

Energy Frontiers Focus Topic

Room: 103 - Session EN+PS-MoM

Plasmas for Photovoltaics & Energy Applications

Moderator: S. Agarwal, Colorado School of Mines

8:20am EN+PS-MoM1 **Plasma Energy R&D at National Fusion Research Institute (NFRI): Fusion Energy, Silicon Quantum Dot Solar Cell, and Plasma-Enhanced Coal Gasification**, S.J. Yoo, National Fusion Research Institute, Republic of Korea **INVITED**

National Fusion Research Institute (NFRI) is a unique national laboratory dedicated to conducting research and development of the most powerful plasma energy application, the fusion energy, in Korea. We have constructed and a fully superconducting Tokamak device named KSTAR (Korea Superconducting Tokamak Advanced Research) which is now successfully in operation, and actively involved in the world's largest joint fusion project - International Thermonuclear Experimental Reactor (ITER), in which seven countries are participating to investigate engineering feasibility of fusion power commercialization.

Besides the fusion research, the NFRI has actively developed various plasma applications related to energy harvesting such as silicon quantum dot solar cells and plasma-enhanced coal gasification.

We have challengingly developed a new fabrication method of the silicon quantum dot solar cell by using hyperthermal neutral beams which are neutral beams with an energy range of 1 ~ 100 eV and very effective tools for thin film deposition at much lower substrate temperature without plasma-induced damages. The hyperthermal neutral beams can be effectively applied to each fabrication step of the silicon quantum dot solar cells: Deposition of a silicon thin film consisting of nano-crystal silicon and amorphous silicon matrix, then selective etching of the amorphous silicon matrix by keeping only nano-crystal silicon remained in order to obtain the silicon quantum dots, thereafter dielectric barrier coating on the silicon quantum dot surface, and then repetition of the procedure until a required thickness achieved.

We also have developed a steam plasma torch driven by microwave powers of 2.45 GHz and 915 MHz for effective gasification of various hydrocarbon materials and even low grade coals which can be hardly gasified by conventional thermal gasification methods since the steam plasma torch can produce much more abundant reaction catalysts such as O*, H*, OH*, H₂O₂, and O₃ than the thermal gasification methods. And, furthermore, the microwave plasma torch has a great advantage of the system life time compared to conventional arc plasma torches for which metallic electrodes are inevitable and thus easily eroded by the reaction catalysts produced for the coal gasification.

9:00am EN+PS-MoM3 **Synthetic Fuel Processing through Plasma-Assisted CO₂ Conversion**, S. Welzel, S. Ponduri, F. Brehmer, M. Creatore, M.C.M. van de Sanden, R. Engeln, Eindhoven University of Technology, Netherlands

Continuously increasing green house gas emissions and forthcoming (fossil) fuel depletion has stimulated research in novel fuel processing, cleaner combustion as well as CO₂ capturing and conversion. Conventional fuel processing usually aims at producing syngas (CO/H₂) mixtures that may be further converted into value-added hydrocarbons and oxygenates (C_xH_yO_z). Photocatalytic CO₂ hydrogenation is now considered as alternative approach which would simultaneously lead to a global green carbon cycle. It could reduce atmospheric CO₂ concentrations, while at the same time provide fuels on a renewable basis that can directly be supplied to our present energy infrastructure. Since the efficiency of such an artificial photosynthesis is low, we propose the plasma-assisted hydrogenation of CO_x into hydrocarbons.

This contribution focuses on the efficiency of CO₂ depletion and selectivity of CH₄ production in a low-temperature plasma expansion. The plasma is created from mixtures of argon and hydrogen while CO_x is injected into the expansion part where the dissociation mechanism might be radical- and/or ion-driven. Results on measurements of the (steady state) gas composition obtained by mass spectrometry and mid-infrared tuneable diode laser absorption spectroscopy will be reported.

Especially under argon rich conditions, where the chemistry is mainly driven by combined charge exchange with the Ar ions and dissociative recombination, a CO yield of 50 % was achieved. CH₄ formation was particularly detected at high hydrogen admixtures. C₂H_y hydrocarbons were in most cases absent while H₂O and CO turned out to be the main stable products. The results suggest an inherent syngas step during the plasma-

assisted conversion approach, particularly a successive hydrogenation of CO.

9:20am EN+PS-MoM4 **Effective Light Trapping for Crystalline Silicon Solar Cells by Plasma Texturing**, F.M.M. Souren, Eindhoven University of Technology, Netherlands, J. Rentsch, Fraunhofer Institute for Solar Energy Systems (ISE), Germany, M.C.M. van de Sanden, Eindhoven University of Technology, Netherlands

Currently, in the photovoltaic (PV) industry, wet chemistry based etching is used for saw damage removal and surface texturing. It is known that plasma based dry etching leads to an improved light trapping on multi-crystalline silicon material and, therefore, it has the potential to increase the solar cell efficiency. However, up to now plasma based texturing has not been implemented in the PV industry, because of the very low etch rate (<1 μm/min) and the high cost of ownership. In this study, different front surface textures obtained by means of the Linear Microwave Plasma (LMP, commercialized by Roth&Rau) technique and the high rate Expanding Thermal Plasma (ETP, commercialized by OTB-Solar) technique, are investigated to reduce the overall reflection losses of mono-crystalline silicon solar cells and compared to KOH/IPA (Potassium hydroxide/Isopropanol) which is the standard process in solar cell manufacturing industry. The created textures employing the different etching techniques are characterized by reflectometry (250-1200 nm) to determine the weighted reflection and by Atomic Force Microscopy (AFM) to measure the surface topography so as to determine statistical roughness parameters. We have found that the average scatter angle, determined from the AFM measurements, shows a clear correlation to the measured weighted reflection. Effective light trapping has been obtained for two typical textures based on the described etching techniques. A texture which leads to a successive hit of the incident light ray towards the solar cell surface, can result in effective light trapping, as for example, the KOH/IPA process which creates a pyramidal texture. Efficient light trapping can also be obtained by the creation of a diffuse front surface (resembles the topography of "black silicon"), as for example by using the LMP technique, under the conditions used, which creates micro roughness. This micro roughness can be described as an effective medium with a refractive index between air and silicon and a typical thickness of up to (60±10) nm [1]. The micro roughness leads to an effective light trapping of a broad range of wavelengths from 250 nm up to 1200 nm. The light trapping of the wafer etched by the ETP technique is smaller than the as cut wafer and can be explained by a smaller average scatter angle compared to the as cut wafer. A short post treatment of the ETP textured wafer by the LMP technique, creates a diffuse front surface and results, therefore, in an improved light trapping. Moreover this combination shows great promise for a cost-effective approach towards plasma based texturing.

[1] R.B. Stephens and G.D. Cody, Thin Solid Films 45 (1977) 19.

9:40am EN+PS-MoM5 **RF-PECVD Processes Excited by Asymmetric Voltage Waveforms**, P.-A. Delattre, S. Pouliquen, Laboratoire de Physique des Plasmas, France, E.V. Johnson, Laboratory of Physics of Interfaces and Thin Films, France, J.-P. Booth, Laboratoire de Physique des Plasmas, France

Voltage Waveform Tailoring (VWT) is a promising new technique for Radio-Frequency (RF) process plasma excitation. It is known that asymmetric waveforms resembling *peaks* (short positive and long negative voltage) or *valleys* (long positive, short negative voltage) can produce a voltage self-bias, even in a symmetrical reactor [1], known as the Electrical Asymmetry Effect (EAE). We have implemented a system to provide such voltage waveforms on the RF electrode of our Capacitively Coupled Plasma (CCP) reactor. For a peak to peak voltage (V_{pp}) of 300 V, we can control the self-bias from -190 V to 15 V, without changing any other process parameter. A new differential RF probe gives us the real-time current and voltage derivatives, and therefore, the instantaneous power. For a voltage waveform composed of a 15 MHz fundamental and three harmonics, instantaneous power changes from +1 kW to -1kW in 10 ns. Using a hairpin resonator probe in hydrogen at 13 Pa, we have measured an electron density of 2E8 cm⁻³ with a standard sine waveform, 2E9 cm⁻³ with a valleys waveform and 2E10 cm⁻³ with a peaks waveform (all with V_{pp}= 300V). With a view towards photovoltaic applications, using a gas mixture of 4 % of SiH₄ in H₂ at 65 Pa, we have achieved a deposition rate of high-quality amorphous silicon of 1 Å/s for sine, 2.7 Å/s for valleys, and 3.8 Å/s for peaks voltage waveforms.

¹Brian G Heil *et al* 2008 *J. Phys. D: Appl. Phys.* **41** 165202

10:00am **EN+PS-MoM6 Spontaneous and High Rate Synthesis of Nanocrystalline Silicon by Expanding Thermal Plasma**, *I. Doğan, N.J. Kramer, M.A. Verheijen*, Eindhoven University of Technology, Netherlands, *K. Dohnalova, T. Gregorkiewicz*, University of Amsterdam, Netherlands, *M.C.M. van de Sanden*, Eindhoven University of Technology, Netherlands

Silicon nanocrystals (Si-NCs) draw attention since they exhibit size dependent luminescence, improved charge storing capacity and increased surface reactivity. For instance, the size dependent optical properties of Si-NCs show great promise for increasing the efficiency of solar cells. Si-NCs could be used as spectrum down converters by converting the excess energy of a hot photon to generate multiple exciton pairs. For successful applications, the main issues on Si-NC synthesis are size control and surface engineering for improved optical properties, and high throughput. Among these points, the amount of throughput is highly critical for large scale applications however, it is not possible to achieve with current production techniques. Our research goal is to show that it is possible to fulfill these demands with a novel route by using the remote expanding thermal plasma (ETP) technique. Synthesis of Si-NCs in a remote Ar/SiH₄ plasma occurs by means of a reaction sequence of ion-SiH₄ charge exchange and subsequent addition of SiH₄ molecules. This realizes spontaneous and nearly complete conversion of SiH₄ into Si-NCs with very high throughputs of about 25mg/min, the fastest deposition rate reported in the literature so far. Moreover, ETP has the freedom of tuning the size of the Si-NCs by controlling the flow rates of SiH₄ and Ar, i.e. the residence time in the plasma. Synthesized Si-NCs have a bimodal distribution of small (4-7nm) and large (50-80nm) sizes as confirmed by TEM, which is a consequence of the plasma expansion and reactor geometry. Bimodality has been analyzed with Raman spectroscopy by studying the asymmetry and shift in the transverse optical vibration mode of bulk-Si at 521cm⁻¹. Photoluminescence spectroscopy confirms the presence of monodisperse size distribution of small Si-NCs (4-7nm) leading to luminescence in the region 600-900nm. Observation of luminescence illustrates the quality of the nanocrystal surface passivated by the rapid native oxidation. Preliminary results show separation of the bimodal distribution can be controlled by means of geometrical isolation of the regions, in which small and large particles are formed.

10:40am **EN+PS-MoM8 SiH₄ and SiF₄ Dissociation in Matrix Distributed ECR Sources, and Potential for High Deposition Rate of Thin Film Silicon Alloys**, *S. Kasout, Total S.A, France, P. Bulkin, P. Rocca i Cabarrocas, LPICM, France*

Depositing at high rates and on ever larger areas are important objectives for the reduction of thin film silicon modules costs. High deposition rates have been achieved so far using different plasma sources but uniformity over large areas is still problematic. Matrix distributed electron cyclotron resonance (MDECR) systems consist of individual ECR plasma sources, which can be arranged in arrays with virtually no size limitations. Deposition rate of silicon alloys exceeding 10 nm/s, has been demonstrated, but little is known so far about the precursors' dissociation and species fluxes onto the surface.

We study here the dissociation of Silicon film precursors, using optical emission spectroscopy and quadrupole mass spectrometry, both in the plasma phase and in the fore line. We correlate the dissociation on the one hand to the electron density and temperature measured using Langmuir probes and microwave interferometry, and to film growth rate and structure on the other.

It is found that more than 90% of SiH₄ is used across a wide range of microwave powers, with a small dependence on gas residence time and pressure. Deposition rate depends primarily on the total flow of SiH₄, and values above 3 nm/s are easily obtained. Transition from amorphous to microcrystalline silicon growth, on the other hand, occurs at high powers, and correlates to the electronic temperature and the high H/Si ratio observed in the gas phase. Direct dissociation of SiH₄ by electron impact, followed by deposition from atomic Si and subsequent crystallization by hydrogen is therefore a satisfactory explanation.

On the contrary, for deposition from SiF₄, consumption is found to be lower than 60%, and independent of the gas residence time and microwave power. The deposition rate is also much lower, on the order of 0.3 nm/s. SiF₄ consumption increases with the total hydrogen flow rate added to the mixture. The total concentration of atomic Si in the gas phase varies linearly with the product of SiF and H species, estimated by actinometry, suggesting fluorine abstraction by hydrogen as a possible mechanism. Deposition rate is also proportional to the Si content in the plasma phase and increases with the hydrogen flow rate added to the plasma. We propose that film growth from MDECR plasmas of SiF₄/H₂ mixtures occurs through the deposition

of atomic silicon, obtained from hydrogen abstraction of fluorine in the gas phase, direct electron impact dissociation of SiF₄ playing a smaller role.

This illustrates the importance of gas phase reaction for achieving high deposition rates, even in the case of high density low pressure plasma sources.

11:00am **EN+PS-MoM9 The Effects of Showerhead Hole Structure on the Deposition of uc-Si:H Thin Films by VHF PECVD**, *S.-S. Wi, Y.-G. Kim, H.-J. Lee*, Pusan National University, Republic of Korea, *D. Kim, D. Hwang, W.S. Chang*, LG Electronics, Republic of Korea

We presents the characteristics of hydrogenated microcrystalline silicon thin films deposited from SiH₄/H₂ in 40 MHz plasma enhanced chemical vapor deposition (PECVD) equipped with multi-hole-array showerhead. The effects of hole array structure are analyzed in terms of their diameter and depth. Cross dependences between the hole structure and process parameters, such as SiH₄ concentration, rf power, pressure, substrate temperature and total gas flow rate, are also investigated. The results show that deposition rate is not a strong function of hole structure compared with other process parameters. However, it is found that uniformity can be controlled by varying the surface density of hole array. With decreasing total flow rate, faster increase in deposition rate is found at the multi-hole array compared with flat electrode. This may be attributed to the high electron density and longer residence time of within the holes. It is demonstrate that the multi hole array electrode can be used as an effective control variable for optimization of Si thin film solar cell PECVD process.

11:20am **EN+PS-MoM10 Plasma-Enhanced CVD and ALD Prepared Nanolayers for High-Efficiency Solar Cell Manufacturing**, *W.M.M. Kessels*, Eindhoven University of Technology, the Netherlands **INVITED**

Photovoltaics has become a very innovative field of research and manufacturing due to the continuous improvement in the solar cell cost/performance ratio and its tremendous growth opportunities (past average annual growth rate of 40%). Several innovations with respect to the improvement of the cell efficiency lie in the field of thin film technology, not only for thin-film solar cells but also for crystalline silicon solar cells which are currently still dominating the market (87% market share in 2010). One particular trend is the application of ultrathin films or "functional nanolayers" for solar cell interface engineering. In crystalline silicon technology these nanolayers have as a main application the reduction of charge carrier recombination at interfaces through "surface passivation". Plasma-based deposition processes such as plasma-enhanced chemical vapor deposition (CVD) are key for the preparation of such films and recently the interest also shifted to (plasma-enhanced) atomic layer deposition (ALD) processes due to their precise growth control and their excellent uniformity and conformality [1]. Moreover, ultrathin films of < 10 nm have been found feasible in terms of reaching very-well passivated surfaces. In this contribution, the application of ultrathin films of various materials such as a-Si:H, a-SiN_x:H, SiO₂, and in particular Al₂O₃ will be addressed. The preparation methods will be described as well as the relevant surface reaction mechanisms during the film synthesis. Passivation and solar cell results will be presented with a main emphasis on the key mechanisms underlying the good passivation performance of the ultrathin films. Also the market feasibility of new ALD technologies, e.g., in terms of high throughput processing, will be addressed.

[1] Atomic layer deposition: prospects for solar cell manufacturing, W.M.M. Kessels, et al., Proc. 33rd IEEE Photovoltaic Specialist Conference, San Diego, U.S.A. (2008).

Energy Frontiers Focus Topic

Room: 104 - Session EN-MoM

Industrial Physics Forum on Energy I

Moderator: R.A. Sears, Massachusetts Institute of Technology, B. Clark, Schlumberger

8:20am **EN-MoM1 Energy Security and Energy Policy**, *W.W. Hogan*, Harvard University **INVITED**

Energy security is broader and different than energy independence. Different definitions of energy security produce different policy prescriptions. A consistent framework for energy security must address basic principles.

9:00am **EN-MoM3 Technology Innovation and China's Skyrocketing Demand for Energy**, *E. Steinfeld*, Massachusetts Institute of Technology
INVITED

9:40am **EN-MoM5 Making Energy Sustainable – Scientific Challenges in Determining the Pathways to the Future**, *E.D. Williams*, BP plc, UK
INVITED

The scale and cost of the energy challenge are immense. Everyone wants secure, reliable, and affordable energy, but climate change, demand growth and, increasingly, resource scarcity, are transforming the energy landscape and it will continue to evolve.

There are many possible technical pathways to a low-carbon energy future, and each presents unresolved technical challenges that will influence the time, money and global-scale asset and infrastructure deployment that will take place over the next decades. BP's energy portfolio demonstrates many of the research challenges in this arena, and some examples from Carbon Capture and Storage and Biofuels will be discussed here specifically. Ultimately, research, technology, policies and partnerships will determine the pace of change.

10:40am **EN-MoM8 Synthetic Biology for Energy and the Environment**, *A.A.N. Patrinos*, Synthetic Genomics (SGI) **INVITED**

Synthetic biology is one of the major "tools" that are converting biology from a concept-driven scientific revolution to a tool-driven scientific revolution. This paradigm shift will enable significant applications of the new biology to major challenges in medicine, energy, and the environment.

11:20am **EN-MoM10 Manufacturing Innovations for a Sustainable Energy Future**, *R. Castro, O. Nalamasu*, Applied Materials, Inc. **INVITED**

Nanomanufacturing technology, the cost-effective and practical manufacturing solutions based on equipment and process solution platforms have been translating the promise of nanotechnology to reality in advancing transforming the electronics and display industries. Technology, Scale and Innovation would continue to be fundamental to meet the global inflections associated with Electronics and Display industries and more importantly, advances in nanomanufacturing technology are critical to solving the energy and environment challenges. In this presentation, I will detail the challenges and opportunities in building a sustainable energy future based on nanomanufacturing innovations.

Monday Afternoon, October 31, 2011

Energy Frontiers Focus Topic

Room: 103 - Session EN+EM+NS-MoA

Nanostructured Materials for Third Generation Solar Cells

Moderator: W.A. Tisdale, Massachusetts Institute of Technology

2:00pm **EN+EM+NS-MoA1 Fabrication of Two-dimensional Array of Sub-10nm GaAs Nanodisk using Bio-template Neutral Beam Etching Process**, S.-H. Lin, X.-Y. Wang, C.-H. Huang, Y. Ohno, M. Igarashi, Tohoku University, Japan, A. Murayama, Hokkaido University, Japan, S. Samukawa, Tohoku University, Japan

Recently, 3-dimensional (3D) or 2-dimensional (2D) quantum dot superlattice are widely investigated to develop the new generation devices, such as quantum dot solar cell. Quantum dot superlattice consists of quantum dots with lower band gap energy in the matrix with higher band gap energy. For the device application, the structure requires high QD density, periodic QD array and uniform dot size and inter-dot spacing. Molecular beam epitaxy (MBE) and Metal-organic chemical vapor deposition (MOCVD) are two attractive methods among various bottom-up fabrication methods to fabricate quantum dots. However, there is limitation of bottom-up process to control the size, spacing and density of quantum dots. To breakthrough these problems, we have proposed the ultimate top-down process by combination of bio-template and damage-free neutral beam etching (NBE) for fabricating defect-free 2D array of quantum dots.

In this study, we developed a series of novel process for fabricating uniform size and high density 2D array of GaAs nanodisk with uniform inter-dot-spacing. Firstly, the hydrogen-radical treatment was used to remove the native oxide on GaAs surface. To utilize two-dimensional array of ferritin (protein including 7-nm-diameter iron core) as an etching mask, the formation of a hydrophilic 1-nm thick GaAs neutral beam oxidation film is key point. It is found that protein shell can be removed with oxygen-radical treatment at a low temperature of 280°C without thermal damage to GaAs. After protein shell removal, the iron oxide cores inside the ferritins remained on the surface. Then, using the iron core as an etching mask, neutral beam could etch the defect-free nanodisk structure of GaAs. Finally, we developed that iron oxide core was removed by wet etching with diluted hydrogen chloride and completed a fabrication process without inflicting any damage to GaAs. The result shows the quantum dot superlattice structure with a two-dimensional array of GaAs quantum dots with a diameter of ~7-nm, a height of ~10-nm, and a quantum dot density of more than $7 \times 10^{11} \text{cm}^{-2}$ was successfully demonstrated without any damage to GaAs.

This work is supported by the Core Research of Evolutional Science and Technology (CREST) of Japan Science and Technology Agency (JST).

2:40pm **EN+EM+NS-MoA3 Solution Processed Quantum Dots for Low Cost Photovoltaics**, E.J.D. Klem, J. Lewis, C. Gregory, G. Cunningham, D. Temple, RTI International

INVITED

For solar energy to be a significant component of our energy supply new technologies are needed that enable the fabrication of low cost, high efficiency solar cells. Research into solar energy devices which incorporate carbon fullerenes and semiconducting polymers represent one such technology. One factor limiting their further advance is their lack of absorption in the infrared (IR). As half the sun's energy lies beyond 700 nm and one third beyond 1000 nm, low-cost device technologies are needed which capture this lost infrared potential. An additional factor limiting the further advance of these devices is the relatively poor electrical transport properties of most semiconducting polymers.

The use of solution processed quantum dots provides a potential route towards overcoming both of these limitations. Solution processed quantum dots can be tuned to absorb light well into the infrared, and quantum dot composite thin films have been shown to have charge carrier mobilities approaching that of amorphous silicon.

In this presentation we will present a brief overview of colloidal quantum dots and the field of quantum dot photovoltaics. We will discuss a range of device architectures and material systems that have been explored experimentally. This includes quantum dot-metal Schottky junctions, quantum dot heterojunctions, and quantum dot-metal oxide junctions.

We will also present a device architecture which is based on the heterojunction formed between infrared-sensitive PbS quantum dots and C_{60} fullerenes. In this device pre- and post-deposition treatments to are used

passivate carrier traps and increase the conductivity of the quantum dot films. A device stack is presented that is designed to steer photo-excited charge carriers to the charge-separating interface, reducing recombination pathways and improving carrier extraction efficiency. Under simulated solar illumination the devices exhibit short circuit current densities greater than 20 mA/cm², power conversion efficiencies greater than 5%, and spectral sensitivity out to 1500 nm. This represents a significant step towards demonstrating the commercial viability of solution processed quantum dot technology

3:40pm **EN+EM+NS-MoA6 Role of Quantized and Mid-Gap States in "Dark" Charge Transport and Photoconductivity in Semiconductor Nanocrystal Films**, P. Nagpal, Los Alamos National Laboratory

Colloidal semiconductor nanocrystals (NCs) have attracted significant interest for applications in solution-processable devices such as light-emitting diodes and solar cells. However, poor understanding of charge transport in NC assemblies, specifically the relation between electrical conductance in dark and under light illumination, hinders their technological applicability. Here, we simultaneously address the issues of "dark" transport and photoconductivity in films of PbS NCs by incorporating them into optical field-effect transistors (OFETs), in which the channel conductance is controlled by both gate voltage and incident radiation. Spectrally resolved photoresponses of OFETs reveal a weakly conductive mid-gap band (MGB) which is responsible for charge transport in dark. The mechanism for conductance, however, changes under illumination when it becomes dominated by band-edge quantized states. In this case, the MGB still plays an important role as its occupancy (tuned by the gate voltage) controls the dynamics of band-edge charges. Our study has broad implications for NC-based electronics and optoelectronics, and specifically, suggests that design guidelines for NC devices might be different depending on whether they are intended for operation in dark (diodes and transistors) or under illumination (photodetectors and solar cells).

4:00pm **EN+EM+NS-MoA7 Using Surface Chemistry to Modulate the Bandgap of Ge Nanowires**, S. Sivaram, M.A. Filler, Georgia Institute of Technology

Small-diameter semiconductor nanowires are highly attractive building blocks for next generation photovoltaic devices because they exhibit highly tunable optoelectronic properties as a result of quantum confinement. Bottom up approaches, such as the vapor-liquid-solid (VLS) growth mechanism, are controllable down to ~20 nanometers but significant challenges exist at smaller length scales where property tuning is maximized. Furthermore, it is expected that the optoelectronic properties of quantum-confined nanowires will be heavily dependent on surface chemistry, yet there are no experimental studies that fundamentally probe this relationship. Germanium is an ideal system to study because of its large Bohr exciton radius, low rate of oxidation, and chemical similarity to silicon. In this work we controllably synthesize germanium nanowires with diameters from 5 to 20 nanometers using gold catalyst particles with a narrow size distribution. To obtain epitaxial Ge nanowires with uniform diameters and lengths, a two-step growth process is employed that includes a brief, high-temperature nucleation (390°C) above the Au-Ge eutectic point, followed by elongation at various process conditions, generally below the eutectic point (280 – 340°C, 1×10^{-7} – 1×10^{-4} Torr). To limit catalyst diffusion and formation of the $\sqrt{3} \times \sqrt{3}$ Au/Si reconstruction on the Si(111) surface, a key problem for controllable sub-20 nm growth, the substrate is passivated with -CH₃ groups prior to nanowire synthesis by introducing small quantities of methylgermane. Nanowire surface chemistry is probed with *in-situ* transmission infrared (IR) spectroscopy both during and after growth. We introduced different adsorbates (-H and -CH₃) and monitored their influence on the band gap as a function of surface coverage. We show that the band gap of Ge nanowires blue shifts with H passivation and red shifts with CH₃ termination.

4:20pm **EN+EM+NS-MoA8 Production of Multi-milligram Yields of Ternary II-VI Semiconductor Nanocrystals Under Non-coordinating Amine Activated Synthesis**, M. Plaisant, P.H. Holloway, University of Florida

Thermolysis of Zn and Cd precursors under a non-coordinating one-pot wet-chemical synthesis has successfully produced a heterogeneous ternary Cd_xZn_{1-x}Se alloy with an extensive spectral red shift of 200nm in the visible range. Large yields of twenty milligram of the Cd_xZn_{1-x}Se alloy are minimally required for inclusion of the material in the active layer of an inorganic/organic photovoltaic device. The facile synthesis of such large yields of ternary semiconductor nanocrystal alloys has not commonly been reported in the literature. Herein we discuss first the thermolytic synthesis

of the material beginning from the ZnSe core through the inclusion of the Cd-precursor. We then discuss the production of the ternary II-VI semiconductor $Cd_xZn_{1-x}Se$ material through a process of non-coordinating synthesis with amine-activation to produce the high multi-milligram yields required for device inclusion.

