdale, W.: EN-ThP6, 27  
 Tran, B.P.: EN+TF-WeM5, 14

— **U** —

Uchida, G.: EN+PS-MoM1, 1  
 Ueda, O.: EN+SS+TF-ThA2, 24



Uher, C.: EN+NS-WeA11, 17  
Upadhyaya, H.M.: EN+PS-MoM6, 2

— V —

van de Sanden, M.C.M.: EN+PS-MoM5, 1;  
EN+PS-MoM9, 2; EN+TF-TuA1, 10;  
NS+EM+EN-WeA8, 18; TF+EN-MoM6, 3  
van der Loop, T.H.: EN+PS-MoM5, 1  
van der Veer, W.E.: NS+EM+EN-WeA10, 19  
van Hest, M.F.A.M.: EN+TF-WeM9, 15  
Vandervelde, T.: EN+EM-TuA9, 9; EN+SS+TF-  
ThA11, 25; NS+EM+EN-WeA2, 18  
Venkatesh, G.: EN+NS-WeA1, 16  
Verheijen, MA.: EN+PS-MoM5, 1  
Veyan, J.-F.: EN+NS-ThM3, 22  
von Huth, P.: EN+TF-WeM3, 14

— W —

Walde, H.: EN+PS-MoM11, 2  
Walls, J.M.: EN+PS-MoM6, 2  
Walukiewicz, W.: EN+TF-TuA11, 11  
Wang, G.T.: NS+EM+EN-WeA1, 17  
Wang, J.: TF+EN-MoM4, 3  
Wang, S.J.: EN+TF-TuA7, 10  
Wang, W.: EN+NS-WeM2, 12  
Wangperawong, A.: EN+TF-WeM5, 14  
Warren, M.V.: EN+NS-WeA11, 17

Washburn, C.M.: EN+NS-WeA2, 16  
Weeks, S.: EN-ThP7, 27  
Weiss, S.: EN+SS+TF-ThA6, 24  
Wessel, S.: EN+AS-ThM2, 20  
Whang, D.M.: EN+NS-ThM2, 22  
Wheeler, D.R.: EN+NS-WeA2, 16  
White, R.G.: EN+AS-ThM6, 20  
Wi, S.-S.: EN+PS-MoM10, 2  
Wilks, G.B.: EN+EM-TuA4, 9  
Williams, K.: EN-ThP6, 27  
Williams, V.O.: EN+NS-ThM12, 23  
Williamson, T.L.: EN+TF-TuA11, 11  
Winter, R.: EN+NS-ThM12, 23  
Wise, F.W.: EN-MoA8, 5  
Wolak, M.A.: EN+NS-WeM12, 13; EN+TF-  
TuA10, 11

Wong, L.M.: EN+TF-TuA7, 10  
Wood, D.: EN+NS-WeA10, 17  
Woodward, P.M.: EN+SS-FrM2, 29  
Wu, I.-T.: TF+EN-MoM4, 3  
Wu, Z.: EN+EM-TuA1, 9

— X —

Xiao, X.: EN+NS-WeA2, 16  
Xue, J.: EN+NS-WeM5, 12; EN+TF-TuA3, 10

— Y —

Yamamoto, N.: EN-TuM3, 7  
Yamamoto, T.: EN-TuM3, 7  
Yan, Y.: EN+EM-TuA1, 9  
Yang, F.: NS+EM+EN-WeA10, 19  
Yang, J.: EN+TF-TuA3, 10  
Yanguas-Gil, A.: EN+NS-ThM12, 23  
Yasuda, Y.: EN+SS+TF-ThA8, 25  
Yeom, G.Y.: EN+PS-MoM8, 2  
Yin, L.: EN+NS-ThM2, 22  
Young, A.: EN+AS-ThM2, 20  
Yu, C.H.: EN+NS-ThM2, 22  
Yu, K.M.: EN+TF-TuA11, 11  
Yu, Z.Q.: EN+AS-ThM3, 20  
Yuan, H.: EN+SS+TF-ThA9, 25

— Z —

Zahn, D.R.T.: EN+TF-TuA2, 10  
Zajec, B.: EN-ThP5, 26  
Zhang, Y.: EN+NS-WeA8, 16  
Zheng, Y.: EN+TF-TuA3, 10  
Zhou, R.: EN+TF-TuA3, 10  
Zhu, X.-Y.: EN-ThP6, 27  
Zhu, Z.H.: EN+AS-ThM3, 20  
Zumer, M.: EN-ThP5, 26