4:40pm **EN+EM+NS-MoA9 Type-II ZnTe/ZnSe Quantum Dots for Intermediate Band Solar Energy Conversion**, *C. Chen, B. Juang, J. Hwang, S. Kim, X. Pan, J. Phillips*, University of Michigan

Intermediate band solar cells and impurity photovoltaics have been proposed to achieve high efficiency solar energy conversion by introducing electronic states within the bandgap of the host material. The intermediate electronic states provide enhanced photocurrent through the addition of sub-bandgap optical transitions while maintaining a voltage that follows the host material. Approaches to realize these solar cells include the incorporation of dopants/impurities, dilute alloys, and nanostructures such as quantum dots. Self-assembled quantum dots such as InAs/GaAs possess excellent optical properties and have been applied to numerous optoelectronic devices including demonstration of the intermediate band solar cell concept. The highly radiative transitions in these type-I materials result in short radiative carrier lifetimes – a feature that is desirable for light emitters, but can be problematic for photodetectors and solar cells. Semiconductor nanostructures with type-II band alignment result in spatially separated electron and hole wavefunctions, resulting in reduced oscillator strength and corresponding reduction in optical absorption, spontaneous radiative recombination rate, and increased radiative carrier lifetime. The tradeoff between carrier lifetime and optical absorption may be effectively used to provide a closer match to the generation-recombination rates desired for intermediate band solar energy conversion. In this work, ZnTe/ZnSe type-II quantum dots are proposed for intermediate band solar energy conversion. The theory of intermediate band solar energy conversion in this material system will be presented along with initial experimental results on the epitaxial growth, structural properties, and optoelectronic response of the materials. The ZnTe/ZnSe quantum dots were grown by molecular beam epitaxy, where three-dimensional island formation is observed via strained layer growth in the Stranski-Krastanow growth mode. Low temperature photoluminescence spectra reveal optical transitions from ZnSe (2.8eV), Te_{Se} isoelectronic centers (2.6eV), and broad emission in the range of 2.0-2.4eV attributed to type-II quantum dots.

Energy Frontiers Focus Topic

Room: 104 - Session EN-MoA

Industrial Physics Forum on Energy II

Moderator: J.W. Rogers, Idaho National Laboratory, J.N.

Hollenhorst, Agilent

2:00pm **EN-MoA1 The Role of Nuclear Energy in a Sustainable Energy Scenario**, *H.F. McFarlane*, Idaho National Laboratory **INVITED**

Only three primary energy sources power the planet for humankind's benefit. Though seldom identified as such, the most familiar is nuclear fusion, which provides the solar flux to warm the earth, power the renewable wind and water cycles, and drive photosynthesis for plant growth. Ancient carbon bonds, formed over millions of years and stored in the form of familiar fossil fuels—oil, natural gas, and coal—comprise plentiful resources that enable most of our transportation and electricity generation. Uranium powers the third, and to many people the most mysterious, energy source, nuclear fission.

Different groups define sustainable energy in different ways, the specific definition usually crafted to advance a particular point of view. In this discussion, I shall use sustainable to mean that the resource and its application are sustainable for hundreds of years, through multiple generations. Five years ago who would have thought that we would be talking about a 100-year supply of affordable natural gas, yet that is what new technology may have brought us—though the environmental consequences are still being sorted out. Renewable energy will serve us as long as we have a clear view of the sun, or until the solar plasma reaches out and kisses earth. Nuclear energy brings emotional baggage. Nuclear energy's sustainability yardstick is multi-dimensional, not merely a question of how long uranium resources will last under various scenarios.

One well-accepted international research, demonstration and development program addresses nuclear sustainability at its core—the Generation-IV International Forum. From 200 candidate technologies, the Forum selected six advanced nuclear systems for possible development. Each system is required to set stretch goals for safety, nuclear proliferation resistance, economic competitiveness, and sustainability. That said, nuclear's

sustainability relies on success in the first three goals as well as public acceptance.

This talk will use the Generation-IV framework applied to existing as well as future infrastructure. It will provide a provocative perspective on resources, safety (including the Fukushima-Daiichi accident resulting from an overwhelming tsunami), and nonproliferation. Nuclear energy's potential role in providing a significant fraction of electrical generation as well transportation fuels will be explored.

2:40pm **EN-MoA3 What's So Smart about the "Smart Grid?"**, *J.G. Kassakian*, Massachusetts Institute of Technology **INVITED**

The "Smart Grid" has received considerable hype in Washington and the popular press. To some it means an automated metering infrastructure allowing consumers to participate in load management. To others it means the interconnection of distributed renewable resources and the introduction of electric vehicles. It is all of these and more. This presentation will provide an overview of the many dimensions of the smart grid vision, including anticipated technical innovations and policy changes necessary for realizing the vision.

3:40pm **EN-MoA6 Electrochemical Energy Storage for Renewable Integration and Grid Applications: Status, Challenges and Opportunities**, *Z.G. Yang*, Pacific Northwest National Laboratory **INVITED**

Growing concerns over the environmental consequences of burning fossil fuels and their resource constraints, along with the increasing world energy consumption, have spurred great interests in renewable energy from sources such as wind and solar. However, the power from these intermittent sources is constantly varied, making quite challenging for its use and dispatch through the aging electrical grid. One effective way to smooth out the intermittency is to employ electrical energy storage (EES). As such EES has been widely considered as a key enabler of the future grid or smart grid that is expected to integrate a significant level of renewable, while providing electricity or "fuel" to hybrid and electrical vehicles. Among the potential technologies are electrochemical energy storage technologies or batteries that are capable of storing a large quantity of electricity and releasing it according to demands. There remain significant challenges however for the current technologies to meet the performance and cost matrices for broad market penetration. This paper offers an overview on varied technologies, in particular batteries, and discusses the status, challenges and research needs.

Tuesday Morning, November 1, 2011

Energy Frontiers Focus Topic

Room: 103 - Session EN+NS-TuM

Ultrafast Charge and Energy Transfer in Nanomaterials

Moderator: J.B. Baxter, Drexel University

8:00am **EN+NS-TuM1 Controlled Deposition of Nanocrystal Quantum Dots on Silicon Surfaces: Demonstration and Application of Forster Resonant Energy Transfer**, *O. Seitz, H.M. Nguyen, Y.N. Gartstein, A.V. Malko*, University of Texas at Dallas, *Y.J. Chabal*, The University of Texas at Dallas

Studying Forster resonant energy transfer (FRET) at semiconductor surfaces has been a challenge because of difficulties in grafting reliably nanocrystal quantum dots (NQDs) onto electronically passivated substrates. Poor control has often resulted in formation of aggregates (3D growth), inhomogeneity, and poor adhesion. In this study, combining IR absorption spectroscopy (IRAS) and X-ray photoelectron spectroscopy (XPS), photoluminescence, atomic force microscopy (AFM) and electrical measurements, we have grafted self-assembled monolayers (SAMs) on both oxidized and oxide-free silicon surfaces with appropriate functionality to obtain dense monolayer of NQDs and to study FRET. SAMs that are directly attached to the silicon via Si-C bonds display a high interface quality with a low density of interface states. This makes it possible to prepare systems with tunable thicknesses necessary for FRET investigation. The time evolution of the fluorescence intensity is in good agreement with the predicted thickness dependence. We are currently developing 3D structures to enhance energy collection for a given surface area. Such hybrid colloidal NQD/Silicon optoelectronic structures could potentially be attractive for both photovoltaic as well as light emitting applications.

8:20am **EN+NS-TuM2 Orbital-dependent Charge Transfer Dynamics in Potential Molecular Wires**, *H. Hamoudi*, Universität Heidelberg, Germany, *S. Nepl*, Technische Universität München, Germany, *P. Kao*, Penn State University, *B. Schüpbach*, Universität Frankfurt, Germany, *P. Feulner*, Technische Universität München, Germany, *A. Terfort*, Universität Frankfurt, Germany, *D.L. Allara*, Penn State University, *M. Zharnikov*, Universität Heidelberg, Germany

Continued progress in technologically important fields such as molecular and organic electronics as well as organic photovoltaics depends on reliable information about the charge transport (CT) through individual molecular groups, above all so-called molecular wires, since these represent important building blocks of a variety of devices. In this context, femtosecond CT dynamics in a series of self-assembled monolayers with oligo(phenyleneethynylene) and oligo(phenyl) backbone, which are prototypes of potential molecule wires, was addressed by resonant Auger spectroscopy using the core hole clock method. The length of the molecular backbone was varied to monitor the respective dependence of the CT time. The CT pathway was unambiguously defined by resonant excitation of the nitrile tailgroup attached to the backbone. Due to the conjugation of the electronic systems of this group and the adjacent terminal phenyl ring of the backbone, a splitting of the degenerated unoccupied molecular orbital (MO) of nitrile occurred, resulting in two different MOs which could be selectively addressed by X-rays and used as the starting points for CT. The characteristic CT times were found to depend strongly on the character of the MO which mediates the CT process. This demonstrates that the efficiency and rate of CT in molecular wires can be controlled by resonant injection of the charge carriers into specific MOs.

8:40am **EN+NS-TuM3 Photophysics of Semiconductor Nanostructures in Relation to Problems of Solar Energy Conversion**, *V.I. Klimov*, Los Alamos National Laboratory

INVITED

This presentation provides a brief overview of research activities in the Center for Advanced Solar Photophysics with focus on spectroscopic properties of semiconductor nanocrystals studied from the prospective of solar energy conversion. One process, which can be used for boosting a photocurrent of solar cells, is carrier multiplication (CM) or multiexciton generation. Our recent activities in this area include the development of reliable methods for efficient screening of CM performance using photon counting with superconducting nanowire detectors, the studies of the impact of "extraneous" processes on CM measurements, and the evaluation of the effects of the nanocrystal composition, dimensions, and shape on CM yields. As part of our effort on controlling excited-state dynamics, we study hot-electron transfer in nanocrystals. We find that the efficiency of this process can approach 10% even with incidental impurity-like acceptors, suggesting that even higher probabilities are possible with engineered

acceptors designed for testing the ideas of hot-electron extraction. We also apply spectroscopic tools for probing the physics of charge transport in nanocrystal assemblies using exploratory devices such as optical field-effect transistors (OFETs). The OFET studies help to understand the nature of conducting states in dark and under illumination and to rationalize many previously unexplained observations including a weak sensitivity of conductance to particles' polydispersity and a significant difference in a photovoltage compared to a nominal band-gap energy. These studies illustrate how key insights into the performance of nanoscale materials are gained through close integration of spectroscopic, materials and device efforts across the Center.

9:20am **EN+NS-TuM5 Hot Electron Transfer from Semiconductor Nanocrystals**, *W.A. Tisdale*, Massachusetts Institute of Technology

INVITED

In conventional semiconductor solar cells, absorption of photons with energies greater than the semiconductor band gap generate "hot" charge carriers that quickly "cool" before all of their energy can be captured – a process that limits device efficiency. Semiconductor nanocrystals (or quantum dots) have been touted as promising materials for photovoltaics because discretization of their electronic energy levels can slow down this cooling process, which might enable the extraction of photogenerated charge carriers before their excess energy is converted to heat.

In this talk, I will demonstrate hot electron transfer from PbSe nanocrystals to delocalized conduction band states of TiO₂ and the concomitant excitation of coherent surface vibrational modes associated with this ultrafast process. In order to make these measurements, we developed the use of optical second harmonic generation (SHG) for femtosecond time-resolved studies of interfacial charge separation. I will discuss the information we obtain from this technique as well as the effect of temperature, nanocrystal size, and surface chemistry, and how these observations inform our understanding of electronic coupling at interfaces between confined states and bulk materials.

10:40am **EN+NS-TuM9 Single Molecule Study of Charge Transfer in 6T-TBPP-Co Molecular Complex**, *Y. Zhang, U.G.E. Perera, S.-W. Hla*, Ohio University

When two molecules having tendency to donate or accept electronic charge are put together, charge transfer between the molecules can take place. By a suitable selection of donor and acceptor molecules, it is possible to engineer an entire class of materials having metallic, semiconducting, insulating, or even superconducting properties [1, 2]. Here, we present a low temperature scanning tunneling microscopy and spectroscopy study of single molecule level charge transfer process between α -sexithiophene(6T) and TBPP-Co molecules on a Cu(111) surface. We form molecular clusters composed of both molecular species on Cu(111). The charge transfer between the molecules is directly evident in the tunneling spectroscopy data, which reveals the shift of 6T HOMO towards the surface Fermi level indicating donation of charge from 6T to TBPP-Co. This work is supported by the US-DOE-DE-FG02-02ER46012 grant.

Reference:

[1] F. Jackel, U. G. E. Perera, V. Iancu, K.-F. Braun, N. Koch, J. P. Rabe, and S.-W. Hla, Phys. Rev. Lett. 100, 126102 (2008).

[2] K. Clark, A. Hassanien, S. Khan, K.-F. Braun, H. Tanaka and S.-W. Hla, Nature Nanotechnology, Vol.5, April, 2010.

11:00am **EN+NS-TuM10 NEGF Quantum Simulation of Nanotip Thermionic Emitters for Direct Energy Conversion**, *T.D. Musho, D.G. Walker*, Vanderbilt University

Wide band-gap diamond nanotip field emission devices have been experimentally shown to have superior performance and lifetime. However, theoretical studies of the electronic emission from these devices using standard Fowler-Nordheim (FN) theory does not fully capture the physics as a result of the fitting parameters inherent to the FN approximation. The following research computationally models wide band-gap nanotip field emission devices from a quantum point of view, using a novel non-equilibrium Green's function (NEGF) approach previously applied to modeling the transport in solid-state electronic devices. In this research the IV characteristics of a single square tip diamond emitter are investigated under several bias conditions. Those bias conditions include both field emission in response to a potential bias and thermionic emission in response to a temperature bias. The NEGF model calculates the ballistic transport using a self-consistent Schrödinger-Poisson solver, calculating the transmission at discrete energy levels which is then used by the Landauer

formalism to determine the total current. Ultimately, this model allows the inherent quantum mechanical transport to be captured without any fitting parameters. Findings from this research have confirmed non-linearities in the FN curve and have demonstrated the experimental transport trends. Additionally, thermionic emission trends suggest that select geometric parameters are target for enhanced emission.

11:20am **EN+NS-TuM11 Mechanisms of Heterogeneous Charge Transfer at the Quantum Dot-Organic Interface**, *A. Morris-Cohen, M. Frederick, L. Cass, E.A. Weiss*, Northwestern University **INVITED**

We examine the rates and mechanisms of electron transfer between colloidal semiconductor quantum dots (QDs) and viologen derivatives using ultrafast transient absorption spectroscopy. Viologens accept electrons from photoexcited QDs on the femtosecond-to-single picosecond timescale. Modifications of the chemistry by which the ligands link to the QD surface, and the density of ligands on the QDs, facilitates control of charge separation and recombination rates, and determination of the operative mechanisms of charge transfer.

Energy Frontiers Focus Topic

Room: 108 - Session EN-TuM

Industrial Physics Forum on Energy III

Moderator: D.G. Seiler, National Institute of Standards & Technology, J.S. Murday, University of Southern California

8:00am **EN-TuM1 Materials for Low Risk Nuclear Reactors**, *T.R. Allen*, University of Wisconsin, Madison **INVITED**

Advanced reactor concepts have been proposed for many reasons that could be attributed to "risk reduction." Risk reduction could mean improved safety margins, more certain economic performance, greater resistance to proliferation, or reduction of risk of exposure during the long-term storage of waste. For many of the envisioned advanced reactor concepts that have been proposed to reduce some form of risk, the ultimate deployment hinges on overcoming challenges in fuels and materials performance. The limits of performance unique to nuclear systems are typically associated with either radiation damage from high-energy particles or due to high-temperature corrosion or stress corrosion cracking. This presentation will provide an overview of the unique operating conditions in proposed reactor concepts and special challenges associated with structural materials operation. Then an overview of two approaches to improve material performance will be presented, specifically use of nanoparticles to improve high temperature strength in radiation fields and the use of tailored systems of grain boundaries to improve corrosion and stress corrosion cracking resistance.

8:40am **EN-TuM3 Battery 500 - the Li-Air Battery Opportunity**, *S.A. Swanson*, IBM Almaden Research Center **INVITED**

In 2009, IBM started a project to develop rechargeable Li-air batteries for electric cars with a range of 500 miles per charge. This type of high density energy storage technology could become a game changer for the widespread adoption of electric vehicles but it also presents enormous technical challenges. Published work on Li-air batteries has only reported small fractions of the theoretical limit with limited rechargeability. Many aspects of the technology, including the lithium-oxygen electrochemistry, appear to have been poorly understood.

This presentation will give an overview of Li-air battery technology. We will describe our ongoing research including our investigation into the decomposition of carbonate based solvents during cell discharge using Differential Electrochemical Mass Spectrometry, the characterization and identification of the cathode electrodeposits, and enhanced cell capacities achieved using alternative aprotic solvents.

9:20am **EN-TuM5 Advanced Thermoelectric Technology for Waste Heat Recovery**, *G.P. Meisner*, General Motors Research & Development **INVITED**

In today's internal combustion engine based vehicles, more than two-thirds of the fuel energy is lost as waste heat. At General Motors Global Research & Development, we aim to demonstrate a viable thermoelectric (TE) generator system to recover that waste heat by converting it into useful electricity using advanced TE technology and thereby reduce vehicular fuel consumption. Essential to the long term success of TE technology in the automobile industry, and for waste heat recovery applications in general, is new materials research, specifically fundamental physics and materials research aimed at discovering and understanding new high performance TE materials, and the development of those materials into robust and high performance TE devices. Our work, which is generously supported by the

U. S. Department of Energy's Vehicle Technologies Program, focuses on (1) bulk TE materials (e.g., filled skutterudites) and their temperature dependent physical, mechanical, and TE properties, and (2) TE device and module development, TE generator design, and prototype TE generator fabrication, assessment, and validation. We have made significant progress on constructing working prototype automotive TE generator and testing it on a GM production vehicle.

10:40am **EN-TuM9 Improving Solar Energy Conversion with Nanoscale Materials**, *S.F. Bent*, Stanford University **INVITED**

With the intensifying global need for alternative energy, there is strong interest in new approaches to materials for sustainable energy devices. A variety of different energy technologies must work in concert to produce, store, and consume the 20 TW of energy that humans will soon demand. Underlying the diverse set of energy conversion devices are similar physical and chemical phenomena, many of which can be controlled with nanoscale materials. This talk will describe research on nanoscale materials for solar photovoltaics and solar fuel production. Synthetic strategies including atomic layer deposition are used to generate nanoscale materials with a high level of control over composition, structure, and thickness. The materials are then tested in energy conversion devices. The prospects and challenges for such materials to contribute to higher energy conversion efficiencies will be discussed.

Thin Film Division

Room: 107 - Session TF+EN-TuM

ALD for Energy

Moderator: W.M.M. Kessels, Eindhoven University of Technology, the Netherlands

8:20am **TF+EN-TuM2 Controlling the Dispersion and Size of Platinum Nanoparticles Using Pt Atomic Layer Deposition and Surface Treatments**, *V.R. Anderson*, University of Colorado, Boulder, *N. Leick*, Eindhoven University of Technology, Netherlands, *K.E. Hurst*, National Renewable Energy Laboratory, *A.S. Cavanagh*, University of Colorado, Boulder, *S. Kocha*, *K. Jones*, *A.C. Dillon*, National Renewable Energy Laboratory, *S.M. George*, University of Colorado, Boulder

Platinum nanoparticles are used as the catalyst on the cathodes of proton exchange membrane (PEM) fuel cells. Controlling the dispersion and size of the Pt nanoparticles is important for efficient and cost-effective fuel cells. When Pt atomic layer deposition (ALD) is performed on oxide or carbon substrates, nucleation difficulties and the high surface energy of Pt lead to Pt nanoparticles rather than continuous films. This research explored strategies to control the dispersion and size of Pt nanoparticles using Pt ALD together with various surface treatments. Pt ALD was performed using Pt hexafluoroacetylacetonate Pt(hfac)₂ and formalin as the reactants. Titanium oxide (TiO₂) and tungsten oxide (WO₃) were explored as the substrates. We used *in situ* transmission Fourier transform infrared (FTIR) spectroscopy to monitor the surface species during Pt ALD. Surface poisoning by hfac species was observed during the nucleation of Pt ALD on TiO₂, in agreement with our previous studies of Pd ALD [1]. Trimethylaluminum (TMA) was able to remove the hfac species from TiO₂ and promote more facile nucleation of Pt ALD, also as expected by our earlier work on Pd ALD [2]. We then used hfacH adsorption prior to Pt ALD to block surface sites, delay Pt ALD nucleation and decrease Pt nanoparticle dispersion. In addition, we used TMA exposures after Pt(hfac)₂ exposures to facilitate Pt ALD nucleation and increase Pt nanoparticle dispersion. The Pt nanoparticles were detected by the rising absorbance baseline of the FTIR spectrum, and transmission electron microscopy images of Pt nanoparticles on TiO₂ and WO₃ particles. The size of the Pt nanoparticles was dependent on the number of ALD reaction cycles.

1. D.N. Goldstein & S.M. George, *Thin Solid Films* (In Press).

2. D.N. Goldstein & S.M. George, *Appl. Phys. Lett.* **95**, 143106 (2009).

8:40am **TF+EN-TuM3 Nucleation & Growth of Continuous and Ultrathin Pt ALD Films for Improved Oxygen Reduction Activity in Fuel Cells Using W ALD Adhesion Layers**, *L. Baker*, *A.S. Cavanagh*, *S.M. George*, University of Colorado, Boulder, *A. Kongkanand*, *F.T. Wagner*, General Motors Research & Development

Transition metals, such as Pt, are important as catalysts in fuel cells. The cost of Pt requires that this metal be utilized as efficiently as possible. Previous studies have demonstrated that flat, continuous Pt surfaces have an activity for the fuel cell oxygen reduction reaction (ORR) per surface Pt atom that is 5-10 times *larger* than the activity of 3 nm Pt nanoparticles on carbon-supported electrocatalysts. Consequently, very thin continuous Pt

layers are needed to achieve high activity per mass of Pt and favorable economics.

Pt has a high surface energy and does not readily wet low surface energy oxide and carbon material surfaces. Instead, Pt nanoclusters are formed during the nucleation of Pt ALD on these low surface energy supports. A continuous Pt film is possible only after the coalescence of the nanoclusters when the film thickness is >5 nm. One possible route to obtain a continuous and ultrathin Pt film is to deposit on an adhesion layer that has a *higher* surface energy than Pt. In this case, the Pt will wet the adhesion layer because the deposited Pt film will lower the surface energy. One material that has a higher surface energy than nearly all other metals, including Pt, is tungsten (W).

W ALD using WF₆ and Si₂H₆ is known to nucleate and grow rapidly on Al₂O₃ ALD surfaces [1]. The surface chemistry of W ALD is able to form chemical bonds to the underlying Al₂O₃ substrate that overcome the surface energy differences. In this study, Pt ALD is performed using MeCpPtMe₃ and H₂ plasma on W ALD adhesion layers grown on Al₂O₃ ALD films. X-ray photoelectron (XPS) and x-ray reflectivity (XRR) studies have demonstrated that Pt ALD nucleates *nearly immediately* on the W ALD adhesion layers. The XPS and XRR data are consistent with a layer-by-layer growth model. Pt ALD films can be deposited that are 1 nm thick, conformal and continuous. Initial electrochemical measurements on these thin films have yielded a large proportion of the anticipated ORR activity benefit.

[1] R.A. Wind, F.H. Fabreguette, Z.A. Sechrist and S.M. George, "Nucleation Period, Surface Roughness and Oscillations in Mass Gain per Cycle during W Atomic Layer Deposition on Al₂O₃", *J. Appl. Phys.* 105, 074309 (2009).

9:00am **TF+EN-TuM4 Engineering Li_xAl_ySi_zO Ion Conducting Thin Films by Atomic Layer Deposition for Lithium-ion Battery Applications**, Y.-C. Perng, J. Cho, D. Membreno, N. Cirigliano, B. Dunn, J.P. Chang, University of California Los Angeles

Lithium (Li)-ion batteries have drawn much attention for their outstanding performance in portable electronics applications. However, formation of the solid electrolyte interphase (SEI) layer on the surface of electrodes during the charge-discharge cycling can reduce battery capacity and the long-term reliability of current battery technology. The use of solid electrolyte layers can effectively suppress formation of the SEI. Another application for thin solid electrolytes is in microbatteries, especially those based on the engineering of electrodes into 3D architectures involving high aspect ratio pillars. To realize this potential, an ultra-thin and highly conformal electrolyte layer is needed to coat the 3D electrode array. The ionic conductor lithium aluminosilicate (LiAlSiO₄) synthesized by atomic layer deposition (ALD), is a promising candidate for these battery applications. The material exhibits high ionic conductivity along its c-axis because of channels formed by the alternating tetrahedra of aluminum-oxygen (Al-O) and silicon-oxygen (Si-O).

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 or electrolyte surface coatings. The metal precursors used in this work are tetraethyl orthosilicate (TEOS), trimethylaluminum (TMA) and lithium t-butoxide (LTB). These precursors, along with water vapor as the oxidant, were used to deposit SiO₂, Al₂O₃ and Li₂O, with deposition rates in the range of 0.8–2 Å/cycle, respectively. The deposition rate of stoichiometric LiAlSiO₄ was ~5 Å/cycle at a temperature of 290°C. The concentration of each metal element in Li_xAl_ySi_zO (LASO) thin films is found to correlate closely to ALD cycles and the associated incubation times. Complex impedance measurements show that the ionic conductivities of as-deposited LASO films are in the range of 10⁻⁷ to 10⁻⁸ S/cm and directly related to the lithium content in the film. The LASO ALD coating on 3D features, such as NWs and nanoparticles (NPs), were confirmed to be conformal and uniform by transmission electron microscopy (TEM) imaging. Further electrochemical tests to check pinhole-free coatings on 2D and 3D features were performed as well. The crystallinity of the films after post-deposition rapid thermal annealing (RTA) was a function of cation concentration. The epitaxial relation of LASO to silicon, a potential anode material, was found to be β-LiAlSiO₄ (-1 2 -1 0) || Si (400) and β-LiAlSiO₄ (1 0 -1 0) || Si (004).

9:20am **TF+EN-TuM5 ALD: Enabling Designer Nanostructures for Energy Applications**, G.W. Rubloff, University of Maryland **INVITED** Nanostructures will dominate next-generation energy technologies. Progress in nanofabrication increasingly allows design flexibility control of structural

geometry and material combinations to achieve high performance multifunctional 3-D nanostructures for energy harvesting and storage. Such designs derive advantage from high surface areas, ultrathin films, structures with high aspect ratios, heterogeneous materials combinations, and control over 3-D profiles of material compositions and nanostructure shapes. Self-assembly, self-alignment, and self-limiting reactions enable both nanofabrication of desired energy nanostructures and their scaling to unprecedented levels of integration.

Atomic layer deposition (ALD) plays a pivotal role in this paradigm because of its intrinsic attributes: thickness control at the atomic scale; exceptional conformality to apply this control in the most demanding of nanogeometries; and a growing portfolio of ALD materials choices from new precursors and processes. As a result, ALD is becoming common, even pervasive, in nanostructure-based energy research, spanning applications from heterogeneous nanowires to passivating electrochemical layers and high-efficiency catalytic nanostructures.

Two primary challenges will determine whether ALD's potential is realized in next-generation energy technology.

First, integration of ALD with other processes into suitable process sequences determines how well nanostructure designs can be fabricated and tailored for the energy application. For example, in high aspect ratio trenches, pores, or aperiodic porous materials, ALD films can be highly conformal or tapered "top-down" to thinner layers deeper in the structure, while electrodeposited films can be grown "bottom-up" from a working electrode at the bottom, together offering more design flexibility in vertical profiles than does either process alone.

Second, scaleup of ALD equipment, processes, and control is required for cost-effective ALD manufacturing. Significant efforts are already underway to develop these technologies, notably including roll-to-roll and other high throughput approaches, as well as atmospheric pressure ALD to circumvent the cost and complexity of vacuum-based equipment.

* Supported by the US Department of Energy, Office of Basic Energy Sciences as part of an Energy Frontier Research Center, and by the Laboratory for Physical Sciences.

10:40am **TF+EN-TuM9 Functionalized Quartz Fibers by Atomic Layer Deposition for Dye-Sensitized Solar Cells**, D. Kim, H.J. Koo, M. Woodroof, J.S. Jur, B. Kalanyan, K. Lee, C.K. Devine, G.N. Parsons, North Carolina State University

Dye-sensitized solar cells (DSCs) are a promising alternative to Si-based photovoltaic cells because of their high efficiency, low cost, and simple processing. To improve the efficiency, the light harvesting properties of the DSC photoanode structure should be improved.

This work shows the ability to improve DSCs efficiency by the incorporation of quartz fiber mats functionalized by ALD with a conformal nanoscale TiO₂ coating for the photoanode. The TiO₂ atomic layer deposition allows precise nanoscale thickness control throughout the quartz fiber mat. In addition, thermal stability of the quartz fiber also enables the annealing of TiO₂ films at high temperatures in order to obtain anatase crystallinity, which is the preferred TiO₂ phase in DSCs due to faster electron transfer kinetics. As a result, we obtained very stable anatase TiO₂ on quartz fibers by annealing at as high as 1050 °C. The micro-sized randomly oriented structure of coated quartz fibers caused high light scattering effect inside the photoanode, so that it increased the photon adsorption. At the same time, TiO₂-coated quartz fibers were successfully sensitized by more dye molecules compared to bare quartz fibers.

The use of the dye-sensitized quartz fiber mats in a DSC framework produces devices with overall efficiency exceeding 7% in our laboratory, compared to ~ 6% for similar devices without the coated fiber scattering layer. We will present X-ray diffraction, morphological changes, and optical properties of TiO₂-coated quartz fibers, as well as I-V and IPCE data for the DSCs. The effects of various integration schemes for introducing quartz fibers into the DSC photoanode will be discussed. Moreover, it is believed that the combination of quartz fiber and ALD is very attractive especially to energy research fields where they need finely tuned nanostructures to meet intricate requirements.

11:00am **TF+EN-TuM10 Angle Dependent Electromotive Force in an Al₂O₃/Al/Thermoelectric Power Generator System Interacting with Infrared Radiation**, *A.J. Vincent-Johnson, K.A. Vasquez*, James Madison University, *A.E. Masters*, Custom Thermoelectric, *X. Hu, G. Scarel*, James Madison University

We present a fundamental study of the interaction between infrared radiation and an Al₂O₃ film on Al sheet placed on a thermoelectric power generator (system 1). We compare the results with those obtained for a system consisting in an Al sheet on a thermoelectric power generator (system 2). The Al₂O₃ film in system 1 is prepared using atomic layer deposition, which provides smooth and well defined air/film and film/substrate interfaces. Infrared spectra show that Al₂O₃ films on the aluminum foil absorb an increasing amount of infrared radiation at increasing angle of incidence. This behavior, known as the Berreman effect, is caused by the radiative surface polaritons excited close to the frequencies of longitudinal optical phonons by the infrared radiation at the interfaces of Al₂O₃/Al. Our work demonstrates that a similar trend occurs when infrared radiation is absorbed by system 1: as the infrared radiation starts illuminating system 1 in its initial condition, the electromotive force jumps up to a maximum (EMF_{max}) and then decays exponentially. The EMF_{max} value and its amplitude increase with the increasing incidence angle of the infrared radiation. Since system 2 exhibits only a weak dependence of the EMF_{max} value and amplitude on the incidence angle of the infrared radiation, we conclude that the behavior of the electromotive force during the transient in system 1 is caused by radiative surface polaritons in Al₂O₃/Al. This research is at a seminal stage and needs further understanding. However many routes can be investigated to enhance the efficiency of the electromotive force production. The results are relevant to energy generation from radiation, sensors, and electromagnetic wave detectors.

Tuesday Afternoon, November 1, 2011

Energy Frontiers Focus Topic

Room: 103 - Session EN+NS-TuA

Nanostructured Materials for Thermophotovoltaics, Thermoelectrics & Plasmonics

Moderator: P. Nappal, Los Alamos National Laboratory

2:00pm EN+NS-TuA1 Thermal Plasmonics as a Route to Photovoltaics?, *D.J. Norris*, ETH Zurich, Switzerland **INVITED**

Patterned metallic films allow the generation and manipulation of special electromagnetic waves known as surface plasmons that propagate along a metal interface. Because these waves allow the concentration of light in nanometer-scale volumes, they have implications for fundamental phenomena as well as applications such as imaging, sensing, and solar cells. Thus, the field of plasmonics has arisen to study and utilize surface plasmons. While light is typically used to create these waves, in some cases it would be more convenient to have a non-optical source for surface plasmons. One route is thermal excitation (*i.e.*, heat). Here, we will explore hot plasmonic structures for obtaining new optical behavior. For example, we will examine metallic films patterned with a series of circular concentric grooves (a bull's eye pattern). We show that, when heated, these films can emit light that is amazingly narrow, both in terms of its spectrum and its angular divergence. Thus, a simple metallic foil can generate a highly directional beam of monochromatic light by a thermal process. This effect has implications for creating efficient thermophotovoltaic devices, which convert heat into electricity. During these studies, we also developed a simple, high-throughput method for obtaining ultrasoft patterned metal films. Previously, roughness in such films has hindered the field of plasmonics. Therefore, our approach solves a critical problem and allows many high-quality plasmonic structures to be available for the first time.

2:40pm EN+NS-TuA3 Nanocrystal Assemblies: A Modular Approach to Materials Design, *D.V. Talapin*, University of Chicago **INVITED**

Colloidal nanocrystals can combine the advantages of crystalline inorganic semiconductors with the size-tunable electronic structure and inexpensive solution-based device fabrication. Single- and multicomponent nanocrystal assemblies, also known as superlattices, provide a powerful general platform for designing two- and three-dimensional solids with tailored electronic, magnetic, and optical properties. Unlike atomic and molecular crystals where atoms, lattice geometry, and interatomic distances are fixed entities, the nanocrystal arrays represent ensembles of "designer atoms" with potential for tuning their electronic structure and transport properties. Generally speaking, nanocrystal assemblies can be considered as a novel type of condensed matter, whose behavior depends both on the properties of the individual building blocks and on the interparticle exchange interactions.

The ability to assemble precisely engineered nanoscale building blocks into complex structures is opening the door to materials where components and functionalities can be added, tuned or combined in a predictable manner. I will show how self-assembly of nanocrystals can lead to a palette of unprecedented phases including superlattices isostructural with the Archimedean tilings and dodecahedral quasicrystals.

Efficient charge transport is crucial for performance of nanocrystal-based electronic and optoelectronic devices. The insulating nature of surface ligands traditionally used for nanocrystal synthesis results in the poor electronic coupling between individual nanocrystals. To facilitate charge transport in nanocrystal solids, we introduced the concept of inorganic ligands for colloidal nanocrystals. These ligands, namely metal chalcogenide complexes, can be applied to a broad range of inorganic nanomaterials. I will demonstrate the power of this approach on several examples of prospective electronic, thermoelectric and photovoltaic materials.

4:00pm EN+NS-TuA7 Photonic and Plasmonic Crystals for Thermophotonics and Energy Conversion, *R. Biswas*, Iowa State University & Ames Laboratory - US DOE **INVITED**

Photonic and plasmonic crystals that have various energy-related applications will be discussed. Metallic plasmonic crystals consisting of an array of nano-holes or nano-pillars on common substrates, with pitch at infrared length scales, have very sharp absorption properties at infrared wavelengths. Such arrays have diverse applications to sensors and thermophotonic applications. The absorption, thermal emission, and angular characteristics from these plasmonic arrays will be described with rigorous scattering matrix simulations and compared to measurements. I will also

survey the rich physics underlying plasmonic nano-arrays at optical length scales, and a few energy related applications.

4:40pm EN+NS-TuA9 Molecular and Hybrid Solution Processible Thermoelectrics, *R.A. Segalman*, *S. Yee*, University of California, Berkeley, *N. Coates*, *J. Urban*, Lawrence Berkeley National Laboratory **INVITED**

Thermoelectric materials for energy generation have several advantages over conventional power cycles including lack of moving parts, silent operation, miniaturizability, and CO₂ free conversion of heat to electricity. Excellent thermoelectric efficiency requires a combination of high thermopower (S , V/K), high electrical conductivity (σ , S/cm), and low thermal conductivity (κ , W/mK). To date the best materials available have been inorganic compounds with relatively low earth abundance and highly complex, vacuum processing routes (and hence greater expense), such as Bi₂Te₃. Molecular materials and hybrid organic-inorganics bring the promise of inexpensive, solution processible, mechanically durable devices. While highly conductive polymers are now common place, they generally demonstrate low thermopower. Our work on molecular scale junctions suggests that nanostructuring of organics allows them to act as thermionic filters between inorganic junctions which can lead to enhanced thermoelectric properties. We have taken inspiration from this fundamental understanding to design material systems in which we combine a high electrical conductivity, low thermal conductivity polymer with a nanoparticle that contributes high thermopower. Additionally, the work functions of the two materials are well-aligned which introduces the possibility of thermionic filtering at the interface and an additional boost to the power factor. The combination of these effects results in a new hybrid, solution processible material with a thermoelectric figure of merit approaching those of Bi₂Te₃. In this talk, I will discuss both the use of thermoelectric measurements to gain insight to molecular junctions and how this insight translates to design principles for polymer and hybrid thermoelectrics.

5:20pm EN+NS-TuA11 Semiconductor Nanowire Networks as Thermoelectric Platforms, *A.J. Lohm**, University of California Santa Cruz, *E. Coleman*, *G.S. Tompa*, Structured Materials Industries, Inc., *N.P. Kobayashi*, University of California Santa Cruz

Current energy production mechanisms for electrical power and transportation are plagued by inefficiencies which results in most of the energy source being lost as heat. In most cases that heat is found in the form of low-grade heat with temperatures below approximately 200 degrees C. Unfortunately, typical methods such as the Rankine cycle for converting heat to electricity suffer from poor efficiency for low-grade heat. Direct thermoelectric conversion is currently struggling to match the efficiency of the Rankine cycle at high temperatures but offers advantages in terms of reduced maintenance and form-factor which enable energy scavenging in places such as the exhaust line of a vehicle where larger systems could not be implemented.

Dominated by recent progress in nanostructured materials, the unitless thermoelectric figure of merit ZT has been increased to well beyond 1 such that efficiencies are reaching a range which makes them cost effective. Typically thermoelectric materials include elements such as lead or tellurium which are toxic and rare therefore alternative materials are being sought. Recent progress in silicon nanowire thermoelectric has shown a reduction in thermal conductivity, and therefore an increase in ZT of two orders of magnitude, making them viable candidates in the thermoelectric marketplace. Decreased cost and toxicity of silicon as compared to conventional thermoelectric materials make it an attractive candidate but to date nearly all studies on thermoelectricity of nanowires have focused on nanowires in isolation. Our platform based on interconnected 3-dimensional nanowire networks grown directly on metallic substrates provides large area thermoelectric modules capable of scavenging low-grade heat for low cost. The materials properties comprising ZT : thermal conductivity, electrical conductivity and Seebeck coefficient will be discussed for undoped, p-type and n-type silicon nanowire networks with particular emphasis on electrical conductivity and Seebeck coefficient within the temperature range of low-grade heat.

5:40pm EN+NS-TuA12 Diamond as an Electrode Material for the Direct Conversion of Thermal to Electrical Energy through Thermionic Emission, *W.F. Paxton*, *J.L. Davidson*, *W.P. Kang*, Vanderbilt University

Introduction

* NSTD Student Award Finalist

Thermionic energy conversion is a candidate technology for the efficient conversion of thermal energy directly to electrical energy. In a thermionic converter, thermally excited electrons are emitted from the surface of a heated cathode into a vacuum gap. These electrons are then collected by a cooler anode and driven through an external load back to the cathode. The thermionic emission current density of a heated cathode can be described by the Richardson Equation (Eq. 1).

$$J = AT^2 e^{-\Phi/kT} \quad (1)$$

where: J: Thermionic emission current density (A/cm²); A: Richardson constant (A/cm² T²); T: Temperature (K); Φ : Material's work function (eV); and k: Boltzmann constant (eV/T)

It can be seen from Eq. 1 that a material with a lower work function, Φ , can achieve higher current densities at lower temperatures than a material with a higher work function, which implies lower work function values translate into better energy converters. Prior attempts to construct efficient thermionic converters were limited by available materials with work function values ranging from 3.5eV to 5eV requiring extreme cathode temperatures in order to achieve useable output power values. In this study, the thermionic emission properties of nitrogen-incorporated diamond films are examined as a potential electrode material to enhance the efficiency of such a device.

Experimental

Polycrystalline diamond films were synthesized on molybdenum substrate via Microwave Plasma-Enhanced Chemical Vapor Deposition (MPCVD). The source gases were H₂, CH₄, and N₂, microwave power was 1.5KW, and the nominal pressure was 50Torr. Scanning electron micrographs of the samples demonstrated uniform film coverage and a thickness of ~100 μ m.

Thermionic emission characterization was performed in a vacuum environment with a base pressure of 1×10^{-7} Torr. The diamond films were resistively heated and the temperature was constantly observed by a dual color pyrometer. Electron emission current was collected with an electrically isolated anode biased at a constant voltage of 100V positioned 0.5cm above the heated cathode.

Results and Discussion

Observation of the electron emission current above the noise level began at 600°C and increased exponentially with temperature up to 800°C. Analysis of this data demonstrated agreement with the Richardson equation with a correlation coefficient of 0.99. From this data, the nitrogen-incorporated diamond samples were determined to have a work function value less than 2eV which is considerably lower than previously mentioned materials. These results exhibit diamond's potential as an interesting cathode material for a thermionic energy converter.

Energy Frontiers Focus Topic

Room: 108 - Session EN+TF-TuA

Thin Films for Solar Cells

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

2:00pm **EN+TF-TuA1 Thin Film Silicon Approaches to Future Generations of PV Materials**, *P.C. Taylor*, Colorado School of Mines **INVITED**

Silicon is a material of choice for photovoltaic (PV) applications for several reasons. First, there is perhaps more known about the properties and processing of Si than any other semiconductor due to its prominence in electronic devices. In addition, Si is a non-toxic, abundant element that is potentially inexpensive to produce in large quantities. The major problems with Si for use in future PV applications are the inefficient absorption of light due to its electronic band structure and a fundamental limit on the efficiency of any single junction bulk device due to transmission of photons below the optical band gap energy and loss of energy to heat for photons above the optical band gap energy (so-called Shockly Queiser limit). Nanostructured films of Si have the potential to overcome these problems by decoupling the absorption length for photons from the collection length for carriers and by introducing additional optically excited carriers due to the quantum confinement in nanostructured films. The most promising possibilities for more efficiently exciting and collecting carriers include the production of more than one electron-hole pair per absorbed photon for photon energies greater than twice the optical gap energy, the absorption of photons of below gap energies by the introduction of an intermediate band of states within the optical energy gap due to the inclusion of quantum confined structures with the appropriate properties, and the collection of excited carriers before they lose their energy to phonons. Progress in utilizing these mechanisms for dramatically increasing the efficiencies of future PV devices based on Si will be discussed.

2:40pm **EN+TF-TuA3 On the Influence of the Amorphous Silicon Microstructure on the Crystallization Kinetics Towards Polycrystalline Silicon for Solar Cells**, *M. Creatore, K. Sharma, M.C.M. van de Sanden*, Eindhoven University of Technology, the Netherlands

Polycrystalline silicon (poly-Si) is considered to be a promising candidate for thin film PV, coupling the high quality crystalline Si technology with large area and low-cost manufacturing. Our initial studies [1] on poly-Si layers have shown grains extending through the whole thickness (1 μ m) upon solid phase crystallization (SPC) of high growth rate plasma deposited amorphous silicon (a-Si:H) films. Furthermore, larger grains are promoted by an increase in the a-Si:H microstructure parameter R* [2], which represents the order (low R*)/disorder (high R*) in the matrix according to the Si-H bond distribution in mono-/di-vacancies (low stretching mode-LSM) and nano-sized voids (high stretching mode-HSM), and it is quantified by the integrated IR absorption band ratio $I_{HSM}/(I_{LSM}+I_{HSM})$.

The SPC of a-Si:H follows the steps of incubation, nucleation and grain growth. With the purpose of providing insight on the crystallization process, this contribution addresses a detailed crystallization kinetic study of plasma deposited a-Si:H films by means of in-situ X-ray diffraction (XRD). a-Si:H films having R* in the range of 0.05-0.6, with an hydrogen content of 5-14 at. %, were annealed at 600 °C.

The medium range order (MRO) of the a-Si:H layers, quantified by the XRD line-width, and representing the most ordered regions in the matrix (up to 15-25 Å from the mono-vacancies), is found to affect the incubation time (t_0), in agreement with [3]: low R* and high MRO promote a faster nucleation (t_0 in the range of 50-100 min), since the most ordered regions act as nucleation centers; as the structural disorder increases, the MRO decreases and the incubation step is delayed up to 450 min. However, for R* > 0.3 and an hydrogen content above 9%, the incubation time unexpectedly decreases. Therefore, the R* and the MRO evolutions during the annealing step are studied. High R* layers, characterized by hydrogen mainly bonded to nano-sized voids, are more prone to hydrogen out-diffusion upon annealing, as inferred by the quantitative decrease of the HSM mode with respect to the LSM mode. The hydrogen evolution is then followed by the rearrangement of the a-Si:H into more ordered regions, as witnessed by the increase of the MRO upon annealing, promoting a decrease in incubation time. In conclusion, next to the established role of the MRO, the nano-sized voids play also a role in the crystallization kinetics, as they affect the overall microstructure and medium range order upon annealing.

[1] Illiberi et al., *Material Letters* **2009**, *63*, 1817.

[2] Sharma et al., *Advanced Energy Materials* **2011**, DOI: 10.1002/aenm.201000074

[3] Mahan et al., *Adv. Funct. Mater.* **2009**, *19*, 2338.

3:00pm **EN+TF-TuA4 Deposition of Microcrystalline Silicon Thin Films by Radio Frequency PECVD using Voltage Waveform Tailoring**, *S. Pouliquen, P.-A. Delattre, E.V. Johnson, J.-P. Booth*, Ecole Polytechnique (Palaiseau), France

This paper shows the feasibility of depositing thin films of hydrogenated microcrystalline silicon (μ c-Si:H) for photovoltaic applications by radiofrequency discharge using voltage waveform tailoring. Contrary to typically used sinusoidal waveforms, the films were deposited using asymmetric voltage waveforms, resembling "peaks" and "valleys", composed of a fundamental frequency of 15 MHz and three harmonics. Such waveforms lead to an electrical asymmetry effect in the plasma, and a different ion bombardment energy on each electrode. For these experiments, we used a gas mixture of silane diluted in hydrogen (from 1-4%), a total flow rate less than 100 sccm, and a range of pressure from 100 up to 1000 mTorr. We show that the chemical, optical and structural properties - as measured by FTIR, spectroscopic ellipsometry, Raman scattering and profilometry - are strongly determined by the shape of the voltage waveform, and therefore the ion bombardment energy. We observe this effect on the Si-Si bond configuration (microcrystalline vs amorphous peaks in Raman scattering between 480 and 520 cm⁻¹) as well as on the Si-H bond configuration (FTIR peaks at 2000-2100 cm⁻¹). We examine the strength of the effect for varying process parameters, including pressure, total gas flow, voltage amplitude, and SiH₄/H₂ dilution ratio. For the range of parameters used, a growth rate for highly microcrystalline silicon of up to 3 Å/s was achieved without exceeding a pressure of 100 mTorr.

4:00pm **EN+TF-TuA7 Amorphous and Nanocrystalline Silicon Thin Film Photovoltaic Technology on Flexible Substrates**, *B. Yan, A. Banerjee, J. Yang, S. Guha*, United Solar Ovonic LLC **INVITED**

Because of the rapid increase of energy demand and growing concern of environmental impact, renewable energy from photovoltaic (PV) has gained a great deal of attention in the last decade. Various PV technologies have been developed. However, solar panels using conventional crystalline

silicon have dominated the market. Thin film silicon is one of the so-called second generation PV technologies. Nowadays, majority of thin film silicon PV products are made with hydrogenated amorphous silicon (a-Si:H) and amorphous silicon germanium (a-SiGe:H) alloy. The advantages of a-Si:H based technology are low cost, capability of large scale manufacturing, abundance of raw materials, and no environmental concerns. One disadvantage of a-Si:H PV technology is its lower efficiency than solar panels made of crystal silicon and compound crystal thin film semiconductors. To resolve the low efficiency issue, significant effort has been made by the researchers. In order to use the solar spectrum effectively, multi-junction structures are normally used by incorporating a-SiGe:H in the bottom cell. In recent years, hydrogenated nano-crystalline silicon (nc-Si:H) has been used as a potential replacement of a-SiGe:H bottom cell in multi-junction structures. The pros of nc-Si:H are its stability under sun light, high photocurrent capability, and no Ge-containing gases required in the process; the cons are thick intrinsic layer that needs high rate deposition and technical challenges for large-area deposition. United Solar has been heavily involved in research and development of a-Si:H and nc-Si:H based PV technology. We have made significant progress in efficiency improvements of a-Si:H and nc-Si:H multi-junction solar cells and modules. We have achieved (i) a 15.4% initial active-area (~0.25 cm²) solar cell efficiency, (ii) an NREL measured stable total area (~0.25cm²) efficiency of 12.5%, and (iii) NREL measured initial and stable module (~400 cm²) efficiencies of 12.0% and 11.4%, which all set new record efficiencies achieved by a-Si:H, a-SiGe:H, and nc-Si:H multi-junction cell structures. Based on these achievements, we have started working on the development of roll-to-roll manufacturing technology for a-Si:H and nc-Si:H multi-junction structures on flexible substrates. We expect to launch 12% stable aperture area a-Si:H and nc-Si:H product in 2012. In this presentation, we will review the progress made by the community and challenges a-Si:H and nc-Si:H PV technology face.

4:40pm **EN+TF-TuA9 High Efficiency, Large Area Silicon Thin Film Solar Modules**, **L. Li, T. Guo, Y. Meng, Z. Xu, F. Dai, F. Zhang, W. Li, Z. Lei, C. Cai, H. Li, B. Tang, D. Zhou**, ENN Solar Energy Co. Ltd. **INVITED** Hydrogenated amorphous and microcrystalline silicon based thin film solar cells have long shown great potential for various photovoltaic applications due to its better electricity generation under low light and high temperature, shorter energy payback time and greener manufacturing processes, as well as unique applications for BIPV. However, this technology hasn't fully realized its market potential, as low module efficiencies at mass-production level being one of the major limiting factors. In this paper we report over 9% stabilized module efficiencies in volume production achieved on 5.7 m² substrates from a-Si:H/uc-Si:H tandem junction solar modules, which reflects significant efficiency improvement by process tuning of silicon thin films, back contact, and device structure, etc.. Several application case studies are also reported which demonstrate excellent field performance of ENN silicon thin film solar modules.

5:20pm **EN+TF-TuA11 Metal-Modulated Epitaxy Growth of InGaN/GaN p-i-n Solar Cells**, **B. Gunning, M.W. Moseley, J.E. Lowder, W.A. Doolittle**, Georgia Institute of Technology, **J. Wierer, S. Lee, D. Koleske, Q. Li**, Sandia National Laboratories InGaN alloys have great potential in the field of photovoltaics due to their excellent light absorption and tunable bandgap (0.7-3.4eV) which spans the visible spectrum. However, the growth of this material remains a challenge due to thermal decomposition, indium surface segregation, and phase separation. To combat these issues, low substrate temperatures and high growth rates must be implemented in combination with in situ surface monitoring via RHEED. Metal modulated epitaxy (MME) has been shown to achieve single-phase InGaN alloys throughout the miscibility gap with sub-nm RMS roughness.

In this study, MME is applied to the growth of n-GaN/i-InGaN/p-GaN solar cells. Unintentionally doped InGaN layers 50/200nm thick with 16% In composition are grown on a 3μm n-type GaN template. The topmost layer consists of p-type GaN with varying hole concentrations. Transient RHEED signals are monitored closely during InGaN growth to prevent indium surface segregation and ensure a smooth film.

The absorption characteristics are determined as shown in Figure 1, and the material is characterized via AFM, XRD and PL prior to being fabricated into device structures. The InGaN layers are found to be approximately 80% strain relaxed as determined by XRD analysis of the (20-25) reflection (Figure 2). During device testing, the solar cells exhibit low turn-on voltages below the expected value, as well as low external quantum efficiency. These inconsistencies indicate carrier loss due to electrical shorts and defects. The scanning TEM images in Figure 3 show striations in the InGaN layer similar to those in a superlattice structure but with a period that

does not correspond to the shutter cycles. Even though the x-ray diffraction indicates predominantly relaxed epitaxy, TEM images are unable to resolve individual threading dislocations. It is not clear at present if this is indicative of extremely large dislocation density or a new method of relaxation related to the above mentioned striations. Finally, post-growth annealing processes are explored as possible ways to improve device performance.

The work at Georgia Tech was supported by Air Force Office of Scientific Research, under a basic science grant managed by Kitt Reinhardt.

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Wednesday Morning, November 2, 2011

Energy Frontiers Focus Topic

Room: 103 - Session EN+EM+NS-WeM

Quantum Dot and Nanowire Solar Cells

Moderator: K. Leschkes, Applied Materials Inc.

8:00am EN+EM+NS-WeM1 **Hybrid Quantum-Dot/Organic Solar Cells Based on Silicon Nanocrystals**, *U. Kortshagen, C.Y. Liu, Z. Holman, J. Yang*, University of Minnesota **INVITED**

Organic solar cells based on bulk heterojunctions between acceptor and donor semiconductors have attracted significant attention due to their low cost, compatibility with roll-to-roll processing, and relative lack of health and environmental concerns. However, the stability of organic semiconductors under solar irradiation remains to be a challenge. Producing bulk heterojunction solar cells based entirely on inorganic materials thus has become an attractive proposition.

In a first step into this direction, we have produced solar cells from silicon nanocrystals (Si NCs) and poly-3-hexylthiophene (P3HT). Silicon NCs 3–5 nm in diameter were synthesized by dissociating silane gas in a nonthermal radio frequency plasma, and collected on a mesh downstream of the plasma. The silicon-hydride terminated NCs were dispersed with P3HT in 1,2-dichlorobenzene. Films of this blend with thicknesses of 100–200nm were spin-cast onto an indium tin oxide (ITO) substrate pre-coated with 50 nm of poly(3,4-ethylenedioxythiophene)/poly(styrenesulfonate) (PEDOT:PSS). Metal electrodes (2mm wide, 100 nm thick) were then evaporated on top of the Si NC/P3HT film.

The Si NCs were found to be efficient electron acceptors. The optimal weight ratio of Si NC to P3HT was 50 wt%. The effects of annealing and different metal electrodes on Si NC/P3HT hybrid solar cells were studied. After annealing at 150 °C, Si NC/P3HT solar cells exhibited power conversion efficiencies as high as 1.47%. The hole mobility in the P3HT phase extracted from space-charge-limited current measurements of hole-only devices increased from 2.5×10^{-10} cm²/V-s to 1.1×10^{-9} cm²/V-s after annealing, resulting in better transport in the solar cells. A quenching of the open-circuit voltage and short-circuit current was observed when high work function metals are deposited as the cathode on Si NC/P3HT hybrid devices.

Devices with silicon-hydride terminated Si NCs were plagued by poor film morphology. Hence we studied functionalizing Si NCs with organic ligands. Functionalization with 1-octene and 1-dodecene led to improved film morphology but the transport in the Si NC network became worse. However, excellent stability with respect to air exposure of these cells was observed. Efforts to improve the dispersability of Si NCs without inhibiting transport in the Si NC network are in progress.

This work was supported primarily by the MRSEC Program of the National Science Foundation under Award Number DMR-0819885 and by the DOE Energy Frontier Research Center for Advanced Solar Photophysics.

8:40am EN+EM+NS-WeM3 **Precision Engineering of Semiconductor Nanowires for Advanced Photovoltaic Devices**, *N. Shin, I.R. Musin, S. Sivaram, M.A. Filler*, Georgia Institute of Technology **INVITED**

Semiconductor nanowires offer exciting opportunities to engineer light absorption and carrier transport for ultrahigh efficiency photovoltaic devices. The precise control of crystal structure and geometry is required to achieve a desired behavior, especially in highly confined nanoscale systems. In the ideal situation, the combination of nanowire diameter, lattice structure (e.g. diamond cubic, wurtzite), crystal orientation (e.g. <111> vs. <110>), and sidewall faceting that yields the most robust device performance would be known and could be rationally synthesized. Unfortunately, an inadequate understanding of nanowire chemistry-structure and structure-property relationships prevents the accomplishment of this task with bottom-up syntheses at the present time. This presentation will provide an overview of our recent efforts to bridge this knowledge gap. In our research, *in-situ* infrared spectroscopy is combined with an ultrahigh vacuum growth environment to fundamentally correlate nanowire chemistry with photophysics, while circumventing the sample degradation that can obscure the intrinsic properties of nanoscale structures. Group IV nanowires and their heterostructures are a model system and are fabricated with the vapor-liquid-solid (VLS) growth technique. The critical influence of surface-bound species near the three-phase boundary and their impact on nanowire crystal structure will be discussed in detail. This fundamental knowledge opens a generic and highly tunable route to engineer multiple classes (e.g. group IV and III-V, etc.) of semiconductor nanowires,

heterostructures, and superstructures for advanced photovoltaic device applications.

9:20am EN+EM+NS-WeM5 **Electrophoretic Deposition of CdSe Nanocrystals in Quantum Dot Sensitized Solar Cells**, *N.J. Smith*, Middle Tennessee State University

Electrophoretic deposition (EPD) of nanocrystal thin films from the solution phase has received increasing attention due to its simplicity and ability to rapidly create controlled thickness films. In this presentation, we will discuss the impact of solvent choice, deposition time, and electrode voltage on the properties of CdSe nanocrystal films deposited by EPD for solar cell applications.

While hexanes are a commonly used solvent for depositing CdSe nanocrystals, resulting film formation by EPD is often not reproducible for different batches of nanocrystals. In this work, we report that adding acetone to solutions of nanocrystals in hexanes enables the consistent deposition of CdSe nanocrystal thin films of controllable thickness. These films form within a few seconds and require comparatively low electrode voltages for the deposition process. The addition of acetone appears to mitigate the effects of impurities in the precursor chemicals, the presence of solvents left over from nanocrystal synthesis, and variable environmental conditions that may otherwise compromise the quality of the resulting EPD nanocrystal films.

Quantum dot sensitized solar cells have been fabricated using the EPD process with CdSe nanocrystals solvated in hexanes with acetone. By modifying the EPD parameters, both the density and thickness of the nanocrystals films deposited on titanium dioxide coated ITO slides were affected. We will discuss the relationship between the EPD parameters and the resulting I-V characteristics and efficiency of the CdSe nanocrystal sensitized solar cells. Preliminary studies suggest that proper choice of EPD parameters can lead to more than one order of magnitude improvement in the solar cell performance metrics.

9:40am EN+EM+NS-WeM6 **Selective and Highly Efficient Photo-Induced Activity Over Nano-Scale Sites in Porous Silicon: Potential Application for Hybrid Organic-Silicon PV**, *M. Asscher*, The Hebrew University of Jerusalem, Israel, *G. Toker, A. Nahor, O. Berger, S. Yitzchaik, A. Sa'ar*, Hebrew University, Israel

Photo-induced processes over solid surfaces are of great basic and technological interest with applications in e.g. photolithography, sensing, catalysis and photovoltaics. Photo activity within porous silicon (PSi) following UV (193-266nm) irradiation has been studied. Unusually efficient, non-thermal, morphology and wavelength dependent photo-induced desorption (PID) of Xe was recorded. It is a selective process, revealing more than 3 orders of magnitude enhancement within pores, at the vicinity of nano-scale silicon tips, over atoms adsorbed on top of flat surfaces. Remarkably large cross sections up to $\sigma_{\text{PSi}} = 2 \cdot 10^{-15}$ cm² were recorded, significantly larger than any previously published photo-induced events on solid surfaces at this wavelength range. Long lived, photo-induced positive charges (holes) located at inner surface nano-tips is proposed to stabilize transient negative Xe adsorbate ions as the precursor for this new photo-desorption process.

These results were utilized for the construction of hybrid conducting polymer-porous silicon photovoltaic cell. Proof of concept and preliminary results are discussed.

10:40am EN+EM+NS-WeM9 **High-Performance, Low-Cost Nanopillar Array Photovoltaics**, *A. Javey*, University of California Berkeley **INVITED**

Semiconductor nanowires (NWs) hold great promise for fabrication of high-performance, low-cost solar cells. These materials have been extensively studied, both computationally and experimentally. The key advantage of NW solar cells resides in the ability to grow single crystalline NWs non-epitaxially on support substrates. Additionally, by varying the NW geometry, the electrical, optical and mechanical properties of the solar cells can be controlled, providing opportunities unavailable to planar thin-film solar cells. Here we discuss our work on bottom-up CdS/CdTe nanopillar (NPL) solar cells, optical engineering of NPL arrays, and top-down fabrication of InP solar cells.

Bottom-up NPL solar cells were fabricated on anodized aluminum oxide (AAO) templates. Due to the 3-D geometry, the templated NPL architecture orthogonalizes the light absorption and carrier collection directions,

enabling cells to be optimized even for poor quality materials. First-generation CdS/CdTe solar cells on low-cost Al foil exhibited 6% efficiency, 0.6 V open circuit voltage, V_{OC} , and 21 mA/cm² short circuit current, J_{SC} , despite significant (>30%) optical reflection from the top contact. Additionally, detailed electronic simulation was used to examine the design trade-offs involved with the NPL architecture. We found that even for a poor quality CdTe absorber layer, through proper design, moderate efficiencies of ~15% could be achieved. Additionally, all the processes used to fabricate the cell were roll-to-roll compatible. Thus, the combination of experiment and modeling show the promise of this method for fabrication of low-cost, high-performance solar cells.

The AAO templated growth enables a high degree of control over the geometry and dimensions of the NPL arrays. For single-diameter Ge NPL arrays embedded in AAO, increasing the Ge material filling ratio both increases the reflectance and decreases the transmittance. The absorbance of an array is shown to strongly increase for increased diameter NPL arrays. Thus, by fabricating arrays of dual-diameter Ge NPLs, ~99% of incident light was absorbed with a film only 2 μ m thick. This behavior is caused by the smaller NPL diameter at the interface between the material and incident light, and the higher diameter base then absorbs the light.

Finally, radial p-n junction solar cells are fabricated from InP NPLs generated from a top-down etching procedure. The main challenge with radial p-n junctions is the ability to form ultra-shallow and conformal junctions along the radial axis. By utilizing a sulfur monolayer doping scheme, conformal junction depths of <10nm with high electrically active dopant concentrations (~10¹⁹ cm⁻³) are achieved. The fabricated solar cell exhibited a power conversion efficiency of 8.1%, a V_{OC} =0.54 V, and a J_{SC} =25 mA/cm².

In summary, we have presented both top-down and bottom-up approaches for fabricating NPL solar cells, from both crystalline starting materials as well as low-cost Al foil. The templated AAO growth method also enabled optical engineering of NPL arrays, allowing a single material to maximize absorption and minimize reflection. Finally, the utilization of a previously-developed conformal, ultra-shallow doping scheme was shown to enable radial InP solar cells.

11:20am **EN+EM+NS-WeM11 Extremely Thin Absorber Solar Cells Based on CdSe-Coated ZnO Nanowires**, *H. Majidi, T.P. Le, G.W. Gaglietta, J.B. Baxter*, Drexel University

Solar cells can provide an abundant, clean, and sustainable source of electricity, but high costs have limited their implementation. The use of sensitized nanostructured architectures may enable both low-cost processing and high efficiency by decoupling the functions of light harvesting and charge transport into different materials. Sensitized solar cells consist of a bicontinuous interpenetrating network of electron- and hole-transporting materials with an interfacial absorber layer. In this architecture, interfacial recombination is the dominant loss process, so controlling the interfacial chemistry during deposition is critical.

We report on the use of n-type ZnO nanowire arrays sensitized with thin CdSe coatings and covered with p-type CuSCN in extremely thin absorber (ETA) solar cells. Low temperature, solution deposition methods were used for each material, offering the potential for inexpensive and scalable nanomanufacturing. Nanowire arrays provide direct pathways for electron transport as well as sufficient surface area for sensitization. The electrodeposited CdSe coatings are nanocrystalline and conformal with well-controlled thickness. CuSCN is electrodeposited into the pore volume between nanowires. Morphology and microstructure of CdSe and CuSCN depend sensitively on bath chemistry and deposition potential. By controlling nucleation and growth rates, conformal and void-free materials can be deposited.

A combination of solar cell measurements and ex situ materials characterization for both planar thin film stacks and nanowire arrays have been used to direct the selection of optimal ETA cell architectures. For example, ultrafast transient absorption spectroscopy demonstrates that interfacial electron transfer from photoexcited CdSe to the ZnO is much faster than recombination (~3 ps vs ~50 ps) for thin coatings. Planar solar cells were used to identify the optimal coating thickness of ~70 nm for these materials. External quantum efficiency measurements show efficient sensitization throughout the visible region of the solar spectrum. However, interfacial recombination limits overall energy conversion efficiencies.

11:40am **EN+EM+NS-WeM12 Hybrid Photovoltaics Devices Based on Quantum Dot Functionalized ZnO Nanowire Arrays Embedded in a Polymer Matrix**, *N. Harris, L. Butler, G. Shen, N. Dawahre, S. Wilbert, W. Baughman, S. Balci, P. Kung, S. Kim*, University of Alabama

There is an increasing need to develop new low-cost materials and architectures for high efficiency solar cells in an attempt to provide a cost effective alternative to fossil fuels. Dyes, polymers and quantum dots have received tremendous amounts of attention due to their potential for solution

processing and high absorption coefficients. Polymers and quantum dots are an attractive option for replacing dyes as the next generation low-cost absorber material due to their improved electronic properties and increased longevity. Bulk-heterojunction polymer based cells suffer from low carrier mobility and short carrier lifetimes which lead to high recombination rates. Quantum dots are promising sensitizing material because they potentially have improved stability over polymers and can potentially generate multiple excitons per photon. However, charge transport in solar cells based solely on quantum dots is generally accomplished through the hopping-mechanism and leads to increased recombination rates.

In this talk, we present a hybrid photovoltaic device structure based on quantum dot (QD)-functionalized single crystalline ZnO nanowire arrays embedded into a polymer matrix in order to achieve improved charge collection efficiencies from the QDs and transport through the cell. A number of issues need to be addressed, such as the enhancement of the coverage of the nanowires with quantum dots to increase photon absorption, as well as implementing a hole-transport medium that does not degrade the quantum dots and can potentially serve as a secondary absorber material that could potentially greatly improve device longevity, reproducibility and efficiency.

In this work, the specific photovoltaic device structure consisted of an InP/ZnS core-shell QD functionalized ZnO nanowire array that is embedded into a poly-3(hexylthiophene) (P3HT) hole transport matrix. The QD sensitized ZnO nanowires were characterized by optical absorption, confocal Raman and photoluminescence spectroscopy, as well as high resolution and scanning transmission electron microscopy. In addition, interface between QDs and ZnO NWs were studied by Atom Probe Tomography. QDs with different absorption bands were concurrently functionalized onto the same nanowire arrays in order to broaden the final device absorption bandwidth. The ZnO:P3HT matrix was then planarized using inductively coupled plasma etching. The performance of planarized, quantum dot functionalized devices was subsequently compared to as-deposited and non-functionalized devices and the effect of QDs on device efficiency is presented. These include the study of the charge transfer mechanism using terahertz time domain spectroscopy.

Energy Frontiers Focus Topic

Room: 209 - Session EN+NS-WeM

Organic Photovoltaics

Moderator: R.A. Quinlan, Naval Surface Warfare Center, Carderock Division

8:00am **EN+NS-WeM1 Sol-gel Prepared Ca Doped ZnO and Its Application in Polymer-Oxide Bilayer Hybrid Solar Cells**, *M. Wang, I. Hill*, Dalhousie University, Canada

Conjugated polymer/metal oxide hybrid photovoltaic devices have received considerable attention in recent years due to their potential for scalable, low-cost manufacturing. To improve device efficiency, most research has focused on increasing the fill factor and short circuit current. In this article, calcium doped zinc oxide ($Zn_xCa_{1-x}O$) is used as electron acceptor in the hybrid poly(3-hexylthiophene) ($Zn_xCa_{1-x}O$) bilayer solar cells to modify the band offsets and increase the open circuit voltage. XRD results show the sol-gel prepared Ca doped ZnO films have a hexagonal wurtzite phase with no indication of calcium separation. Atomic force micrographs indicate the $Zn_xCa_{1-x}O$ surface becomes decorated with interconnected ridges approximately 100 nm in height. The rms surface roughness increases with increasing Ca. The band gap obtained from UV-vis absorption spectra widens from 3.20 to 3.60 eV as the Ca concentration increases from $x=0$ to $x=0.12$. The work function of the $Zn_xCa_{1-x}O$ films measured by Kelvin probe is seen to decrease with increasing Ca composition for values of x up to 0.12, which indicates a decrease in electron affinity. The open circuit voltage of hybrid P3HT/ $Zn_xCa_{1-x}O$ devices increases from 570 mV at $x = 0$ up to 800 mV for $x = 0.10$. Work is under way to incorporate Ca doped ZnO nanoparticles into bulk heterojunction solar cells to optimize device efficiency.

8:20am **EN+NS-WeM2 The Influence of ITO Surface Treatments on Spatially Localized Photocurrent Variation in Organic Photovoltaic Devices**, *B.J. Leever*, Air Force Research Laboratory, *I.P. Murray*, Northwestern University, *M.F. Durstock*, Air Force Research Laboratory, *T.J. Marks, M.C. Hersam*, Northwestern University

The fabrication process for bulk heterojunction (BHJ) organic photovoltaic (OPV) devices nearly always includes anode modification steps ranging from solvent cleaning to haloacid treatments to the deposition of interfacial layers such as polymer blends or transition metal oxides. The role of these

treatments is not yet fully understood, but they are thought to modify the anode work function, contribute to electron-blocking, alter the anode surface energy, and prevent shunts among other functions. In separate work, conductive atomic force microscopy (AFM) and derivative techniques have been used to simultaneously probe both the morphological and electrical properties of BHJ photovoltaic layers. Previous work has demonstrated a correlation between BHJ nanostructure and properties such as photocurrent at the same scale (~ 20 nm) as the phase separation in these films. Photocurrent variability has also been observed at a length scale orders of magnitude larger than the domains in the BHJ layer, and this variation has been speculated to have an origin in the anode or interfacial layers in the OPV architecture.

In this work, a correlation between indium tin oxide (ITO) surface treatment and spatially localized photocurrent variation has been found in OPV devices with a poly(3-hexylthiophene):[6,6]-phenyl-C-61-butyric acid methyl ester (P3HT:PCBM) BHJ layer. Atomic force photovoltaic microscopy (AFPM) was used to scan arrays of functioning 2 μm solar cells with varied ITO surface treatments. The standard deviation of the average photocurrent was found to be 11.4% for devices fabricated on untreated ITO, 8.6% for devices with a poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) interlayer, and 6.7% for devices with a HCl-treated ITO surface. These results suggest that conductive non-uniformity in the ITO surface is transferred through the P3HT:PCBM film and that improving the anode conductive uniformity could be an important role of OPV interfacial layers or anode surface treatments.

8:40am **EN+NS-WeM3 Electronically Monodisperse Single-Walled Carbon Nanotube Thin Films as Transparent Conducting Anodes in Organic Photovoltaics**, T.P. Tyler, R.E. Brock, H.J. Karmel, T.J. Marks, M.C. Hersam, Northwestern University

Carbon nanomaterial thin films are being increasingly investigated for use as transparent electrodes in a variety of optoelectronic devices [1-3]. These flexible and solution-processible films are ideal candidates for organic electronics, including organic photovoltaics (OPVs), where low production costs and mechanical robustness are essential. While carbon nanotube networks have begun to be explored in such devices, the inherent polydispersity of the samples—namely the mix of both semiconducting and metallic species—has prevented the realization of their full potential in these devices and convoluted a complete understanding of their implications on device operation. Herein we report the use of single-walled carbon nanotubes (SWNTs) sorted by electronic type via density gradient ultracentrifugation as the transparent anode in poly(3-hexylthiophene) (P3HT) [6,6]-phenyl-C₆₁ butyric acid methyl ester (PCBM) organic photovoltaic devices. Through a combination of dip coating and nitric acid treatment we achieve film roughnesses comparable to typical transparent oxides such as indium tin oxide. While carbon nanotube films are often electronically doped during processing, either intentionally or as a byproduct of roughness-reducing acid treatments, we find that the application of the quintessential electron-blocking interlayer poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) removes sufficient adsorbed dopant groups to return the semiconducting nanotubes to their original state, vastly reducing their contribution toward current collection and transport. This is observed by both sheet resistance increases and UV-vis-NIR spectrophotometry. Further investigation using X-ray photoelectron spectroscopy reveals that the weakly-bound nitric oxide groups on the surface are almost entirely removed by PEDOT:PSS. By varying the semiconducting and metallic content in the electrodes, we find that metallic content greater than 70 percent yields devices with efficiencies 50 times greater than those comprised of almost entirely semiconducting SWNTs. This observation is counterintuitive considering that freshly acid-treated semiconducting SWNT films often possess a lower sheet resistance than their metallic counterparts [4]. This underscores the advantage of using metallic-enriched populations for transparent conductors, where unstable doping of semiconducting carbon nanotubes complicates processability and ultimately reduces device performance.

- [1] T. M. Barnes; et al. *Appl. Phys. Lett.* **2010**, *96*, 243309.
- [2] S. Kim; et al. *Adv. Funct. Mater.* **2010**, *20*, 2310.
- [3] J. Li; et al. *Nano Lett.* **2006**, *6*, 2472.
- [4] J. L. Blackburn; et al. *ACS Nano* **2008**, *2*, 1266.

9:00am **EN+NS-WeM4 In Situ Characterization of Lifetime and Morphology in Operating Bulk Heterojunction Organic Photovoltaic Devices by Impedance Spectroscopy**, B.J. Leever, C.A. Bailey, Air Force Research Laboratory, T.J. Marks, M.C. Hersam, Northwestern University, M.F. Durstock, Air Force Research Laboratory

Numerous reports have established that improving the performance of bulk heterojunction (BHJ) organic photovoltaic (OPV) devices requires not only the development of materials systems with improved spectral response and

higher charge carrier mobility but also the ability to understand and tailor the morphology of these systems. Approaches for morphological characterization have included microscopic techniques such as scanning electron microscopy, transmission electron microscopy, and various atomic force microscopy techniques. Other methods have provided indirect information about active layer morphology by enabling the determination of charge carrier lifetimes. These approaches have included transient absorption spectroscopy, transient photovoltage, and time-of-flight techniques among others. While these methods have proven quite informative, the relationships between nanoscale morphology, device performance, and the underlying electrical characteristics of functioning devices are not yet fully understood.

Recently, impedance analysis has begun to be applied to BHJ OPV devices. These reports demonstrate that the impedance analysis framework established for dye-sensitized solar cells can, to some extent, be extended to bulk heterojunction devices in order to calculate average charge carrier lifetime, electron densities-of-states, and charge carrier concentrations. However, a detailed analysis of the impedance response of active devices, and its dependence on device processing history, morphology, and operating conditions is still needed. In this work we acquire and analyze the impedance behavior of operating P3HT:PCBM bulk heterojunction devices and its dependence on illumination and bias conditions, active layer composition, and annealing history. We also report a simplified equivalent circuit model that successfully describes bulk heterojunction devices over a range of illumination conditions and applied biases. We use this model to extract relevant device performance characteristics such as average electron lifetime and find, in agreement with other reports, that bimolecular recombination losses play a significant role in these devices. To this end, we demonstrate a correlation between device efficiency and lifetime, and describe how values extracted from the present equivalent circuit model can be used to optimize device performance with new materials systems.

9:20am **EN+NS-WeM5 Singlet Exciton Fission in Tetracene and Diphenyltetracene**, P. Jadhav, A. Mohanty, J. Sussman, M. Baldo, Massachusetts Institute of Technology **INVITED**

Singlet exciton fission is a process by which a high energy singlet spontaneously decomposes into two low energy triplets. It is an example of a multi-exciton generation process that could allow the efficiency of solar cells to reach beyond the Shockley-Queisser limit. In this talk we examine singlet exciton fission in solar cells based on tetracene and diphenyltetracene (DPT). Notably we find that the photocurrents in each cell have opposite dependencies on the application of a magnetic field, suggesting that fission increases the photocurrent in tetracene-based solar cells, but decreases the photocurrent in DPT-based solar cells.

We report an organic semiconductor solar cell using tetracene and CuPC (Copper Phthalocyanine) as donors, and C60 as the acceptor. Tetracene absorbs photons in the 450-550-nm region, generating high energy singlets which split into two lower energy triplets, potentially doubling the photocurrent in this part of the spectrum. CuPC extends the absorption of the solar cell to the red part of the spectrum. We also demonstrate bulk heterostructure tetracene-C60 devices and tested them for singlet exciton fission.

We observe that: (i) The addition of the CuPC layer does not affect the flow of excitons from tetracene to the CuPC – C60 junction significantly because of similarities in triplet energies of tetracene and CuPC, (ii) The application of a .5T magnetic field shows ~1.5% change in photocurrent, confirming singlet fission, (iii) Low temperature quantum efficiency measurements show a drop in the tetracene IQE (internal quantum efficiency), and a singlet fission yield of 72% at room temperature. The drop in performance at low temperature is expected since singlet exciton fission in tetracene is a thermally activated process. (iv) Singlet exciton fission has a very high yield even in bulk heterostructure devices and can be potentially used to improve the performance of polymer solar cells.

In comparison, we observe that solar cells consisting of DPT-C60 exhibit a large positive (+5%) effect of the magnetic field on the photocurrent, +5% at ~.4T. We explain the anomalous magnetic field effect and demonstrate that it can be increased beyond 100% by biasing the device close to open circuit, potentially leading to applications as an anisotropic magnetic field detector.

10:40am **EN+NS-WeM9 Charge Separation and Relaxation in Phthalocyanine-C₆₀ Photovoltaic Systems**, G.J. Dutton, University of Maryland -College Park, S.W. Robey, National Institute of Standards and Technology

Organic photovoltaic (OPV) structures depend on charge transfer processes occurring within 10's of nanometers of donor-acceptor interfaces. Charge generation in these devices involves successive steps of (1) optical absorption to create excitons, (2) diffusion of the exciton population to the donor-acceptor interface, (3) exciton dissociation and charge transfer at the

interface and (4) charge transport and collection at electrodes. The charge separation step depends critically on electronic level alignment between the donor and acceptor. Also, because exciton diffusion to the interface occurs on timescales of several to 10's of picoseconds (ps), relaxation processes occurring on sub-ps and ps timescales as the exciton diffuses can impact the energy available for charge separation at the interface. We have investigated the exciton relaxation and charge separation processes close to phthalocyanine (Pc)-C₆₀ interfaces by combining time-resolved two-photon photoemission (TR-2PPE) with organic MBE to form donor-acceptor interfaces layer-by-layer. Pc $\pi \rightarrow \pi^*$ transitions are excited by a pump pulse to generate singlet (S₁) excitons. The resulting population dynamics are then probed with a time-delayed UV pulse to follow the relaxation and charge separation as a function of energy. For CuPc /C₆₀ interfaces, we compared the decay dynamics as a function of CuPc thickness, and thus distance from the C₆₀ interface, to allow determination of the rate of charge transfer at the interface. We find a charge transfer rate of $\approx 8 \times 10^{12} \text{ sec}^{-1}$ for the initial exciton population formed immediately after pumping. For CuPc, the exciton population also undergoes vibrational relaxation and intersystem crossing (ISC) on a timescale of $\approx 1-2 \text{ ps}$, ultimately resulting in the production a triplet exciton population at significantly lower energy. By again comparing results for thin and thick Pc layers we estimate that the charge transfer rate of this lower energy triplet population is reduced by at least a factor of ≈ 1000 , giving charge transfer rates closer to $8 \times 10^9 \text{ sec}^{-1}$. We will also discuss measurements for the case of H₂Pc and C₆₀ where ISC of the Pc singlet excitons to triplet levels is negligible. Our results will be discussed within the context of the Marcus theory of charge transfer and connections will be made to calculated charge transfer rates for similar donor-acceptor interfaces.

11:00am **EN+NS-WeM10 Low Energy Ion-Assisted Modification of PbS Nanocrystal-Sexithiophene Composite Films**, *F.D. Pleticha*, University of Illinois at Chicago, *L. Donghwa*, University of Florida, *I.L. Bolotin*, University of Illinois at Chicago, *S.R. Phillpot*, *S.B. Sinnott*, University of Florida, *L. Hanley*, University of Illinois at Chicago

The properties of semiconductor nanocrystal-organic films are of interest for applications in photodetectors, light-emitting diodes and photovoltaics. The versatility of these films arises from the ability to tune the bandgaps by adjusting the PbS nanocrystal size. Nanocrystalline photoelectric properties are also strongly affected by the chemical environment presented to them and by their bonding to the surrounding organic films. PbS nanocrystals are simultaneously deposited under vacuum into an organic matrix of evaporated α -sexithiophene while concomitantly modulating the film interface with 50 eV acetylene ions. Cluster beam deposition has been shown to allow the preparation of PbS nanocrystals that are surface terminated with either Pb or S [1]. Surface polymerization on ion assisted deposition (SPIAD) has shown an ability to increase the conjugation of oligothiophenes and otherwise lead to their chemical modification [2-4]. Cluster beam deposition and SPIAD are combined here to modulate the interface between the PbS and the organic matrix by introducing acetylene ions during the formation of the film. X-ray photoelectron spectroscopy analysis shows chemical shifts indicative of acetylene ion modulated interaction between the nanocrystals and sexithiophene. The deposition process was also simulated by a linearly scaled density functional theory method. These computer simulations indicate chemical bonding between the nanocrystals and sexithiophene, which is consistent with the chemical shifts observed by XPS.

1. A. M. Zachary, I. L. Bolotin, D. J. Asunskis, A. T. Wroble, and L. Hanley ACS Appl. Mater. Interf. 1 (2009) 1770
2. S. Tepavcevic, A. M. Zachary, A. T. Wroble, Y. Choi, and L. Hanley, J. Phys. Chem. A 110 (2006) 1618
3. S. tepavcevic, Y. Choi, and L. Hanley, Lang. 20 (2004) 8754
4. W. -D. Hsu, S. Tepavcevic, L. Hanley, and S. B. Sinnott, J. Phys. Chem. C 111 (2007) 4199

11:20am **EN+NS-WeM11 Molecular Modulation of Solar Cells: Where Inorganic, Molecular and Organic Electronics Meet**, *D. Cahen*, *R. HarLavan*, *O. Yaffe*, Weizmann Institute of Science, Israel

Organic materials present a promising direction for potentially cheaper solar cells. One way to use them and increase our understanding (e.g., define basic physical cell performance limits), is hybrid, organic / inorganic photovoltaics (PV). We explore 2 main directions to hybrid PV - with molecules as dipolar films, i.e., use electrostatics

- with molecular monolayers as electronic transport medium.

While we find that incomplete partial dipolar monomolecular films can control solar cell behavior for /single, poly- and nano-crystalline cells, for current to pass through the molecules, we need dense monolayers. Alkyl chain monolayers help form near-ideal Metal-Insulator-Semiconductor (MIS) diodes, with significant PV activity. Surprisingly, though we can

actually make *MIS* cells without a separate *I*(nsulator) layer, suggesting that 'MIS' effects are at least partly more "chemical than is often thought.

In this way we demonstrate a near-ambient, simple, potentially low-cost approach to make and modify semiconductor solar cells, using a monolayer of molecules, as short as two carbons, that self-assembles onto the semiconductor (absorber) surface, passivating and buffering it. Good passivation is necessary to express the molecule-induced interface dipole, which can change the semiconductor electron affinity by up to 1 eV.

Good, stable interface passivation along with strong inversion allows minority carriers, generated by absorbed light, to move laterally within the semiconductor top layer, for collection by a minimal-area grid, deposited on the conducting polymer and also minimizes photo-current losses, due to sheet resistance. Thus, $\leq 1 \text{ nm}$ thick organic molecules appear to convey a unique advantage over inorganic passivation or buffer layers.

11:40am **EN+NS-WeM12 Correlation of Interfacial Electronic Structures and Open Circuit Voltages in Organic Solar Cells**, *M.H. Chen*, National Dong Hwa University, Taiwan, Republic of China, *W.H. Tseng*, *J.Y. Wang*, *C.T. Tseng*, *C.I. Wu*, National Taiwan University

In this study, the interfacial electronic structures and energy band diagrams of polymer/fullerene bulk heterojunction (BHJ) solar cells are investigated. To study the device performance influenced by the interlayer, poly(3-hexylthiophene) (P3HT) mixed with 6,6-phenyl C61-butyric acid methylester (PCBM) are used as an active layer and bathocuproine (BCP) and calcium (Ca) are incorporated respectively with the cathodes. Since the mechanisms leading to the improvement of power conversion efficiency are more chemically and electronically complicated and have not been understood, the ultraviolet and x-ray photoemission spectroscopy (UPS and XPS) are used to investigate the properties of energy band, electronic structures and the interface chemistry at the interface. For the devices incorporated with BCP, highest occupied molecular orbital (HOMO) level of PCBM is pulled down about 0.3 eV with respect to the Fermi level after the deposition of BCP. It indicates that the BCP layer could modify the energy band by shifting the energy level of acceptors, causing the increase of built-in potential (V_{bi}). Thus, the open circuit voltage (V_{oc}) attributed to the increase of V_{bi} resulted from BCP could be enhanced. Moreover, AFM image indicates that BCP molecules cannot form a uniform layer on the active layer surface, pointing out the band modulation is the key reason to the V_{oc} improvement. For the devices with Ca as cathodes, the UPS results with deposition of Ca illustrate a 0.8 eV-downward shift in energy levels of P3HT, but not in those of PCBM. Therefore, the energy difference between the HOMO of P3HT and the LUMO of PCBM is widened, resulting in the increase of V_{oc} and the enhancement of device efficiency. Moreover, from the XPS spectra, there is an extra new peak appear at the lower binding energy about 162 eV, which suggests that the addition of electrons around the reactive sulfur (S) atoms in P3HT molecules after Ca deposition. The combinations of S and Ca spectra imply that the formation of Ca-S bonding at the Ca/P3HT interface, which is in good agreement with the findings of UPS spectra.

Wednesday Afternoon, November 2, 2011

Energy Frontiers Focus Topic

Room: 103 - Session EN1+TF-WeA

Thin Film Chalcogenide Solar Cells (CIGS, CZTS, CdTe and Related Materials)

Moderator: L.W. Rieth, University of Utah

2:00pm **EN1+TF-WeA1 Comparative Study of Structure and Morphology of $\text{CuIn}_{1-x}\text{Ga}_x\text{S}_2$ and $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ Thin Film Absorbers Using EBSD**, A. Kaul, E. Schneller, N.G. Dhere, Florida Solar Energy Center, H.R. Moutinho, National Renewable Energy Laboratory

Electron backscatter diffraction (EBSD) in scanning electron microscopy (SEM) is a powerful technique that allows crystallographic information such as the grain orientation, grain boundaries and also the grain size to be obtained. Crystalline maps are formed in EBSD while the electron beam of a SEM scans the sample surface providing information about crystalline orientation of individual grains as well as features such as twin boundaries. This study relates to EBSD investigation of $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ (CIGSe) and $\text{CuIn}_{1-x}\text{Ga}_x\text{S}_2$ (CIGS2) samples that were prepared by a two stage process which is easily scalable to large area manufacturing. Since sample polishing is very critical for generation of very good quality Kikuchi pattern formed by back scattered electrons, the earlier work was focused on optimizing the sample polishing technique. Efforts were also made to develop a database to facilitate proper indexing and corresponding accurate determination of preferred orientation of the pseudo-quaternary compound absorber films. Eventually, high quality Kikuchi patterns and EBSD maps have been obtained. It is essential for the research and development of the chalcopyrite thin film absorbers to elucidate the effect of variation of processing conditions (temperature, time and composition) on the growth and development of microstructure. Therefore, in the current work, CIGSe and CIGS2 absorber films were synthesized under different processing conditions and their EBSD maps and patterns are being compared in terms of grains size, grain orientation and grain boundaries as a necessary and vital step prior to undertaking the study of the still more complex compound $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_{2-y}\text{S}_y$ (CIGSeS) being used in large-volume production of photovoltaic solar cells and modules.

2:20pm **EN1+TF-WeA2 Improving the Damp-Heat Stability of Copper Indium Gallium Diselenide Solar Cells**, B.S. Tosun, University of Minnesota, R.K. Feist, The Dow Chemical Company, S.A. Campbell, E.S. Aydil, University of Minnesota

While copper indium gallium diselenide (CIGS) thin film solar cells with laboratory efficiencies exceeding 20 % have been reported, these high efficiencies may degrade with time as the devices are exposed to humid environments. It is well known that grain boundary diffusion of water through the ZnO to the CIGS-CdS interface is implicated in long-term degradation of the solar cell performance.¹ This penetration must be reduced or stopped to increase the solar cell lifetime. Herein, we show that amorphous tin dioxide (SnO_2) layers deposited by radio frequency (RF) magnetron sputtering on top of the completed CIGS solar cells can significantly increase the device lifetime by forming a barrier against water diffusion. Specifically, with approximately 0.2 micron and thicker SnO_2 layers deposited on top of the completed CIGS solar cells we have demonstrated that initially 11.1 % efficient CIGS solar cells lose less than 7 % of this peak efficiency and still exhibit efficiencies greater than 10 % (factor of 10%) after 150 hours at 85 °C and 85 % relative humidity. In comparison, under identical test conditions, the solar cells without the SnO_2 layer lost nearly 80 % of their initial efficiency within 24 hours after commencing the test. We studied the effects of deposition conditions and film thickness for different film structures on the solar cell stability in damp-heat tests. The deposited SnO_2 films tend to be amorphous when deposited at room temperature or when the films are thin, but show increased crystallinity for thicker films and films deposited at 150 °C. We found that solar cells coated with polymorphous SnO_2 films exhibit better damp-heat stability than those coated with polycrystalline films. By polymorphous we mean films that consist of nanocrystalline SnO_2 embedded in amorphous SnO_2 . We attribute this difference to the lack of grain boundary diffusion in polymorphous SnO_2 films. Replacing the crystalline ZnO window layer with a SnO_2 film can provide further protection of the CIGS solar cells. We demonstrate a 8.2±0.2 % efficient CIGS solar cell with a SnO_2 window layer. Same solar cell fabrication process and CIGS film with ZnO window layer resulted in 8.2±0.6 % overall efficiency. The open circuit voltages of the two cells were the same indicating that the band alignment with the SnO_2 film is suitable for CIGS. These SnO_2 films were deposited using magnetron sputtering at 5 mTorr

and 150-250 W RF power using Ar as the sputtering gas without substrate heating.

¹R. Feist et al, IEEE Photovoltaic Specialist Conference, 2009.

2:40pm **EN1+TF-WeA3 Progress Towards a High-Efficiency Cu-Zn-Sn-S-Se Thin-Film PV Technology**, D.B. Mitzi, O. Gunawan, T.K. Todorov, D.A.R. Barkhouse, S. Bag, R. Haight, T. Gokmen, T. Goislard de Monsabert, S.J. Chey, S. Thiruvengadam, IBM T.J. Watson Research Center

INVITED

A key criteria for achieving terawatt-compatible photovoltaic (PV) technology is the ability to fabricate high power conversion efficiency (>10%) solar cells using a low-cost process (< \$1/watt) and readily available, abundant and preferably non-toxic materials. The kesterites, $\text{Cu}_2\text{ZnSn}(\text{S},\text{Se})_4$ (CZTSSe), are considered a promising PV technology for meeting this goal because of similar electronic properties to the two leading thin-film chalcogenide technologies, CdTe and $\text{Cu}(\text{In},\text{Ga})(\text{S},\text{Se})_2$ (CIGSSe), achieved while employing low-cost, readily-available constituents. This talk will discuss recent developments that have enabled the demonstration of the first CZTSSe solar cells with certified power conversion efficiencies of over 10%, using a glass/Mo/CZTSSe/CdS/i-ZnO/ITO structure and a simple liquid-based deposition approach. We also present a device characterization study that compares the CZTSSe devices with higher-performing CIGSSe analogs, elucidating some of the key performance bottlenecks in CZTSSe cells, including dominant buffer-absorber recombination, high series resistance and a relatively short minority carrier lifetime. These studies help to elucidate key areas for improvement for the CZTSSe cells in the effort to develop a high performance pervasive technology.

4:00pm **EN1+TF-WeA7 Solar Cells from Colloidal Dispersions of $\text{Cu}_2\text{ZnSnS}_4$ Nanocrystals**, A. Khare, Y. Li, B. Chernomordik, B.S. Tosun, A.W. Wills, D.J. Norris, E.S. Aydil, University of Minnesota

Copper zinc tin sulfide ($\text{Cu}_2\text{ZnSnS}_4$ or CZTS) is emerging as a promising photovoltaic material for thin film solar cells. CZTS has a band gap of ~1.4 eV, the ideal value for converting the maximum amount of energy from the solar spectrum. In addition, CZTS has a high absorption coefficient (> 10^4 cm⁻¹ in the visible region of the electromagnetic spectrum) and its constituent elements are all abundant in the earth's crust and are non-toxic. We have synthesized CZTS nanocrystals from metal dithiocarbamate complexes. The diameter of the nanocrystals can be varied from 2-7 nm by changing the temperature and synthesis time. A suite of methods including Raman spectroscopy, optical absorption, electron energy loss spectroscopy and X-ray diffraction were used to characterize these nanocrystals and show that they are phase-pure CZTS. Nanocrystals with diameters less than 3 nm exhibit quantum confinement. These quantum dots were used to assemble quantum dot solar cells. In a second approach to making solar cells, thin films of CZTS nanocrystals are annealed to form thin films with large grains. Nanocrystals melt at temperatures much less than the bulk temperature and recrystallize to yield larger CZTS grains. These films were then used for making conventional thin film solar cells.

4:20pm **EN1+TF-WeA8 Surface Structure of Pyrite Thin Films Grown by MOCVD**, M. Cheng, Y. Liu, N. Berry, A. Margarella, J.C. Hemminger, M. Law, University of California, Irvine, H. Bluhm, Z. Liu, Lawrence Berkeley National Laboratory

Iron pyrite (FeS_2) has been considered one of promising materials for use in solar cells due to its large absorption coefficient, suitable band gap and elemental abundance. In-lab X-ray photoelectron spectroscopy and tunable-energy synchrotron X-ray photoelectron spectroscopy were used to explore the surface structure of pyrite thin films grown by metal organic chemical vapor deposition (MOCVD). The influence of sodium diffusion on the growth of pyrite thin films on glass substrates was examined. By using synchrotron X-ray photoelectron spectroscopy, the different types of sulfur chemical states on the surface of pyrite thin films were resolved. The mechanism of pyrite oxidation after exposure to different oxidizing environments indicated that the surface monosulfide species were oxidized first. In addition, the band gap of pyrite thin films was determined by combining valence band spectroscopy with X-ray absorption spectroscopy compared to traditionally ultraviolet-visible absorption spectroscopy. The discrepancy between the two measurement techniques will be discussed.

4:40pm **EN1+TF-WeA9 Effect of the Use of a c-CdS Nanocrystalline Layer on the Photovoltaic Characteristics of the Screen Printed CdS/CdTe Heterostructure**, *L.G. Rangel-Chavez*, UAM-Azcapotzalco, Mexico, *M. Garcia-Aguirre*, *F.A. Cuevas-Ortiz*, Cinvestav-IPN, Mexico, *M.I. Neria-Gonzalez*, Instituto Tecnológico de Estudios Superiores de Ecatepec, Mexico, *M.A. Melendez-Lira*, Cinvestav-IPN, Mexico

The fact that the efficiency for the CdS/CdTe system has remained without any change for several years until now requires employing new approaches in order to increase it. In this work it is reported the effect on the photovoltaic characteristics of the CdS/CdTe system by employing as source of the CdS the one obtained as a by-product from bio-remediation of heavy metals in residual waters. By using a novel sulfate-reducing bacterium (*Desulfovibrio alaskensis* 6SR) particles of the CdS semiconductor are obtained. Structural and optical characterization by XRD, UV-vis, Raman and photoluminescence spectroscopies shown that nanoparticles of cubic CdS are obtained. The nanoparticles of cubic CdS are deposited on CdTe films by screen printing and then subject to a mild thermal treatment. It is expected that the employment of CdS with cubic rather than hexagonal crystal structure will reduce the number of defects at the CdS/CdTe interface improving the transport of minority carriers through it. We will report the effects on the spectral response and filling factor obtained for the CdS/CdTe heterostructure by employing nanostructured cubic CdS as compared to those obtained employing hexagonal CdS.

*: Work partially supported by CONACyT-Mexico.

5:00pm **EN1+TF-WeA10 Surface Structure and Chemistry of AgInSe₂ Studied by Scanning Tunneling Microscopy**, *P. Peña Martin*, *J.W. Lyding*, *A. Rockett*, University of Illinois at Urbana-Champaign

Chalcopyrite semiconductors such as (Cu,Ag)(In,Ga)(S,Se)₂ show great promise in thin film solar cells as they exhibit high optical absorption and excellent performance even as polycrystalline layers. The alloy AgInSe₂ (AIS) is a promising candidate for solar applications, as it has a nearly ideal energy gap (1.2 eV), high absorption coefficient, and shows sharper photoluminescence emissions than do the Cu-containing alloys. The surface of the material forms the heterojunction and determines many aspects of device performance. These semiconductors also contain a large number of intrinsic point defects, which are probably responsible for minority carrier recombination in the depletion region. Therefore understanding the surface and near surface nanostructure and nanochemistry are critical to device optimization. To characterize the structure and buried point defects near the surface, we used ultra high vacuum scanning tunneling microscopy (UHV-STM) to obtain atomic-scale topographic and electrical information.

We report the first atomically-resolved STM images and current-voltage profile measurements of AIS. Epitaxial layers were grown on epi-ready substrates of p-GaAs(111)A by hybrid technique, in which Ag and In are sputtered concurrently with effusion cell evaporation of Se. The resulting film was transported in a N₂ ambient to the STM laboratory, mounted under normal lab air as quickly as possible, and introduced to vacuum, with a total atmosphere exposure of about 20 minutes. The sample was degassed at ~100°C to drive off water and other contaminants. Electrochemically-etched W tips were used for scanning. The STM measurements were carried out in a home-built system with a base pressure of 1.2x10⁻⁸ Pa (9x10⁻¹¹ Torr). Topographic images reveal atomically-resolved regions on the surface with the periodicity expected for the polar metal-terminated [112] plane, 0.34 and 0.36 nm along rows oriented 60° from each other. This indicates that the surface does not reconstruct, unless by swapping one type of metal atom for another. Current-voltage spectra confirm that the material exhibits n-type behavior with an energy gap close to the bulk value of 1.2 eV. Some regions exhibit more fluctuations in the bandgap for a series of current spectra taken along a different line, indicating that there are variations in the electronic properties due to defects. We attempt to correlate these with topographic features in order to identify the defect responsible. Understanding and controlling these defects should lead to improved device performance, and some of the results may even carry over to CIGS devices.

5:20pm **EN1+TF-WeA11 Imaging and Phase Identification of Cu₂ZnSnS₄ Thin Films using Confocal Raman Spectroscopy**, *A.-J. Cheng*, *M. Manno*, *A. Khare*, *C. Leighton*, *S.A. Campbell*, *E.S. Aydil*, University of Minnesota

Copper zinc tin sulfide (Cu₂ZnSnS₄ or CZTS) is a potential candidate for next generation thin film solar cells because it contains abundant and nontoxic elements and exhibits high light absorption. Thin films of CZTS are typically synthesized by sulfidizing a stack of zinc, copper and tin films. In addition to CZTS, a variety of binary and ternary metal sulfides can form and distinguishing among phases with similar crystal structure can be difficult. Herein, we show that confocal Raman spectroscopy and imaging can distinguish between CZTS and the other binary and ternary sulfides [1]. Specifically, Raman spectroscopy was used to detect and distinguish between CZTS (338 cm⁻¹), Cu₂SnS₃ (298 cm⁻¹) and Cu₄SnS₄ (318 cm⁻¹)

phases through their characteristic scattering peaks. Confocal Raman spectroscopy was then used to image the distribution of coexisting phases and is demonstrated to be a useful tool for examining the heterogeneity of CZTS films. We show that, during sulfidation of a zinc/copper/tin film stack, ternary sulfides of copper and tin, such as Cu₂SnS₃ form first and are then converted to CZTS. The reason for formation of Cu₂SnS₃ as an intermediary to CZTS is the strong tendency of copper and tin to form intermetallic alloys upon evaporation. These alloys sulfidize and form copper tin sulfides first, and then eventually convert to CZTS in the presence of zinc. As a consequence, films sulfidized for 8 hours at 400 °C contain both CZTS and Cu₂SnS₃ while films sulfidized at 500 °C contain nearly phase-pure CZTS. In addition, using Cu K α radiation, we identify three CZTS X-ray diffraction peaks at 37.1° [(202)], 38° [(211)] and 44.9° [(105) and (213)], which are absent in ZnS and very weak in Cu₂SnS₃.

[1] A.-J. Cheng, M. Manno, A. Khare, C. Leighton, S. A. Campbell, and E. S. Aydil, *J. Vac. Sci. Technol. A*, in press (2011).

5:40pm **EN1+TF-WeA12 Synthesis of CZTS Solar Cells using Non-Toxic Sulfur Precursor**, *P. Vasekar*, *L. Ganta*, *D. Vanhart*, *T. Dhakal*, *C.R. Westgate*, The State University of New York at Binghamton

Thin film solar cells based on Cu(In,Ga)(S,Se)₂ and CdTe have demonstrated significant improvement in last few years and they are also being transferred to production level. However, both CIGS and CdTe based thin film solar cells are hindered by potential environmental hazard issues and scarcity issues associated with the constituent elements, mainly Te, In, Ga and to some extent Se. Recent research trends are moving towards finding alternatives based on earth-abundant and non-toxic elements. An alternative material Cu(Zn,Sn)(S,Se)₂ is being explored these days by the thin film photovoltaics community which contains earth abundant materials like Zn and Sn. CZTS structure can be derived from CuInS₂ chalcopyrite structure by replacing one half of the constituent indium atoms by zinc and other half by tin. The resulting bandgap varies in the range of 0.8 eV for a selenide structure to 1.5 eV for a sulfide structure. Copper and sulfur in earth's crust are 50 and 260 ppm respectively and while abundance of zinc and tin is 75 and 2.2 ppm in respectively. As compared to this, indium in earth's crust is 0.049 ppm and selenium 0.05 ppm. CZTS also has a large absorption coefficient in the order of 10⁴ cm⁻¹. There are vacuum-based as well as non-vacuum based approaches for the synthesis of CZTS solar cells. Among vacuum based approaches, generally sulfurization in H₂S atmosphere is carried out on sputtered CuZnSn precursors. However, there are toxicity issues involved with the use of H₂S gas. We subscribe to the philosophy of sticking to a non-toxic approach of synthesizing thin film solar cells and for the first ever time introduced a non-toxic sulfur precursor called di-tertiray-butyl-disulfide (TBDS) for the sulfurization of CZT layer. Initial results are quite encouraging and device quality CZTS cells are already being synthesized. The CZTS cells are characterized using materials characterization techniques such as SEM, XRD, XPS and photovoltaic parameters are being extracted under AM 1.5 conditions and also analyzed using quantum efficiency measurement. This is the very first attempt to successfully synthesize CZTS solar cells using a non-toxic sulfur source.

Energy Frontiers Focus Topic

Room: 106 - Session EN2+TF-WeA

Thin Films for Solar Fuels

Moderator: A.J. Muscat, University of Arizona

4:00pm **EN2+TF-WeA7 N-doped SrTiO₃(100) Epitaxial Films for Fundamental Studies of Visible Light Active Photocatalysts**, *T. Luttrell*, *M. Batzill*, University of South Florida

N-doping of photocatalysts, in particular TiO₂, has been extensively studied for its ability to increase visible light activity. However, the solubility of N in TiO₂ is limited to ~ 2% and thus limits the visible light absorption. One reason for the low solubility of nitrogen is the different preferred charge state of nitrogen (3-) compared to the substituted oxygen (2-) anions. Here, we investigate the less studied perovskite SrTiO₃, which has similar photocatalytic activity to TiO₂. Because a wide range of oxides crystallize in the perovskite structure, we anticipate that charge compensating co-doping in N:SrTiO₃ can be more easily accomplished than in TiO₂. Such co-doping may result in a higher achievable N-concentration. In our studies, the stability of N-doping in SrTiO₃ and the effect of co-doping have been investigated in thin films. High quality pure and N-doped epitaxial films of SrTiO₃ have been grown on LaAlO₃(100) substrates by pulsed laser deposition (PLD). The structural and electronic properties have been investigated, by x-ray and UV photoemission spectroscopy (XPS and UPS) and ex-situ atomic force microscopy (AFM). N-doping was accomplished by deposition in an ammonia atmosphere. N³⁻ ions are substituting for O²⁻

ions in the SrTiO₃ matrix and thus cause a charge imbalance that is compensated for in pure films by formation of oxygen vacancies. To avoid this defect formation, substitution of the quadrivalent cations in SrTiO₃ by co-doping with La⁵⁺ is investigated. La co-doping allows a higher nitrogen solubility in SrTiO₃. Nitrogen doping causes a band gap narrowing due to formation of filled N-2p states at the top of the valence band and thus an increase in visible light adsorption. The UV and visible light photocatalytic activity is assessed by decomposition of methyl orange.

4:20pm **EN2+TF-WeA8 Photoelectrochemical Water Splitting by Hematite Nanostructures Prepared by Chemical Bath Deposition.** R. Morrish, Colorado School of Mines, M. Rahman, J.M.D. MacElroy, University College Dublin, C.A. Wolden, Colorado School of Mines

Hematite (α-Fe₂O₃) is a promising material for sustainable generation of H₂ due to its low cost, widespread availability, chemical stability, and ability to absorb a significant fraction of visible light. However numerous challenges remain in order for this material to approach its theoretical potential of 15% solar to hydrogen efficiency. Nanorod geometries are an ideal configuration for this material, decoupling the different length scales required for photon absorption and efficient carrier transport. Unfortunately such structures have historically yielded poor photoelectrochemical performance (<5 mA/cm²).¹ We recently demonstrated that nanorods synthesized by chemical bath deposition (CBD) could be activated through the use of appropriate annealing treatments.² Photocurrents >500 mA/cm² were achieved at 1.23 V versus RHE, and the photoanodes displayed low onset potentials. These changes were correlated with significant amount of tin diffusion from the underlying FTO substrate into the Fe₂O₃ matrix occurs during high temperature annealing process. The benefits of this process may include enhanced conductivity as well as improvement of the FTO/ Fe₂O₃ interface. Despite these advancements, significant room remains for further improvement. In this paper we describe a number of strategies to reach this goal. First, the nanostructure of the hematite can be further improved. This is explored by varying the CBD chemistry, optimizing the post-deposition annealing conditions, and through subtractive processing. A second issue is electron transport at the hematite/FTO interface, and this is explored through the use of novel treatments of the FTO prior to deposition. Finally, the addition of an electrocatalyst can further reduce the onset potential. Each of these three strategies has demonstrated enhanced photocurrent over our previous results. We plan to integrate these advancements in order to maximize performance. Detailed characterization of the structure, composition, and electrochemical changes observed with these processes will be used to provide fundamental insight into the mechanisms underlying the improvements.

References

- [1] N. Beermann, L. Vayssieres, S.-E. Lindquist & A. Hagfeldt, "Photoelectrochemical Studies of Oriented Nanorod Thin Films of Hematite", 2456-2461, (2000).
- [2] R. Morrish, M. Rahman, J. M. D. MacElroy & C. A. Wolden, "Activation of hematite nanorod arrays for photoelectrochemical water splitting", 474-479, (2011).

4:40pm **EN2+TF-WeA9 Nanostructured Thin Films for Solar Water Splitting.** K. Sivula, Ecole Polytechnique Federale de Lausanne, Switzerland **INVITED**

Solar energy can be converted to chemical energy stored in hydrogen through water splitting using a photoelectrochemical device. However, decades of research have failed to identify one semiconducting electrode material that can perform the water splitting reaction with adequate efficiency, stability and material cost. Here I present a system that overcomes the limitations of conventional materials to afford direct solar hydrogen production by taking inspiration from natural photosynthesis and using two photosystems in tandem. In addition, to reach the terawatt energy scale needed to have a global impact, I describe the use of abundant and inexpensive semiconducting materials. Specifically, progress developing hematite (Fe₂O₃) photoanodes and cuprous oxide (Cu₂O) photocathodes will be presented. I will show that our water splitting tandem cell, using these materials and inexpensive processing techniques, is capable of solar-to-hydrogen conversion efficiencies of over 5 % at standard conditions. I will further detail how the progress in developing the electrode thin films has been enabled by exploiting recently developed techniques like aerosol-assisted chemical vapor deposition and atomic layer deposition.

5:20pm **EN2+TF-WeA11 TiO₂ N-doped Nanofibers Deposited by Electrospinning for Photocatalytic Applications.** D. Di Camillo, F. Ruggieri, L. Lozzi, S. Santucci, University of L'Aquila, Italy

Titanium dioxide (TiO₂), thanks to its interesting properties as nontoxicity, low cost and high chemical stability, has been extensively investigated for several application in which, following light absorption, the generated charges can be usefully applied, as for photovoltaic applications or for

photocatalytic devices. However, due to the wide intrinsic energy gap of TiO₂ (between 3.0 and 3.2 eV, depending on the crystalline structure), only a small fraction of the solar spectrum can be used to promote the light absorption [6]. In the photocatalytic devices one of the most important goal of the recent research is to be able to prepare photocatalyst which can be active by absorbing the visible light, in order to increase the application of TiO₂-based system in poor regions (where it could be difficult to use UV light sources) or to reduce the application cost. In order to increase the fraction of the solar spectrum that can be absorbed, different approaches have been used, mainly by doping TiO₂ with metals or anions.

One of the most studied doping is using nitrogen. TiO₂ doped with nitrogen atoms can be prepared in different ways, as powders, as thin films by sol-gel or reactive sputtering.

In this paper we will show the photocatalytic results obtained depositing TiO₂ N-doped nanofibers (NF) prepared by means of electrospinning (ES) and near-field electrospinning (NF-ES) techniques for the photo-degradation of methylene blue (MB) in water under visible light. The ES preparation technique allows a quick deposition of fibers on wide surfaces using a cost-effective system. Instead NF-ES method allows the growth of a well ordered NF net, with a spacing lower than few microns.

The NFs were deposited using different deposition and post-deposition parameters (solution composition, annealing temperature and atmosphere) and have been characterized by using X-ray photoemission spectroscopy (XPS), X-ray diffraction (XRD) and Secondary Electron Microscopy (SEM). The photocatalytic properties have been studied recording the variation of the optical absorption of MB when the sample is illuminated by an halogen lamp (visible spectrum).

The annealing process determines a partial loss of nitrogen and the formation of the Anatase crystalline phase. The TiO₂ N-doped NFs have shown interesting degradation properties, which are much better than those observed when TiO₂ NFs are used.

5:40pm **EN2+TF-WeA12 Fabrication of Palladium Nanoscale Structures for Hydrogen Sensing Applications.** D. Rodríguez-Vindas, University of Puerto Rico at Rio Piedras, C. Ortiz, V. Pantojas, University of Puerto Rico at Cayey, W. Otaño, University of Puerto Rico at Cayey and Institute for Functional Nanomaterials

Palladium (Pd) metal is one of the most prominent materials studied for the detection of hydrogen gas. Hydrogen rapidly dissociates on its surface and diffuses into subsurface layers forming palladium hydride with consequent changes in optical, mechanical and electrical properties that are easily detected. Materials with nanoscale morphologies are promising to improve sensor performance as they provide large surface areas for adsorption, and smaller crystallite size reducing the time needed for "bulk" diffusion. The amount of sites available for hydrogen adsorption per Pd atom is also higher in the surface and subsurface layers resulting in higher sensitivity. In this project, Pd nanoribbons and nanoshells are prepared by magnetron sputtering deposition on top of the mat of polymer fibers, which act as a template that shapes the morphology of the palladium being deposited while providing support to the metallic scaffold that is created. Sputtering is a line-of-sight deposition process and the fibers become a variable angle-substrate for the incoming Pd flux. A larger amount of palladium is deposited on top of the fiber where the incoming flux is perpendicular to the surface compared to the sides where the flux is incident at a glancing angle. The top and sides of the fibers shadow their bottom parts closer to the substrate preventing any substantial deposition there. The end result of the deposition is the formation of Pd nanostructures, thicker in the middle region than at the edges, with a large void network. Process parameters such as deposition time, sputtering pressure, and power can be used to produce nanoshells with different thickness and crystallinity. The high sensitivity and response time shown to 1% or less of hydrogen in nitrogen is understood to result from the reduced dimensions combined with this unique nanostructure. A description will be given of the conductance changes with hydrogen concentration as result of the competing mechanisms of percolation and scattering. This work shows the use of nanotechnology combined with unique processing approaches to produce new sensor geometries with different behavior and morphology than simple thin film or wire approaches.

Thursday Morning, November 3, 2011

Energy Frontiers Focus Topic

Room: 103 - Session EN+NS-ThM

Nanostructures for Energy Storage and Fuel Cells I

Moderator: J. Lewis, RTI International

8:00am EN+NS-ThM1 Exploring Intercalation Chemistry of Modified Graphene with Ionic Liquids for Energy Storage Applications, *M. Acik*, The University of Texas at Dallas, *D.R. Dreyer*, *C. Bielawski*, The University of Texas at Austin, *Y.J. Chabal*, The University of Texas at Dallas

One of a real-world application of Electrochemical Double Layer Capacitors (EDLCs) is their use in prototype electric vehicles. An EDLC simply consists of two non-reactive, porous electrodes and an electrolyte separated with a membrane. Activated charcoals are one of a commonly used electrode systems which has drawbacks such as limited energy storage due to their large ion size. Therefore, a replacement electrode system with a higher surface area is necessary for a superior EDLC performance. Modified graphene is one of a promising candidate with its high theoretical surface area (2630 m²/g). EDLC working principle also depends on how effectively it can polarize the electrolyte solution. In principle, ionic liquids are promising electrolyte systems with their high non-volatility, non-flammability, thermal stability and good solvating ability.

This study focuses on the intercalation studies of ionic liquids such as N-methyl-N,N,N-tris(2-hydroxyethyl)ammonium iodide, N-methyl-N,N,N-tris(2-hydroxyethyl)ammoniummethyl sulfate, 1-butyl-3-methylimidazoliummethylsulfate and N-octyl-N-methylpiperidinium methylsulfate. To achieve a high surface area material with modified graphene, it is essential to understand the interfacial interactions upon intercalation of ionic liquids.

We study powder X-Ray Diffraction Analysis to characterize the interlayer distance of modified graphene. For instance, its d-spacing increases by about 4-12 Å after intercalating as-synthesized graphite oxide (GO, ~9Å) with N-methyl-N,N,N-tris(2-hydroxyethyl)ammonium methylsulfate (IL) at room temperature. Annealing at 300-500°C, (002) orientation of GO disappears as a result of thermal exfoliation. In addition, *in-situ* Infrared Absorption Spectroscopy (IRAS) measurements were performed to explore the intercalation chemistry of modified graphene in the presence of ionic liquids. Therefore, we perform thermal reduction studies in vacuum coupled with IRAS measurements to characterize the chemical interactions during thermal exfoliation of reduced GO. After annealing GO intercalated with this IL, the loss of C-N and C-O containing species is identified at ~1000-1500 cm⁻¹ and 800-1200 cm⁻¹ with contribution from C-OH groups at 3000-3700 cm⁻¹. Complete removal of these species is observed after a ~500°C anneal resulting in a weak infrared absorbance intensity of sp²-hybridized C=C species at ~1580 cm⁻¹. The presence of new formation of sheet-to-sheet linking or bonding motifs was also studied with X-ray Photoelectron Spectroscopy (XPS).

*Research supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering under Award DE-SC001951.

8:20am EN+NS-ThM2 Electronic Structure and Chemical Composition of Candidate Conversion Material Iron Oxyfluoride, *R. Thorpe*, *S. Rangan*, *R.A. Bartynski*, *O. Celik*, *N. Pereira*, *G. Amatucci*, Rutgers University

Transition metal fluorides have recently gained interest as possible electrode materials in lithium ion conversion batteries. Owing to their large band gaps, they operate at high voltages and enable high energy densities. However this large band gap inhibits charge conduction and thus impedes efficient charge and discharge. One path to overcome this limitation is the use of metal oxyfluorides, which are characterized by a slightly smaller energy gap and thus a higher electronic conductivity. Currently, little is known about the electronic structure of metal oxyfluorides, particularly the relation between chemical structure, composition, and energy gap. Hence, we have produced model oxyfluoride systems in order to characterize the conversion mechanism using surface science tools.

Of all metal fluorides, iron-based compounds are the most promising to maximize energy density. Ultra-thin FeF₂ films have been synthesized via the fluorination of clean Fe foil exposed to XeF₂, following a self-limited Mott-Cabrera mechanism. The FeF₂ films have then been sequentially exposed to a partial pressure of O₂ of 2x10⁻⁶ Torr at 285°C in order to produce iron oxyfluoride. Using x-ray and ultraviolet photoemission as well as inverse photoemission, we have probed the electronic structure of these

FeO_xF_y samples and characterized the occupied and unoccupied states near the band gap of the material.

It has been found that oxygen insertion into the FeF₂ matrix can be controlled until complete oxidation occurs. As expected for a Mott-Hubbard insulator, the valence band and conduction band of FeF₂ can be interpreted using a simple crystal field approach. In the case of Fe₂O₃, strong charge transfer effects need to be taken into account in order to interpret the band edges. To explore the conversion process, Li has been evaporated onto these iron oxyfluorides *in-situ*. Preliminary results addressing the reactivity of lithium at the surface of these materials will also be presented.

8:40am EN+NS-ThM3 Lithium Ion Batteries: Present and Future Technologies, *K. Amine*, *W. Wu*, *I. Belharouak*, *A. Abouimrane*, *Z. Zhang*, *J. Lu*, Argonne National Laboratory **INVITED**

In its goal of developing more fuel efficient vehicles, the US Department of Energy in collaboration with the US auto industries are focusing on high-power and high energy lithium-ion batteries to meet the energy storage requirements for HEV and PHEV applications. Under these auspices, Argonne National Laboratory is investigating several different lithium ion chemistries in order to address the calendar life, cost and safety of high power and high energy lithium ion batteries for transportation applications

To meet the high-energy requirement that can enable the 40-miles electric drive P-HEVs, It is necessary to develop very high energy cathode or anode that offers 5,000 charge-depleting cycles, 15 years calendar life as well as excellent abuse tolerance. These challenging requirements make it difficult for conventional cathode materials to be adopted in P-HEVs. In this paper, we report on several advanced battery chemistry that could be used to power Hybrid electric vehicles. We also discuss several future high energy battery technologies that can enable 40 miles Plug in Hybrid and long range electric vehicles.

9:20am EN+NS-ThM5 Templating of Porous Materials for Energy Storage and Generation, *A. Stein*, *J. Davidson*, *N. Petkovich*, *Y. Qian*, *S. Rudisill*, *L. Venstrom*, *A. Vu*, University of Minnesota **INVITED**

Materials containing pores in size ranges from micropores to macropores offer interesting features for a number applications involving energy storage and conversion, such as batteries, fuel cells, hydrogen storage, and sunlight-to-fuel conversion. Depending on the specific application, they can provide large surface areas for reaction, interfacial transport, or dispersion of active sites; they can provide nanostructured features which enhance reactivity, alter materials properties, or shorten diffusion paths; they can act as host materials to stabilize other active components; or, in the case of porous carbons, they can provide electrically conductive phases as well as intercalation sites. However, the higher reactivity brought about by nanostructured features can also lead to decreased stability, particularly in applications where phase changes may alter the structure of the material or where high temperatures are employed. This talk will focus on two redox systems (lithium-ion batteries and sunlight-to-fuel conversion) in which templated porous materials provide a platform for either electrical energy storage or light-to-chemical energy conversion. In the first system the role of pore architecture in carbon-based electrodes will be discussed. Improved rate capabilities for lithiation/delithiation are observed for hierarchically porous carbon electrodes. In composites with tin or tin oxide for anodes these structures maintain electrical contact between tin-based particles, even when those particles undergo significant volume changes during cycling, and hence the composite anode maintains good capacities over multiple cycles. Composites of hierarchically structured carbon with poorly conducting but otherwise desirable electrode materials (like sulfur or LiFePO₄) can be used to overcome limitations in electrical conductivity of those materials, increasing the choice of useful electrode materials. In the second system, we investigate the role of porosity in ceria-based materials of interest for solar thermal splitting of water or carbon dioxide to produce hydrogen or carbon monoxide fuels, respectively. Dopants for ceria are examined to stabilize the porous structures at the high reaction temperatures. The interplay between composition and morphology of these materials, thermal stability, and conversion efficiencies will be discussed.

11:00am EN+NS-ThM10 Exploration of the Effects of Si Nanowire Length and Doping on Li-ion Battery Anode Performance, *F. Rusli*, *V. Chakrapani*, *M.A. Filler*, *P.A. Kohl*, Georgia Institute of Technology
Silicon nanowires have recently garnered significant attention as a potential candidate to replace graphite as the negative electrode in a lithium-ion battery. Silicon's earth abundance, extensive knowledge base, and its theoretical capacity of 4200 mAh/g make it an attractive material for this purpose. While the high incorporation of lithium presents a problem as silicon undergoes a significant specific volume expansion upon

intercalation (up to 400%), nanowires permit facile radial strain relaxation and allow lithiation without pulverization. In this work, we report on the first systematic study of nanowire length and doping on the cycling performance of NW electrodes. Silicon nanowires were grown on stainless steel substrates via the vapor-liquid-solid technique in a cold-wall low pressure chemical vapor deposition reactor. Growth times ranging from 5-60 minutes and doping concentrations between 10^{18} – 10^{20} atoms cm^{-3} were studied. The half cells were cycled against lithium metal between (1) 0.01 and 2.0 V and (2) 0.07-0.7 V at a C/20 rate for 20 cycles. Cycling performance at different depths of discharge was also studied. Nanowires grown at short and long times both exhibit lower capacities than those grown at intermediate times. We attribute this effect to the loss of nanowire contact at the interface between the stainless steel and nanowire array for long nanowires, while the percolation network formed by short nanowires is not sufficiently robust to prevent loss of electrical connectivity upon wire breakage further from this interface. Nanowires at higher doping concentrations were not found to improve cycling performance drastically, which we attribute to the dopant effects on the growth mechanism of the nanowires and placement of dopant atoms in the silicon matrix that may have inhibited lithium atom insertion. We will present novel electrode fabrication routes that overcome these two challenges.

11:20am **EN+NS-ThM11 In Situ TEM Electrochemistry of Anode Materials in Lithium Ion Batteries, J.Y. Huang**, Sandia National Laboratories **INVITED**

We created the first nano-battery inside a transmission electron microscope (TEM), allowing for real time atomic scale observations of battery charging and discharging processes. Two types of nano battery cells [1], one ionic liquid based, and the other all solid based, were created. The former consists of a single nanowire anode, an ionic liquid (IL) electrolyte and a bulk LiCoO_2 cathode; the latter uses Li_2O as a solid electrolyte and metal Li as anode. Four case studies will be presented: 1) Upon charging of SnO_2 nanowires in an IL cell, a reaction front propagates progressively along the nanowire, causing the nanowire to swell, elongate, and spiral. The reaction front contains high density of dislocations, which are continuously nucleated at the moving front and absorbed from behind. This dislocation cloud indicates large in-plane misfit stresses and is a structural precursor to electrochemically-driven solid-state amorphization. 2) In charging Si nanowires, the nanowires swell rather than elongate. We found the highly anisotropic volume expansion in lithiated Si nanowires, resulting in a dumbbell-shaped cross-section which developed due to plastic flow and necking instability. Driven by progressive charging, the stress concentration at the neck region led to cracking, eventually splitting the single nanowire into sub-wires. 3) Carbon coating not only increases rate performance but also alters the lithiation induced strain of SnO_2 nanowires. The SnO_2 nanowires coated with carbon were charged 10 times faster than the non-coated ones. Intriguingly, the radial expansion of the coated nanowires was completely suppressed, resulting in reduced tensile stress at the reaction front, as evidenced by the lack of formation of dislocations. 4) The lithiation process of individual Si nanoparticles was observed in real time in a TEM. A strong size dependent fracture behavior was discovered, *i.e.*, there exists a critical size with a diameter of ~ 150 nm, below which the particles neither cracked nor fractured upon lithiation, above which the particles first formed cracks and then fractured due to lithiation induced huge volume expansion. For very large particles with size over 900 nm, electrochemical lithiation induced explosion of Si particles was observed. This strong size-dependent fracture behavior is attributed to the competition between the elastic energy and the surface energy of the nanoparticles. These results highlight the importance of in-situ studies in understanding the fundamental sciences of lithium ion batteries.

1. J.Y. Huang *et al.*, **Science** 330, 1515-1520 (2010); **Nano Lett.** (revised); **ACS Nano** (in press).

Thursday Afternoon, November 3, 2011

Energy Frontiers Focus Topic

Room: 102 - Session EN+MS+VT-ThA

Photovoltaics Manufacturing

Moderator: V. Ku, Satcon Technology Corporation

2:00pm EN+MS+VT-ThA1 **Waste Not, Want Not**, *L.V. Maness, Jr.*, South Park Platinum, Inc. **INVITED**

Rapidly increasing demand for certain geological commodities, in particular semi-conductors, rare earth elements (REE) and those with other desirable characteristics, are making the extraction of formerly ignored elements of significant financial interest for miners, recyclers and other commodity producers. This need is tempered by legal and regulatory requirements that minimize pollution. Historically, miners, smelters and others have used almost all the physical, chemical and electromagnetic characteristics of ores as a means of extraction and concentration – with the exception of the unique benefits afforded by processing in vacuums. Vacuum use enables the clean separation and capture of many commodities that heretofore were wasted, either up smokestacks, in water, or in waste dumps, etc. As a side-benefit, the coating with certain REE, etc., of heated surfaces will enable the selective emission of optimized thermal frequencies for use in generating electricity using Thermal PhotoVoltaics (TPV) technologies: this major improvement in TPV efficiency will result from the suppression in a vacuum of transfer of energy via conduction and convection. In addition, for the many commodities that vaporize selectively in vacuums, a vacuum-smelter would enable the non-polluting capture of all processed materials. Such capabilities will enable revolutionizing the economics of many operations, since the removal of one component from a mix will increase proportionally the relative percentages of the other components. This development will bring closer the goal of “*No Waste Mining*” and of the separation and use of certain otherwise useful constituents, such as arsenic, which are considered harmful, are tightly regulated and whose disposal is presently a very high cost-item.

2:40pm EN+MS+VT-ThA3 **The U.S. PV Manufacturing Consortium – Bringing the Supply Chain Together**, *P. Haldar, H. Efstathiadis*, College of Nanoscale Science & Engineering and U.S. Photovoltaic Manufacturing Consortium **INVITED**

The U.S. Photovoltaic Manufacturing Consortium (PVMC) – a \$300 million partnership between SEMATECH and the College of Nanoscale Science and Engineering (CNSE) of the University at Albany – will bring together the entire supply chain of companies to enable the development of advanced PV-related manufacturing processes. Created as part of the U.S. Department of Energy’s (DOE) SunShot initiative, which is designed to reduce the cost of photovoltaic solar energy systems by about 75 percent over the next decade, the PVMC will engage over 40 companies and organizations from throughout the solar community. Through PVMC, SEMATECH and CNSE will spearhead a unique research and development collaboration through which industry, academia and government will accelerate the development, commercialization and manufacturing of next-generation copper indium gallium selenide (CIGS) thin film PV manufacturing technologies, increasing performance while driving down the cost and risk of bringing them to the marketplace. By integrating the industrial research consortium and manufacturing development facilities models, PVMC offers lab-to-fab capabilities that will support rapid commercialization of new technologies and incubation of new start-up firms. PVMC offers the Federal government an unparalleled opportunity to promote the competitiveness of the U.S. PV industry.

4:20pm EN+MS+VT-ThA8 **Potentials and Challenges for High Efficiency Multi Junction Solar Cells**, *Bedair*, North Carolina State University **INVITED**

The developments of multi junction solar cell will be outlined. The major challenges facing this structure will be discussed. There are several current approaches to improve the efficiency of MJ solar cells. They include: lattice matched structure, metamorphic s structure, inverted structure and GaAsN based approach. We will discuss the concept of strain balanced strained layer super lattices in improving the converting efficiencies of lattice matched MJ solar cells.

The advantages and the limitations of each of these approaches will be presented and discussed. We also discuss the limitations facing the applications of MJ solar cell at high solar concentrations. We will address the tunnel junction issues for concentration exceeding 1000 suns. Series resistance and heat dissipation issues will also be outlined.

Finally the cost issues will be addressed with their limitations on the potential applications of this approach.

Energy Frontiers Focus Topic

Room: 103 - Session EN+NS-ThA

Nanostructures for Energy Storage and Fuel Cells II

Moderator: J. Lewis, RTI International

2:00pm EN+NS-ThA1 **Charge-Storage Processes in Model MnO₂-Li-HOPG Systems: UHV-STM Investigations**, *S.C. Bharath, W. Song, J.E. Reutt-Robey*, University of Maryland, College Park, *K.R. Zavadil*, Sandia National Laboratories

Nanostructured materials have the potential to substantially improve the speed, efficiency, and cyclic lifetime of energy storage systems such as the lithium-ion battery (LIB). Nanometer-scale oxide cathodes elements allow for greater extent of lithium incorporation due to improved strain accommodation relative to conventional cathode structures. Exposed surface facets in structures with high surface/volume ratio will act as gateways to lithium insertion, playing an important kinetic role in charge storage. However, detailed mechanisms of lithium insertion and their dependence on oxide facet orientation and grain size and shape are largely unknown. As a platform for fundamental investigations of charge-transfer processes in nanocrystalline materials, we have developed a MnO₂-Li-HOPG model system. This system consists of low-dimensional β -MnO₂ and cubic spinel Li_{1+x}Mn_{2-x}O₄ nanocrystallites, synthesized by the reactive co-deposition of elemental Mn and molecular oxygen on native and modified graphite (C(0001)) supports under ultrahigh vacuum conditions. Nanocrystallite phase and composition has been confirmed using single particle electron diffraction, as well as TOF-SIMS and scanning AES. Morphology of individual nanocrystallites, and their registration to the C(0001) support, have been determined with ambient AFM and UHV STM methods. The morphological response of β -MnO₂ nanocrystallites to Li⁺ insertion has been preliminarily explored under solid-state conditions with UHV-STM. The sensitivity of these methods are currently limited by low β -MnO₂ – C(0001) electrical conductivity, and efforts to overcome this limitation will be described. Additionally, alkali seeded growth of MnO₂ nanocrystals will be presented as a means to guide the formation of alternative MnO₂ polymorphs.

Supported by the Science of Precision Multifunctional Nanostructures for Electrical Energy Storage (NEES), an Energy Frontier Research Center funded by the U.S. Department of Energy (DOE), Office of Science, Office of Basic Energy Sciences (BES) under award DESC0001160.

2:20pm EN+NS-ThA2 **The Influence of Surface Chemistry as a Function of Salt Composition on the Rate Capability of LiNi_{0.5}Mn_{0.5}O₂ Composite Electrodes for Li-ion Rechargeable Batteries as Investigated using XPS**, *R.A. Quinlan*, Naval Surface Warfare Center, Carderock Division, *Y.C. Lu*, Massachusetts Institute of Technology, *A.N. Mansour*, Naval Surface Warfare Center, Carderock Division, *Y. Shao-Horn*, Massachusetts Institute of Technology

LiCoO₂ is currently the most commonly used cathode material in commercial Li-ion battery technology because of its high working voltage, structural stability and long cycle life. However, cobalt is expensive and there are safety and toxicity concerns. Therefore, there has been a considerable amount of work on developing cheaper alternatives for the positive electrode of large-scale lithium ion batteries. LiNi_{0.5}Mn_{0.5}O₂ (LNMO) has emerged as one of the best options due to its high specific capacity, thermal stability and low material costs. Previous studies have illustrated that decreasing the interlayer mixing can increase the rate capability and that increasing the heat-treatment temperature can also increase the rate capability. Recently, the influence that surface chemistry has on the rate capability of LNMO composite electrodes was investigated and it was shown that an additional annealing treatment after quenching the material during synthesis increased the device performance from 50 mAh/g to 180 mAh/g at 55°C and 8C. Via an inspection using X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS), it was shown that the annealing treatment did not result in significant changes in the lattice parameters or in the cation distributions of the layered structure. However, the annealing treatment was shown to be responsible for removing surface impurity phases such as lithium carbonate species and Mn³⁺-containing species, which was associated with the observed increase in performance.

In this study, we further investigate the role that surface chemistry, as developed during the operation of the cell, has on the device performance.

LNMO electrodes were constructed using quenched and annealed LNMO starting material. Both the quenched and annealed electrodes were cycled in the range of 2.0 V – 4.6 V in 1M LiPF₆/EC:DMC (1:1) or 1M LiClO₄/EC:DMC (1:1). The composite electrodes (in the discharged state) were disassembled in an Ar environment glove box and transported to the XPS analysis chamber without exposure to ambient. Cycling performance shows enhanced capacity retention and device performance for annealed electrodes cycled in LiPF₆, with the little to no enhancement observed for annealed electrodes when cycled in LiClO₄. Our initial analysis indicates the formation of both Ni and Mn fluorides/oxyfluoride species on the surface of electrodes cycled in LiPF₆. Additional changes in the surface chemistry and the influence on the rate capability will be discussed.

2:40pm **EN+NS-ThA3 Hydrogen Storage in Metal Organic Frameworks (MOFs)**, *N. Nijem*, University of Texas at Dallas, *L. Kong, H. Wu, Y. Zhao, 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 (MOFs) 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 MOFs using infrared (IR) absorption spectroscopy to characterize its interaction. IR spectroscopy can distinguish possible H₂ binding sites based on the perturbation of the internal H₂ 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 H₂-H₂ 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 H₂ depends greatly on parameters such as geometry of adsorption site and H₂-H₂ interactions. Measurements performed at low temperatures on MOF-74 show that IR shifts of H₂ is greatly red shifted (an additional ~30 cm⁻¹) due to H₂-H₂ interactions on close proximity adsorption sites, and that dipole moments of adsorbed H₂ can appreciably vary with loading.

Our analysis indicate that the intensity of H₂ IR band cannot always be a measure of the amount of adsorbed H₂, therefore methods such as variable temperature IR (VTIR) used to deduce binding energies cannot always be implemented.

3:00pm **EN+NS-ThA4 Nanostructure Engineering and Modeling of 3D Electrostatic Nanocapacitors**, *L.C. Haspert, G.W. Rubloff, S.B. Lee*, University of Maryland, College Park

Increasing energy demands require innovative nanofabrication techniques for efficiently storing and supplying available energy. This talk discusses how anodic aluminum oxide (AAO) and atomic layer deposition (ALD) technologies are implemented and designed for creating high performance nanoelectrostatic metal-insulator-metal (MIM) capacitors. The densely porous (~10¹⁰ pores/cm²) self-aligned, self-assembled AAO nanostructure serves as a complex nanostructured template in which the self-limiting and conformal ALD process can uniformly coat this complex 3D structure. Thus, combining these two technologies results in a nano-capacitor with high power density and increased energy density, comparable to electrochemical batteries.

AAO template fabrication is a two-step anodization process, in which pores self-order in the first anodization. Then, the oxide is removed, leaving in a pre-patterned scalloped Al surface. Peak asperities are rounded with a barrier anodic alumina (BAA) and the rounded structures are retained during the subsequent anodization. Mild anodization (MA) chemistries provide interpore spacings, D_{int} (in nm), equal to 2.5x the anodization voltage, V_{anod} (in V), whereas hard anodization chemistries provide D_{int} ~ 2xV_{anod}. In this work, oxalic acid MA results in pores spaced 100nm apart and 40nm in diameter. A final step etches pore sidewalls, increasing pore diameters up to 85nm. MIM layers are deposited by sequentially depositing 10nm of Al-doped ZnO (AZO), 8nm of Al₂O₃ and ~100nm AZO.

The porous structure increases the available surface area on which charge is stored, thus increasing the energy density since E=½CV². The capacitance increases with increasing depth, where planar, 1µm, 1.5µm and 2µm pore depth have capacitance of ~1, 11, 19 and 26µF/cm², respectively. Introducing the BAA reduces leakage currents to ~10⁻¹⁰A/cm² and breakdown fields are increased to 9.3MV/cm. A model simulates performance of the 3D nanogeometry, distributed resistances and dielectric capacitances, and internal non-linear resistance of the capacitor as a function of voltage. Additionally, trade-offs between pore size vs. layer thickness, AAO template interpore spacings vs. capacitance, pore depth vs. electrode series resistance are considered.

The ability to create scalable nano-structured devices is highly desirable for integrating with energy harvesting technologies. The fully self-aligned, self-assembled and self-limiting MIM nanocapacitors fabricated with ALD deposition in AAO templates demonstrate excellent electrical performance. Simulating device performance will aid in further increasing device performance and energy densities.

3:40pm **EN+NS-ThA6 Atomic Scale Engineering for Energy Conversion Efficiency**, *F. Prinz, N.P. Dasgupta, C.-C. Chao*, Stanford University **INVITED**

The benefits of utilizing nanoscale materials include high surface to volume ratios, short transport lengths, tunable optical and electronic properties, and the ability to take advantage of quantum mechanical effects in low-dimensional structures. Simple scaling laws indicate how nano scale structures may help improving energy conversion efficiency.

Our group has been focusing on two primary application areas of ALD for energy conversion: fuel cells and photovoltaics. In the area of fuel cells, ALD presents several opportunities for reducing efficiency losses. By fabricating oxide-ion conducting electrolyte materials with thicknesses below 100nm which are pinhole free, we have been able to minimize ohmic losses due to ionic transport, allowing for a reduction in the operating temperature of solid oxide fuel cells (SOFCs)[1]. Furthermore, by fabricating 3-D fuel cell architectures[2] and modifying the surface of the electrolyte with a thin ALD layer[3], we have been able to reduce activation overpotentials in these cells and increase power density.

In the field of solar cells, we have been applying ALD to build quantum confinement structures for bandgap engineering. ALD of PbS thin films was performed, and measurements of the localized density of states (DOS) show the ability to tune the bandgap simply by controlling the number of ALD cycles[4]. We have demonstrated a new technique to directly fabricate quantum dots (QDs) during the initial nucleation cycles of ALD PbS[5]. These QDs were deposited directly on nanowire surfaces, suggesting the ability to combine light trapping in nanostructured templates with quantum confinement effects.

[1] J. H. Shim, C.-C. Chao, H. Huang and F. B. Prinz, *Chem. Mater.* **19**, 3850 (2007).

[2] P.-C. Su, C.-C. Chao, J. H. Shim, R. Fasching and F. B. Prinz, *Nano Lett.* **8**, 2289 (2009).

[3] C.-C. Chao, Y. B. Kim and F. B. Prinz, *Nano Lett.* **9**, 3626 (2009).

[4] N. P. Dasgupta, W. Lee and F. B. Prinz, *Chem. Mater.* **21**, 3973 (2009).

[5] N. P. Dasgupta, H. J. Jung, O. Trejo, M. T. McDowell, A. Hryciw, M. Brongersma, R. Sinclair and F. B. Prinz, *Nano Lett.* **11**, 934 (2011).

4:20pm **EN+NS-ThA8 Nanoscale Characterization of Water Distributions in PEM Fuel Cell Membrane Electrode Assemblies Measured by Scanning Transmission Soft X-ray Microscopy**, *A.P. Hitchcock, V. Berejnov*, McMaster University, Canada, *D. Susac, J. Stumper*, Automotive Fuel Cell Cooperation Co, Canada

Successful water management in proton exchange membrane (PEM) fuel cells requires a delicate balance of fuel, oxidant and water transport through a variety of length scales from ~ 1 mm in fuel channels, through ~10-100 nm in the gas diffusion media, to 1-10 nm in the catalyst layer. The combination of a high degree of porosity in the reaction zone, complex composition, heterogeneous wetting properties, and the presence of water in two phases (gas, liquid) makes optimization of the performance of PEM fuel cell challenging. We are studying water distributions *in situ* in thin sections of membrane electrode assemblies (MEA) equilibrated with water vapor under feed-back controlled relative humidity conditions using scanning transmission X-ray microscopy (STXM). The intrinsic soft X-ray absorbance properties of the constituent materials allows direct *in-situ* visualization of water uptake into MEAs and the differentiation and mapping of the gaseous and liquid/sorbed water. The method provides maps of liquid and gaseous water distributed over the catalyst layer, with coincident maps of the ionomer and carbon support in the catalyst layer, as

well as the polymer electrolyte membrane. Condensation at specific sites is observed when the relative humidity at the MEA is higher than ~80%.

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

4:40pm EN+NS-ThA9 Optimization of the Delta Phase in Bismuth Oxide Thin Films, *P. Silva-Bermudez, O. Garcia-Zarco*, Universidad Nacional Autónoma de México, *E. Camps, L. Escobar-Alarcón*, Instituto Nacional de Investigaciones Nucleares, México, *S.E. Rodil*, Universidad Nacional Autónoma de México

Bismuth oxide Bi_2O_3 has interesting technological applications, which have not been largely used due to the particular polymorphism of the material. Bismuth Oxide has five polymorphic forms: α , β , γ , δ and ω - Bi_2O_3 . Among them, the low-temperature α and the high-temperature δ phases are stable and the others are metastable phases, as has been established by bulk solid-state studies. Each polymorph possesses different crystalline structures and various electrical, optical and mechanical properties. The face-centered cubic δ - Bi_2O_3 is stable over a narrow temperature range 729–825 °C (melting point) and it has the peculiarity of being among the few materials presenting high ionic conductivity at moderate temperatures (600–700°C). In this research, we aim to obtain δ - Bi_2O_3 thin films as possible ionic conductors for the development of micro solid state fuel cells. However, the first challenge is to find the deposition conditions of the magnetron sputtering system to ensure the formation of the desired δ - Bi_2O_3 , which is only thermodynamically stable at high temperatures. Based on previous results of Fan et al. (Fan 2006), we choose as the deposition variables the substrate temperature (room temperature to 300 °C) and the power (100–200 W). Our target was pure Bi_2O_3 , but the first results indicated that it was necessary to compensate oxygen losses; therefore the atmosphere was a mixture of Argon and Oxygen, where the Oxygen flow was 20% of the total. The results from the different characterization techniques suggested that substrate temperatures between 150 and 200°C are appropriate to obtain the δ - Bi_2O_3 phase at a high deposition rate, between 1.5 to 2 nm/s. X-ray diffraction (XRD) as a single technique to identify the film crystalline structure demonstrated to be rather difficult, since there is a large overlapping between the diffraction peaks corresponding to the α , β , γ and δ phases. However, we showed that by combining XRD and Raman spectroscopy, it was possible to clearly prove the presence of the δ -phase. The explanation for the stabilization of the high temperature phase might be related to the 2-dimensional confinement and/or then effect of the small crystalline size. The physical properties of the δ - Bi_2O_3 thin films were further investigated; optical properties by transmission spectroscopy and ellipsometric spectroscopy in the ultraviolet-visible range, surface resistivity by the four-points method, composition by X-ray photoelectron spectroscopy and X-ray energy dispersion.

Fan H. T, et al. Thin Solid Films 513 (2006) 142.

5:00pm EN+NS-ThA10 Probing Physical and Interfacial Confinement Effects on Multilayered Piezoelectric Polymeric Films using Second Harmonic Generation Laser Spectroscopy, *J. Jones*, Fisk University, *H. Park*, Vanderbilt University, *L. Zhu*, Case Western Reserve University, *N.H. Tolk*, Vanderbilt University, *R. Mu*, Fisk University

Piezoelectric materials may arguably be the most functional, versatile and widely used materials with a wide range of applications including mechanical sensors, actuators, energy storage and energy harvesting devices. The well established applications are largely based on inorganic piezoelectric materials. The successful employment of polymeric piezoelectric materials, such as polyvinylidene fluoride (PVDF) and its related co-polymers, although light weight, flexible, optically transparent and cost effective, are limited by relatively low piezoelectric coefficients, thermal stability, and durability. The focus of the group is to develop a multilayered piezoelectric PVDF system for improved energy harvesting and energy storage efficiency. These systems are fabricated using enabling technology in co-extrusion which allows more cost effective and large area device production as opposed to more conventional layer-by-layer techniques. Many efforts have been made by the team to fabricate these micro- and nano-layered systems resulting in much improved device performance. A three-time improvement of capacitive electrical energy density has been demonstrated. The focus of this research is to understand the physics of why these multilayered systems perform better than a single layer by developing a characterization technique using both confocal second harmonic generation (SHG) and electric field induced second harmonic (EFISH) laser spectroscopy. Our results have shown that SHG is a very sensitive, non-destructive and versatile technique that can be used to study the piezoelectric and structural properties of layered systems. When combined with EFISH this technique allows the interrogation of electrical properties within the individual layers and at the interfaces between the layers. Further, the proposed techniques can be readily employed *in-situ*

which can provide information in real time during sample processing with static and time-resolved spectroscopic measurements.

5:20pm EN+NS-ThA11 Electrical Transport in Ultrathin Ruthenium Films formed by Atomic Layer Deposition, *K.E. Gregorczyk*, *P. Banerjee*, *G.W. Rubloff*, University of Maryland, College Park

Next generation nanostructured devices require ultrathin layers of different materials (e.g. current collectors found in solar cells, batteries, and charge storage and memory devices, etc.). However, in the ultrathin regime, expectations from bulk resistivity can be misleading in designing such nanostructures. Here, we show the example of ultrathin (5–24nm) Ru films produced by atomic layer deposition (ALD), where resistivity is dramatically increased: at 5nm resistivity is ~7X higher (~135 $\mu\Omega$ cm) than at 24nm (~20 $\mu\Omega$ cm) and ~18X higher than bulk Ru (7.4 $\mu\Omega$ cm). The drastic differences seen here are explained through Mayadas-Shatzkes (MS) theory, which defines the increase in resistivity through geometrical constraints (e.g. film thickness and grain boundaries). Using MS theory the grain boundary reflection coefficients were calculated as ~0.32 for an 18nm thick film and ~0.66 for a 5nm film. Furthermore, the electrical transport properties of these films were studied as a function of both temperature (80–340K) and film thickness (5–24 nm). Finally, we show that the ALD Ru films are p-type, in agreement with the theory of compensated metals, and report both the temperature coefficient of resistivity and charge carrier mobility as a function of film thickness.

Energy Frontiers Focus Topic

Room: East Exhibit Hall - Session EN-ThP

Energy Frontiers Poster Session

EN-ThP1 Development of Analysis System for Evaluating Carrier Lifetime in Organic Thin Film Solar Cell. *K. Naito*, KAST, Chuo Univ., Japan, *M. Sakai*, *H. Takei*, KAST, Japan, *K. Nakata*, KAST, Tokyo Univ. Sci., Japan, *K. Katayama*, Chuo University, Japan, *K. Takagi*, KAST, Japan, *A. Fujishima*, KAST, Tokyo Univ. Sci., Japan

Recently, photovoltaic cell is expected as new green technology replacing fossil fuel. Because of a next-generation photovoltaic cell with flexibility, portability and low cost, organic thin film solar cell (OTFSC) is currently the subject of great interest and intensive study. OTFSC is composed of organic electronic materials, which have differences in electron affinity and ionization energy, between two metallic conductive electrodes. The layer of the material with higher electron affinity and ionization potential is electron acceptor, and the other layer is electron donor. The hole-electron pairs (exciton) generated in either material, when OTFSC was photoinduced. When most of excitons reach the interface of the electron acceptor and electron donor, excitons break into carriers of electrons and holes efficiently. Electrons and holes move in the acceptor and donor, respectively. The carriers are collected by the electrode in contact with each layer. In the latest report, OTFSC has exceeded 8 percent of conversion efficiency. However, it was difficult to increase the area of OTFSC with high conversion efficiency. For instance, the conversion efficiency depended on the layer defects, which was caused by contamination of dust and H₂O, oxidation and inhomogeneous coating. The defects influenced the carrier lifetime in OTFSC. Hence, the inspection technique, which was evaluated in two dimensions XY, was required to measure the carrier lifetime. The present inspection technique (Laser beam induced current method) had to contact electrodes with electric wires and pass an electric current through OTFSC. Because the carrier lifetime was measured by the decay of electric current, the value was influenced by every interface of circuitry in OTFSC. Therefore, it was necessary to detect the pure carrier lifetime in the organic semi conductivity layer. In this study, to investigate the pure carrier lifetime in the OTFSC, we developed the analysis system employing micro wave photoconductivity decay (μ PCD). The carrier life time was discussed from the viewpoints of electrochemistry and quantum mechanics.

EN-ThP2 Reactivation of Thermionic Electron Emission from Nitrogen Doped Diamond Films by Atomic Hydrogen Exposure. *M. Zumer*, *V. Nemanic*, *B. Zajec*, Jozef Stefan Institute, Slovenia, *F.A.M. Koeck*, *R.J. Nemanich*, Arizona State University

Thermionic electron emission from nitrogen doped hydrogen terminated diamond film has been evaluated 18 months after it had been deposited on a 25 mm diameter molybdenum substrate by microwave plasma assisted chemical vapour deposition. A hydrogen enriched surface layer, enabling a negative electron affinity, was formed during the film deposition procedure. The initial thermionic emission current density of the aged film obtained at 500 °C and 0.2 V/micrometer electric field was stable but relatively low compared to the value measured on a freshly deposited film. The value at a base pressure of 2×10^{-7} mbar was $\sim 1.4 \times 10^{-9}$ A/cm². Such a low current density is presumed to be a consequence of oxidation, surface adsorption of contaminants and hydrogen depletion from the surface layer, all processes which proceed during ambient atmosphere exposure since the manufacturing date. Reactivation of the surface was achieved by introducing atomic hydrogen, generated by the hot filament cathode of the ionization gauge. A stable current density of $\sim 2 \times 10^{-6}$ A/cm² (an increase factor of ~ 1400) was achieved after exposure to hydrogen at the base pressure of 2.2×10^{-4} mbar for 2 hours again at 500 °C and 0.2 V/micrometer. The atomic hydrogen exposure rate was estimated by subsequent measurement of the change in optical transmittance of the tungsten phosphate glass plates. The increase in emission with hydrogen was ascribed to two effects: 1) reactivation of the surface, and 2) molecular assisted emission.

Research at ASU is supported through the Office of Naval Research and at JSI through the Slovenian Research Agency (grant BI-US/09-12/021).

EN-ThP3 Self-powered Environmental Sensor System Driven by Nanogenerators. *M. Lee*, *J. Bae*, Georgia Institute of Technology, *J.H. Lee*, Seoul National University, Republic of Korea, *C. Lee*, Korea Electronics Technology Institute, Republic of Korea, *S. Hong*, Seoul National University, Republic of Korea, *Z. Wang*, Georgia Institute of Technology

A self-powered sensor for toxic materials can be the most desirable and promising prototype of the future monitoring systems for environmental protection/detection. Wiring power-source to sensors that are placed in every corner of our surroundings not only causes a vast amount of labours, resources and budget, but also potential contamination to be produced by the batteries. Although solar energy is most attractive, it depends on the weather, season and has day and night difference. However, regardless of day and night, mechanical energy is one of the most abundant/sustainable sources practically to be utilized through piezoelectric materials. ZnO nanowires (NWs) not only have piezoelectricity, but also are environmental friendly and biological compatible, which make it a strong candidate for energy-harvesting for environmental sensors. Here, we have demonstrated a fully stand-alone, self-powered environmental sensor driven by nanogenerators with harvesting vibration energy. Such a system is made of ZnO nanowire-based nanogenerator, a rectification circuit, a capacitor for charge storage, a signal transmission LED light and a carbon nanotube-based Hg²⁺ ion sensor. The circuit lights up the LED indicator when it detects mercury ions in water solution. It is the first demonstration of nanomaterial-based, self-powered sensor system for detecting a toxic pollutant.

EN-ThP4 Effect of Inserting a Thin Buffer Layer on Obtainable Efficiency in n-ZnO/p-Cu₂O Heterojunction Solar Cells. *T. Minami*, *T. Miyata*, *Y. Nishi*, *J. Nomoto*, Kanazawa Institute of Technology, Japan

The effect of inserting a thin-film buffer layer on the obtainable efficiency in n-ZnO/p-Cu₂O heterojunction solar cells was investigated with a transparent conducting Al-doped ZnO (AZO) thin film/Cu₂O sheet structure. To improve conversion efficiency, various heterojunction solar cells were fabricated by forming an AZO/thin-film buffer layer/Cu₂O structure on the front surface of thermally oxidized Cu₂O sheets that function as the active layer as well as the substrate. It was found that achieving higher efficiency Cu₂O-based heterojunction solar cells fabricated by depositing various thin films on Cu O sheets requires that the surface of the Cu₂O sheets always be treated using a low-damage deposition technology at a low deposition temperature.

The Cu₂O sheets, with electrical properties such as resistivity on the order of 10^3 Ω cm, hole concentration on the order of 10^{13} cm⁻³ and Hall mobility above 100 cm²/Vs, were prepared by a thermal oxidation of copper sheets under appropriate conditions. The AZO thin film and the thin-film buffer layer were prepared by a pulsed laser deposition (PLD) using an ArF excimer laser. As an example of AZO/buffer layer/Cu₂O heterojunction solar cells, AZO/ non-doped ZnO (ZO)/Cu₂O solar cells were fabricated by inserting a ZO thin film as the buffer layer. It was found that the obtainable conversion efficiency in AZO/ZO/Cu₂O heterojunction solar cells increased markedly as the deposition temperature of the AZO and ZO thin films was decreased from approximately 300°C to room temperature (RT), i.e., non-intentionally heated Cu₂O sheets. In addition, when the ZO thin films were prepared on non-intentionally heated Cu₂O sheets by PLD, the efficiency (η) increased considerably as the introduced O₂ gas pressure was increased; η , approximately 3 % with a ZO thin-film layer deposition at an O₂ gas pressure of 0.1 Pa, gradually increased as the O₂ gas pressure was increased up to approximately 1.2 Pa, and then decreased markedly at a pressure of approximately 1.5 Pa. The optimal thickness of the ZO thin-film layer was in the range from 30 to 50 nm. The obtained increase of η as the ZO film thickness was increased up to approximately 50 nm may be attributable to an improvement of film quality; in contrast, the decrease of η as the ZO film thickness was increased above approximately 50 nm may be attributable to the short lifetime of minority carriers in the n-ZO thin film. An AZO/ZO/Cu₂O heterojunction solar cell fabricated under optimal preparation conditions exhibited an efficiency of 3.83% under simulated AM1.5G solar.

EN-ThP5 Surface Texturing of Silicon for Solar Cells for CMOS Technology. *A.R. Silva*, *J. Miyoshi*, *F.A. Cavarsan*, *L.P.B. Lima*, *J.A. Diniz*, State University of Campinas, Brazil

The solar cell efficiency is hardly connected with device fabrication processes, such as texturing silicon surface, which increases the surface absorption area of incident radiation on the cell and, consequently, reduces the substrate reflectance. Nowadays, solar cells based on silicon substrate are fabricated with texturing surfaces to increase the device efficiency. These surfaces are obtained by anisotropic wet etching in KOH and NaOH

alkaline solutions [1]. The disadvantage of these solutions are K⁺ and Na⁺ ions from KOH and NaOH, which are mobile charges in Metal-Oxide-Silicon structures. Thus, these solutions are not compatible for CMOS technology, which is used for integration circuits and devices on silicon surface. As an advantage, using these alkaline solutions, the <111> planes of silicon substrate with (100) crystallographic orientation are exposed, resulting in groups of pyramid on silicon surface. The pyramids induce many reflections and scatterings of the incident radiation, which increase the light absorption on the surface. This effect is defined as light trapping [1]. In this work, the silicon substrate texturing is carried out by an anisotropic wet etching, with an alkaline solution based on NH₄OH, because this solution can form pyramids on the surface, does not release alkaline products/reagents on the silicon surface and is fully compatible with the CMOS technology. With this solution (concentration of 9%wt of NH₄OH and four magnetic stirring velocities) the <111> planes of silicon substrate with (100) crystallographic orientation are exposed and these planes can form some pyramids on surface. Scanning Electron Microscopy analysis presents that these pyramids are observed all long on the surface, indicating that the wet etching was uniform on the substrate. Furthermore, the pyramid height values are between 3.5 and 7.2 μm, and the silicon etching wet rate was about of 0.7 μm/minute. The reflectance measurements show that the surfaces with and without texturing present reflectance values of about 16% and 38%, respectively. The reflectance values of about 16% with texturing are similar to the results from references [1], which have used KOH solution. This result indicated that our texturing process based on NH₄OH, which is fully compatible with the CMOS technology, can be used to fabricate Si-based solar cells [2].

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EN-ThP7 Carrier Life Time of Several Organic Photovoltaic Cells by using Micro Wave Photoconductive Decay. *M. Sakai*, Kanagawa Academy of Science and Technology (KAST), Japan, *K. Naito*, KAST, Chuo Univ., Japan, *H. Takei*, KAST, Japan, *K. Nakata*, KAST, Tokyo Univ. Sci., Japan, *K. Katayama*, Chuo University, Japan, *K. Takagi*, KAST, Japan, *A. Fujishima*, KAST, Tokyo Univ. Sci., Japan

Recently, the importance of developing the future energy is recognized in various industries. In one of the green innovations, there are great expectations to develop organic photovoltaic cells; Dye sensitized solar cell (DSSC) and Organic thin film solar cell (OTFSC). Organic photovoltaic cells with inexpensive and low resource constraint are currently the subject of great interest and intensive study. DSSC is composed of photo-sensitized anode using molecular dye placed on a porous layer of titanium dioxide nanoparticles, and an electrolyte solution. The photo electrochemical system was known as the Grätzel cell. Electrons at the dye excited because of sunlight move into the titanium dioxide, and are collected by the electrode. On the other hands, OTFSC is composed of organic electronic materials, which have differences in electron affinity and ionization energy, between two metallic conductive electrodes. The layer of the material with higher electron affinity and ionization potential is electron acceptor, and the other layer is electron donor. The hole-electron pairs (excitons) generated in either material, when OTFSC was photoinduced. When most of excitons reach the interface of the electron acceptor and electron donor, excitons break into carriers of holes and electrons efficiently. Electrons and holes move in the acceptor and donor, respectively. The carriers are collected by the electrode in contact with each layer. In either solar cell, the carrier life time would influence the performance of the solar cell, because the carriers (electrons) move through the semiconductor and reach the electrode. Therefore, we investigated the carrier life time of several organic photovoltaic cells by using micro wave photoconductive decay (μPCD). The difference of the carrier life time was discussed from the viewpoints of electrochemistry and quantum mechanics.

EN-ThP8 Making Molecular Multilayers using "Click" Chemistry: Growth, Characterization, and Application in p-Type Dye Sensitized Solar Cells. *P.K.B. Palomaki, P.H. Dinolfo*, Rensselaer Polytechnic Institute

Bottom-up approaches to creating molecular multilayer assemblies using layer-by-layer (LbL) techniques give one the ability to tailor the surface properties of an interface through molecular control. LbL assembly methods can provide molecular level control of structure in one dimension from simple solution deposition processes. We have developed a versatile LbL fabrication method using copper(I)-catalyzed azide-alkyne cycloaddition (CuAAC) or "click" chemistry in the construction of multilayer assemblies on oxide surfaces. 1,2 These reactions occur in minutes at room temperature

allowing for the facile creation of complex, covalently attached multilayer assemblies. Multilayers containing synthetic porphyrins, perylenes, and mixtures of the two have been constructed in order to highlight the versatility of this method. The fabrication of this new type of molecular multilayer thin film will be discussed along with characterization of the photophysical, electrochemical, and structural properties. Initial results pertaining to the use of these films as light harvesting systems in p-type dye sensitized solar cells will be presented.

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EN-ThP9 Powder-Sputtered Cu(In,Ga)Se₂ Thin Films: Nonstoichiometric Influences on Optical and Electrical Characteristics. *N. Kim, J. Jeon, W. Lee*, Chosun University, Republic of Korea

The thin film solar cell efficiency of 19.2% (0.41 cm²) was accomplished by using Cu(In,Ga)Se₂ (NREL, 2003), which has been fabricated by using the three stage co-evaporation process. There are two general methods for Cu(In,Ga)Se₂ thin film fabrication: selenization after sputtering and thermal co-evaporation. The novel method of powder-sputtering was employed for the preparation of Cu(In,Ga)Se₂ to deposit the thin film over the large area with a good uniformity without selenization of toxic H₂Se because the co-evaporation method requires very strict controls during the deposition process of Cu(In,Ga)Se₂ thin film. This method has the advantages of the production of target, change of stoichiometry, and easy doping of impurities. The composition of the starting powder target was changed by $x = 0.1, 0.3, 0.5, 0.7, \text{ and } 0.9$ in the deposition process of Cu(In_xGa_{1-x})Se₂ thin film while Cu(In+Ga) ratio was '1'. The compositions of the starting powder target and the deposited samples with 1 μm-thickness were comparatively analyzed by electron probe microanalysis (EPMA). The crystal structure, surface morphology, optical properties, and electrical characteristics of Cu(In_xGa_{1-x})Se₂ thin films were analyzed by using X-ray diffraction (XRD), atomic force microscope (AFM), UV-Visible spectrophotometer, and a Hall effect measurement system to investigate the influence of nonstoichiometry on the characteristics. The optimized composition was selected through the comprehensive analysis of the characteristics.

EN-ThP10 Indium-Doped CdS Thin Film by He-Ne Laser Exposure for CIGS Solar Cells. *K. Myung, N. Kim, W. Lee*, Chosun University, Republic of Korea

Cadmium sulfide (CdS) is a direct and wide band gap (2.42 eV at room temperature) II-VI semiconductor, which is a very desirable window layer for many photovoltaic solar cells including CIGS solar cell. CdS thin film has been paid to the considerable attention due to its band gap, high absorption coefficient, reasonable conversion efficiency, stability and low cost. It is generally known that the undoped CdS thin film has the high electrical resistivity. Some impurities were employed for doping CdS to produce less resistive films. Especially, indium (In) showed the improvement of resistivity and optical transmittance when it was doped into the sputtering-deposited CdS thin film. In this study, the structural, optical, electrical, and morphological properties of indium-doped CdS thin films prepared by the effective method with He-Ne laser at room temperature. Indium was deposited on the 200 nm-thickness of CdS thin film by the sputtering method with 10 nm-thickness. He-Ne laser (632.8 nm) was exposed with a small energy by a change of exposure time. The remained indium layer was removed with the chemical solutions. The doping effects of indium on the CdS thin films were investigated by analyzing the structural, optical, electrical, and morphological properties of CdS thin films by using X-ray diffraction (XRD), Auger electron spectroscopy (AES), UV-Visible spectrophotometer, Hall effect measurement system, and atomic force microscope (AFM). AES depth profile was employed to examine the indium-doped CdS thin film with a change of He-Ne laser exposure time. The doping uniformity and amount of indium into the depth of CdS thin film was compared to the characteristics of CdS thin film. The optimization of indium-doping process was achieved to enhance the electrical and optical characteristics including resistivity and optical transmittance.

EN-ThP11 Three-Terminal Tandem Devices for PV, TPV and CPV Applications. *M. Emziane*, Masdar Institute, United Arab Emirates

One of the key approaches for achieving very-high efficiency for photovoltaic (PV) devices is to use, instead of single junctions, double or multi-junction devices due to an extended solar spectral coverage leading to an enhanced overall power output from the multi-junction PV devices.

In this study, we investigated two-junction solar cells based on group IV materials, i.e. Si and Ge, for top and bottom sub-cell, respectively. Unlike the conventional and widely used monolithic series-connected two-terminal device configuration that was shown to deliver a slightly lower output, these double-junction cells were assembled with three terminals and operated independently [1, 2].

The main advantages of choosing these materials and device configuration are: (i) cheapest, largest and easiest group IV substrates; (ii) extended spectral coverage leading to more photons being converted; and (iii) no current matching or the associated tunnel junctions between the two sub-cells.

We have undertaken a comprehensive modeling analysis for the device optimization and performance prediction. n/n/p as well as p/p/n device structure configurations were investigated and optimized with regard to the thicknesses and doping levels of both top and bottom active junctions that lead to the highest device performance. Due to the split of the incident solar spectrum between the top and bottom sub-cells, the latter only receives the light to which the former is transparent (mainly in the near infrared) and therefore behaves differently from the single-junction cell counterpart.

Optimal current-voltage and power-voltage characteristics were generated for individual cells together with the corresponding quantum efficiency spectra. The applications of these devices in conventional PV, concentrator PV and thermal PV were assessed and the output PV parameters were predicted as a function of the simulated operating conditions.

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EN-ThP12 The Advantage of State of the Art DC Power Supplies Over the Pulsed DC Power Supplies for TCO Magnetron Sputtering. P. Rozanski, P. Ozimek, M. Zelechowski, P. Lach, W. Glazek, J. Abraham, Huettinger Electronic Company, Poland

Non-pulsing DC power supplies for highly arcing processes are gaining more and more interest slowly pushing out older pulsing DC power supplies as more efficient and more cost optimal. The importance of arc management in DC power supplies is taking on a new meaning as most advanced DC generators are more and more successful in sputtering highly arcing and difficult materials, providing high deposition rates at competitive investment.

It has been developed as the answer to the market's demand to limit arc energy during an arc occurrence in sputtering. Industrial implementation has been already successfully performed with air-cooled DC power supplies that have been on the market for years. The possibility of using DC power supplies for sputtering highly-arcing materials is the result. It is the beginning of a new age in magnetron sputtering technology. Further improvement and optimization by using more efficient water cooling and faster transistors has resulted in a new generation of power supplies with state-of-the-art arc management parameters. A complementary feature of the newly-developed arc management circuitry is software that supports efficient arc handling: self-adjusting arc management settings and an internal oscilloscope.

EN-ThP13 Photogenerated Current Enhanced by Surface Plasmon Resonance in Metal Grating. D.J. Lee, Inha University, Republic of Korea

Photogenerated current enhanced by surface plasmon resonance excited in metal grating was confirmed in Au/p-type a-Si Schottky structures. Conduction electrons in metal absorb the incident photon of energy $h\nu$ (h is the Planck's constant and ν is the optical frequency) through the a-Si film, gaining enough energy to cross over the Schottky barrier into the semiconductor, where they are swept across the depletion region and collected as photocurrent under reverse bias. In addition, the surface plasmon polariton is excited in metal grating fabricated on the photoresist layer, and excited electrons will flow over the Schottky barrier. This additional photocurrent added to that directly induced by incident light and enhanced the responsivity of the photodetector.

EN-ThP14 The Science of Precision Multifunctional Nanostructures for Electrical Energy Storage. A. Predith, University of Maryland, College Park

Nanostructures for Electrical Energy Storage (NEES) is a five-year Energy Frontier Research Center investigating nanoscale behavior in lithium-ion

battery materials. Funded by the US Department of Energy, the Center studies the properties of composite nanostructures containing an oxide or silicon as a charge storage material and low dimensional forms of carbon as an electronic conductor or mechanical support. NEES is particularly interested in nanostructures that are precise and regularly ordered. These structures provide a unique test bed for uncovering to the science of electrochemistry at the nanoscale.

The two Science Thrusts of the Center investigate nanotubes, nanowires, and layers of MnO₂, silicon, and carbon electrode materials as well as nanoporous membranes in an electrolyte. They examine the mechanical behavior, electrochemical properties, and interfacial phenomena that arise in heterogeneous material combinations. The two Enabling Thrusts of the Center develop model systems and characterization instruments for the nanoscale. Ultra high vacuum scanning probe microscopy and first principles modeling provide for the study of pristine systems, and in situ transmission electron microscopy and microelectromechanical systems are allowing members of NEES to observe electrochemical processes as they unfold.

NEES is a collaboration of 19 senior investigators, ~35 postdoctoral associates and graduate research assistants, and many staff members at six institutions. The Center integrates their perspectives to pursue a comprehensive examination of electrical energy storage using precision, multifunctional nanostructures. Members include Philip Collins (University of California-Irvine), Michael Fuhrer (University of Maryland), Sang Bok Lee (UMD), Charles Martin (University of Florida), Reginald Penner (UCI), Zuzanna Siwy (UCI), John Cumings (UMD), S. Thomas Pireraux (Los Alamos National Laboratory & Center for Integrated Nanotechnologies), Mark Reed (Yale University), Chunsheng Wang (UMD), YuHuang Wang (UMD), Kevin Leung (Sandia National Laboratories), Janice Reutt-Robey (UMD), Kevin Zavadil (SNL), Reza Ghodssi (UMD), Jianyu Huang (SNL, CINT), Robert Hwang (SNL), Gary W. Rubloff (UMD), John Sullivan (SNL, CINT), and Ashley Predith (UMD).

EN-ThP15 Photosystem I-Based Solar Cells. D. Gunther, D.E. Cliffl, G.K. Jennings, Vanderbilt University

The long-term success of photosynthetic organisms has resulted in their global superabundance, which is sustained by their widespread, continual mass-production of the integral proteins that photocatalyze the chemical processes of natural photosynthesis. Here, a fast, general method to assemble wet and dry solar cells composed of one such photocatalytic protein complex, Photosystem I (PSI), onto a variety of electrode substrates, including gold, nanoporous gold, and graphene is reported. The resulting PSI films consist of a protein matrix that is permeable to electrochemical mediators in a wet cell and conducting for electron transfer in a dry cell. These results demonstrate how the assembly of micron-thick coatings of PSI on non-biological substrates yields a biohybrid ensemble that manifests the photocatalytic activity of the film's individual protein constituents, and represent significant progress toward affordable, biologically-inspired renewable energy conversion platforms.

EN-ThP16 Thickness Dependent Photo-Voltaic Effect In Ferroelectric PLZT Thin Films. S. Kotru, H.V. Nampoori, The University of Alabama, Tuscaloosa

Ferroelectrics are emerging as potential candidate materials for energy harvesting. Among the class of ferroelectrics, Lanthanum doped Lead Zirconate Titanate (PLZT) is one which possesses high electro-optic coefficient and exhibits high optical transparency thereby makes it an attractive material for PV applications. In this work ferroelectric thin films of $Pb_{0.95}La_{0.05}(Zr_{0.54}Ti_{0.46})O_3$ (PLZT) of various thicknesses were fabricated using chemical solution deposition method. Structural and ferroelectric properties of these films were studied using standard characterizations methods. Capacitor type solar cells were fabricated from these films using Pt as the top electrode. The IV curves were measured for each device where the thickness of PLZT film ranged from 70 nm to 350 nm. For devices, made with films less than 150 nm thickness, no PV response could be measured as an electrical contact could not be made on such films. From the PV curves measured on films with 140 to 350 nm thickness, the photocurrent density was seen to decrease from 597 to 64 nA/cm², where as no major change was observed for the open circuit voltage. Thus thinner films are seen to enhance the PV response in ferroelectric based capacitor type solar cells.

EN-ThP17 Nanostructure Analysis of Diamond Cold-Cathode Field Emitter, T.C. Wade, N. Ghosh, J.E. Wittig, W.P. Kang, Vanderbilt University, L.F. Allard, K. Unocic, Oak Ridge National Laboratory, J.L. Davidson, N.H. Tolk, Vanderbilt University

Chemical-vapor-deposited diamond is an attractive material for electron field emitters because of its low or negative electron affinity, mechanical strength, and chemical inertness. Arrays of ultra-sharp diamond tips with a radius of curvature less than 5nm have been fabricated [1] and show significant improvement in emission brightness and turn-on field compared to conventional field emitters [2,3]. Irregularities in emission behavior between tips were historically attributed to anomalies in the fabrication process: "sharp" or "less sharp" tips. However, we observe large differences in electron emission thresholds between tips that appear to be equally well formed. We examine the emitter's sub-surface structure to provide insight into how surface and subsurface structure affect emission.

Cross-sectional Transmission Electron Microscopy (TEM) samples were prepared by standard Focused Ion Beam (FIB) lift-out techniques with the additional step of using a layer of EBID Pt before the ion-beam Pt deposition in order to preserve the 5 nm field emission tips. TEM images of the emitter tip cross sections were recorded with a sub-angstrom probe in a JEOL 2200FS.

The core of the emitter consists of boron-doped microcrystalline diamond with characteristic diamond cubic twinning. The graphite layers observed are likely specimen preparation artifacts, although the presence of graphitic material in these diamond emitter tips is still an open question. Crystallites on the order of 5 nm in size are evident in the nanocrystalline diamond surface layer. Final thinning using a nanomill (Fischione Co.) with low energy Ar may be the solution for removing any surface artifacts and reducing the sample thickness. Comparison of the nanostructure of emitter tips with variation in field emission characteristics will provide insight into the influence of the nanocrystalline structure on the electronic properties.

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EN-ThP18 Microbial Fuel Cells Development on the Base of *Desulfuromonas Acetoxidans* Bacteria, O.M. Vasylyv, O.I. Bilyy, S.O. Hnatysh, Ivan Franko National University of Lviv, Ukraine

Microbial fuel cells (MFCs) are able to capture the electrons produced during different biochemical microbial processes to generate electricity. They offer the promise of a new sustainable source of energy, produced from biodegradable and reduced compounds. Increased shortcoming of unrenewable fossil fuels causes the need for its less dependence. The enhance of use of renewable fuels requires the development of alternative sources of energy such as waste biomass for environmental benefits. MFCs investigations have attracted substantial interest in development of different devices for generating electricity and removing wastes. The development of processes that can apply bacteria of normal environmental microflora to produce electricity represents a highly effective method for bioenergy production as bacteria are self-replicating, and thus the catalysts for organic matter oxidation are self-sustaining.

Nowadays MFCs is considered to be applied as highly effective and self-sustaining model of wastewater treatment which contains energy in the form of biodegradable organic matter. At the same time wastewater contains high concentrations of xenobiotics, such as different heavy metal ions that have an overwhelming harmful effect towards all living organisms. These elements even in small concentration in the environment cause the intensive inhibition of physiological and biochemical properties of most bacteria. Despite that, some genuses of bacteria possess high toxic heavy metals resistance because of highly-efficient defensive systems functioning. There are *Ferroplasma*, *Streptomyces*, *Thiobacillus* etc.

Desulfuromonas acetoxidans are uncoloured gram-negative sulfur-reducing bacteria. These bacteria are considered to be used as the substrate for microbial-anode fuel cells with high electron recovery, which is more than 80%, to electric current by the interaction between processes of acetate oxidation and S⁰ or Fe³⁺ - reduction. Sulfurbacteria have a great effect on the biogeochemistry of aquatic environments because of their ability to reduce and precipitate toxic heavy metals compounds. It's a result of their particular binding with the final product of bacterial dissimilative sulfur-reduction - H₂S, and formation of the insoluble metal sulfides. It also

serves as self-defensive mechanism of these bacteria against toxic influence of toxic heavy metal ions.

The influence of different of Ni²⁺ and Cu²⁺ concentrations on size distribution and relative content of *D. acetoxidans* bacteria during their life cycle on the base of cells' light scattering properties changes by the new method of measurement has been investigated. The ability of this bacteria to produce electric current in microbial-anode fuel cells under the specific cultivation condition has been shown. Particular heavy metals resistance of *D. acetoxidans* bacteria has been observed. Distribution curves of the cells' size distribution changes were in the range from 0.3 to 1.9 μm under the influence of investigated metal ions. The maximum of cells' size distribution of investigated bacteria was changed from 0.55 to 0.62 μm under the influence of 0.01-10 mM of NiCl₂·6H₂O and CuCl₂·2H₂O during five days of bacterial growth.

EN-ThP19 Investigating CdTe/CdS/TCO Inter-diffusion by AES and XPS, L. Le Tarte, A. Barbuto, J. Courmoyer, K. Dovidenko, H. Piao, General Electric, Global Research Center

CdTe has recently received a lot of attention as the material of choice for thin film solar cells as it converts light to electricity more cost effectively than traditional semiconductors and is compatible with manufacturing scale-up. An in-depth understanding of film composition, morphology and interface integrity is critical for CdTe thin film process development. Clear depth profiles of the buried layers by Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS) are difficult to obtain due to the rough, and thick (~3μm ± 0.5μm), upper CdTe layer. Sputtering through this layer leads to broadened depth profile interfaces which reduces information about inter-diffusion. We have developed a polishing method to thin and smooth this layer prior to analysis. In this poster we will present how this method has improved the Auger depth resolution and therefore the understanding of inter-diffusion between the CdTe, CdS and TCO layers. A novel FIB preparation method for Auger will also be discussed. XPS imaging analyses on AES sputter crater sidewalls provides additional chemical information about the buried layers and interfaces.

Friday Morning, November 4, 2011

Energy Frontiers Focus Topic

Room: 203 - Session EN+AC-FrM

Materials Challenges for Nuclear Energy

Moderator: L. Petit, Daresbury Laboratory, UK

8:20am **EN+AC-FrM1 Multi-Electron Correlation in UO₂ from Soft X-ray Spectroscopy**, *J.G. Tobin, S.W. Yu*, Lawrence Livermore National Laboratory

Resonant Inverse Photoelectron Spectroscopy (RIPES) and X-ray Emission Spectroscopy (XES) have been used to probe the electronic structure of Uranium Dioxide, UO₂. From these variants of soft x-ray spectroscopy, the nature of the main and satellite features at the U4d_{5/2} edge can be ascertained. This leads to important insights into the multi-electronic correlations underlying the ubiquitous satellite features of UO₂ and implications for future experiments with Pu.

Lawrence Livermore National Laboratory is operated by Lawrence Livermore National Security, LLC, for the U.S. Department of Energy, National Nuclear Security Administration under Contract DE-AC52-07NA27344. This work is funded by the DOE Office of Science, Office of Basic Energy Science, Division of Materials Sciences and Engineering. The Advanced Light Source (ALS) is supported by the Director, Office of Science, Office of Basic Energy Sciences.

8:40am **EN+AC-FrM2 New Results from the DOE EFRC on the Materials Science of Actinides**, *P.C. Burns*, University of Notre Dame, **G. Sigmon**, EFRC **INVITED**

The Materials Science of Actinides EFRC has three major themes: (1) Complex actinide materials, with complexity arising from chemistry, structure, and properties; (2) Nanoscale control of actinides; and (3) Behavior of actinide materials in extreme environments of pressure, temperature and radiation fields (including coupled effects). This presentation will cover several recent results that span the range of themes in the EFRC, with emphasis on those that are most significant to the challenges of nuclear energy.

9:20am **EN+AC-FrM4 Proof that UO₂ is an f-f Electron Correlated System**, *S.W. Yu, J.G. Tobin, J.C. Crowhurst*, Lawrence Livermore National Laboratory, *S. Sharma, J.K. Dewhurst*, Max Planck Institute, Halle, Germany, *P. Olalde-Velasco, W.L. Yang*, Lawrence Berkeley National Laboratory, *W.J. Stekhaus*, Lawrence Livermore National Laboratory **INVITED**

We have performed x-ray absorption experiments on uranium dioxide (UO₂) at the O 1s, U 4d, U 4f, and U 5d edges. After comprehensive energy calibrations for O 1s, U 4d, and U 4f spectra, we have used the U 4d and 4f spectra to sort the energetic positions of the 5f and the 6d states in the unoccupied band unambiguously. This demonstrates conclusively that UO₂ is an f-f Mott-Hubbard insulator, where the electronic repulsion between f electrons is responsible for the insulating state. Calculations performed within the U-corrected generalized gradient approximation of the optical response of UO₂ permit direct comparison with the absorption spectra and confirm the experimental results.

Lawrence Livermore National Laboratory is operated by Lawrence Livermore National Security, LLC, for the U.S. Department of Energy, National Nuclear Security Administration under Contract DE-AC52-07NA27344. This work is funded in part by the DOE Office of Science, Office of Basic Energy Science, Division of Materials Sciences and Engineering. This work is also funded in part by Laboratory Directed Research and Development (LDRD) Program (10-SI-016) of Lawrence Livermore National Laboratory. The Advanced Light Source (ALS) is supported by the Director, Office of Science, Office of Basic Energy Sciences, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231. We would like to thank Ian Hutcheon, Patrick Allen, Anthony Van Buuren, Trevor Wiley, and Joseph Zaig for valuable discussions. POV would like to acknowledge CONACyT Mexico.

10:00am **EN+AC-FrM6 Atomistic Models for Actinide-Actinide Oxide Interfaces**, *S.M. Valone*, Los Alamos National Laboratory

An important class of materials problems of great interest to nuclear energy production consists of composites of metals and metal oxides, and in particular, actinide metals and actinide oxides. Individually, either type of material, actinide or oxide, can involve strong electron correlation effects. At an interface, the situation becomes even more complex. In traversing a metal-metal oxide interface, a radical compositional change is encountered.

Most atomistic models address only metals, or only ceramics, but rarely both. In addition, the actinide oxides themselves enter multiple oxidation states, depending on the composition. Thus, in traversing an interface, the oxidation state need not change abruptly. As a result, these sorts of interfaces present new challenges that must be met in order to understand this important class of material systems. To address these needs, a new, "fragment" model Hamiltonian is constructed at the atomistic level, as opposed to the one-electron model Hamiltonians that underlie tight-binding and density functional theory methods. The model encompasses both actinides and actinide oxides, and provision is made for transitioning gradually through multiple oxidation states. The extremes of the models, the dioxides and the metals, map closely to existing models for these materials. The model for metals conforms generally to a modified embedded atom method (MEAM), meaning that the embedding function (atomistic site energy model) is analytical. The differences between the fragment Hamiltonian potential and the existing MEAM models appear in the explicit form of the embedding function and in the fact that there are two distinct terms in the embedding energy in the new model. The second term is critical to strongly-correlated-electron materials, as it is an atomistic analog to

terms appearing in Hubbard models. The model also possesses a sense of electron hopping that imparts ways to both regulate the net charge on sites in the material and to change important energy gaps that determine metallic and insulating behavior.

10:20am **EN+AC-FrM7 Structure and Properties of New Actinide Oxalates, Precursors of Fuel Materials**, *C. Tamain, B. Arab-CHapelet*, CEA Marcoule, France, *M. Rivenet, F. Abraham*, UCCS, France, *S. Grandjean*, CEA Marcoule, France

For future generation nuclear fuel cycle, actinide co-conversion processes are one option for the co-management of actinides. Oxalic acid is a well-known reagent to recover actinides thanks to the very low solubility of An(IV) and An(III) oxalate compounds in acidic solution. Therefore, considering mixed-oxide fuel or considering minor actinides incorporation in ceramic fuel materials for transmutation, oxalic co-conversion is convenient to synthesize mixed oxalate compounds, precursors of oxide solid solutions.

Up to now, only U(IV)-Ln(III) oxalate solid solutions have been completely structurally described started from single-crystals. In these oxalate compounds, a mixed-crystallographic site which accommodates both elements in spite of their different charges has been established. The extent of this study on powder compounds allowed to examine the influence of An(IV) and An(III) nature. The switch of actinide's nature causes unexpected structural modifications underlining the complexity of specific transuranium elements physical chemistry and the need to pursue studies on single crystal on these actinides.

As the existing oxalate single crystal syntheses are not adaptable to the actinide-oxalate system, several original crystal growth methods allowing the formation of mixed actinide oxalate crystals were first developed. Applied to the mixed actinide systems, they lead to the formation of the first mixed An(IV)-An(III) oxalate single crystals. The results, including the different structural resolutions, are presented.

10:40am **EN+AC-FrM8 Recent Work on Magnetism, Actinides and Defects at ORNL**, *G.M. Stocks, B.C. Larson*, Oak Ridge National Laboratory **INVITED**

The extent to which the collective effects of defects can be manipulated and controlled yields the combination of structural materials properties – strength, toughness, and resistance to degradation in extreme chemical and radiation environments. In this presentation I shall outline the scope of studies of the fundamental physics of dislocations and radiation-induced displacement cascades being conducted within the Center for Defect Physics (CDP) at Oak Ridge National Laboratory and its partner institutions. Within the CDP, the focus is on the quantitative measurement and direct quantum simulation of defects at the level of unit dislocation and cascade events. For dislocation interactions, the focus is on high-spatial-resolution techniques such as 3D X-ray microscopy and convergent beam electron diffraction, which measure the local strains/stresses near isolated defects *directly* and thereby *quantify* the interactions and dynamics of defects in the bulk. For displacement cascades, the focus is on quantitative measurement of the formation and time evolution of energetic-ion-induced atomic displacement cascades using ultrahigh-resolution time-resolved X-ray diffuse scattering measurements made possible by the ultrahigh brilliance of femtosecond X-ray pulses produced at the Linac Coherent

Light Source (LCLS) and the time-averaged brilliance of the Advanced Photon Source (APS). Theoretically, the focus is on developing high-fidelity models that treat spin and ion dynamics on an equal footing and to address system sizes and time scales commensurate with experiments. I will outline early progress with respect to addressing the feasibility of experimentally observing unit events and on developing *ab initio* electronic structure based theories of combined atomistic and spin dynamics. For the latter, I will show preliminary results for Fe that address the importance of the disruption of the magnetic state of Fe caused by the introduction of defects such as dislocations and displacement cascades that are based on large scale (~10,000 atom) models and order-N electronic structure methods.

Work supported by the “*Center for Defect Physics in Structural Materials*” which is a Department of Energy, Office of Science, Energy Frontier Research Center (EFRC).

Authors Index

Bold page numbers indicate the presenter

— A —

Abouimrane, A.: EN+NS-ThM3, 20
Abraham, F.: EN+AC-FrM7, 29
Abraham, J.: EN-ThP12, **27**
Acik, M.: EN+NS-ThM1, 20
Allara, D.L.: EN+NS-TuM2, 6
Allard, L.F.: EN-ThP17, 28
Allen, T.R.: EN-TuM1, 7
Amatucci, G.: EN+NS-ThM2, 20
Amine, K.: EN+NS-ThM3, **20**
Anderson, V.R.: TF+EN-TuM2, 7
Arab-CHapelet, B.: EN+AC-FrM7, 29
Asscher, M.: EN+EM+NS-WeM6, **13**
Aydil, E.S.: EN1+TF-WeA11, 18; EN1+TF-WeA2, 17; EN1+TF-WeA7, 17

— B —

Bae, J.: EN-ThP3, 25
Bag, S.: EN1+TF-WeA3, 17
Bailey, C.A.: EN+NS-WeM4, **15**
Baker, L.: TF+EN-TuM3, 7
Balci, S.: EN+EM+NS-WeM12, 14
Baldo, M.: EN+NS-WeM5, **15**
Banerjee, A.: EN+TF-TuA7, 11
Banerjee, P.: EN+NS-ThA11, 24
Barbuto, A.: EN-ThP19, 28
Barkhouse, D.A.R.: EN1+TF-WeA3, 17
Bartynski, R.A.: EN+NS-ThM2, 20
Batzill, M.: EN2+TF-WeA7, 18
Baughman, W.: EN+EM+NS-WeM12, 14
Baxter, J.B.: EN+EM+NS-WeM11, **14**
Bedair, EN+MS+VT-ThA8, **22**
Belharouak, I.: EN+NS-ThM3, 20
Bent, S.F.: EN-TuM9, 7
Berejnov, V.: EN+NS-ThA8, 23
Berger, O.: EN+EM+NS-WeM6, 13
Berry, N.: EN1+TF-WeA8, 17
Bharath, S.C.: EN+NS-ThA1, **22**
Bielawski, C.: EN+NS-ThM1, 20
Bilyy, O.I.: EN-ThP18, 28
Biswas, R.: EN+NS-TuA7, **10**
Bluhm, H.: EN1+TF-WeA8, 17
Bolotin, I.L.: EN+NS-WeM10, 16
Booth, J.-P.: EN+PS-MoM5, 1; EN+TF-TuA4, 11
Brehmer, F.: EN+PS-MoM3, 1
Brock, R.E.: EN+NS-WeM3, 15
Bulkin, P.: EN+PS-MoM8, 2
Burns, P.C.: EN+AC-FrM2, 29
Butler, L.: EN+EM+NS-WeM12, 14

— C —

Cahen, D.: EN+NS-WeM11, 16
Cai, C.: EN+TF-TuA9, 12
Campbell, S.A.: EN1+TF-WeA11, 18; EN1+TF-WeA2, 17
Camps, E.: EN+NS-ThA9, 24
Cass, L.: EN+NS-TuM11, 7
Castro, R.: EN-MoM10, 3
Cavanagh, A.S.: TF+EN-TuM2, 7; TF+EN-TuM3, 7
Cavarsan, F.A.: EN-ThP5, 25
Celik, O.: EN+NS-ThM2, 20
Chabal, Y.J.: EN+NS-ThA3, 23; EN+NS-ThM1, 20; EN+NS-TuM1, 6
Chakrapani, V.: EN+NS-ThM10, 20
Chang, J.P.: TF+EN-TuM4, 8
Chang, W.S.: EN+PS-MoM9, 2
Chao, C.-C.: EN+NS-ThA6, 23
Chen, C.: EN+EM+NS-MoA9, **5**
Chen, M.H.: EN+NS-WeM12, **16**
Cheng, A.-J.: EN1+TF-WeA11, 18
Cheng, M.: EN1+TF-WeA8, **17**
Chernomordik, B.: EN1+TF-WeA7, 17
Chey, S.J.: EN1+TF-WeA3, 17
Cho, J.: TF+EN-TuM4, **8**
Cirigliano, N.: TF+EN-TuM4, 8

Cliffel, D.E.: EN-ThP15, 27
Coates, N.: EN+NS-TuA9, 10
Coleman, E.: EN+NS-TuA11, 10
Cournoyer, J.: EN-ThP19, 28
Creatore, M.: EN+PS-MoM3, 1; EN+TF-TuA3, **11**
Crowhurst, J.C.: EN+AC-FrM4, 29
Cuevas-Ortiz, F.A.: EN1+TF-WeA9, 18
Cunningham, G.: EN+EM+NS-MoA3, 4

— D —

Dai, F.: EN+TF-TuA9, 12
Dasgupta, N.P.: EN+NS-ThA6, **23**
Davidson, J.: EN+NS-ThM5, 20
Davidson, J.L.: EN+NS-TuA12, 10; EN-ThP17, 28
Dawahre, N.: EN+EM+NS-WeM12, 14
Delattre, P.-A.: EN+PS-MoM5, 1; EN+TF-TuA4, 11
Devine, C.K.: TF+EN-TuM9, 8
Dewhurst, J.K.: EN+AC-FrM4, 29
Dhakal, T.: EN1+TF-WeA12, 18
Dhere, N.G.: EN1+TF-WeA1, 17
Di Camillo, D.: EN2+TF-WeA11, 19
Dillon, A.C.: TF+EN-TuM2, 7
Diniz, J.A.: EN-ThP5, **25**
Dinolfo, P.H.: EN-ThP8, 26
Doğan, İ.: EN+PS-MoM6, **2**
Dohnalova, K.: EN+PS-MoM6, 2
Donghwa, L.: EN+NS-WeM10, 16
Doolittle, W.A.: EN+TF-TuA11, 12
Dovidenko, K.: EN-ThP19, 28
Dreyer, D.R.: EN+NS-ThM1, **20**
Dunn, B.: TF+EN-TuM4, 8
Durstock, M.F.: EN+NS-WeM2, 14; EN+NS-WeM4, 15
Dutton, G.J.: EN+NS-WeM9, 15

— E —

Efstathiadis, H.: EN+MS+VT-ThA3, **22**
Emziane, M.: EN-ThP11, 26
Engeln, R.: EN+PS-MoM3, 1
Escobar-Alarcón, L.: EN+NS-ThA9, 24

— F —

Feist, R.K.: EN1+TF-WeA2, 17
Feulner, P.: EN+NS-TuM2, 6
Filler, M.A.: EN+EM+NS-MoA7, 4; EN+EM+NS-WeM3, **13**; EN+NS-ThM10, 20
Frederick, M.: EN+NS-TuM11, 7
Fujishima, A.: EN-ThP1, 25; EN-ThP7, 26

— G —

Ganta, L.: EN1+TF-WeA12, 18
García-Aguirre, M.: EN1+TF-WeA9, 18
García-Zarco, O.: EN+NS-ThA9, 24
Gartstein, Y.N.: EN+NS-TuM1, 6
George, S.M.: TF+EN-TuM2, 7; TF+EN-TuM3, 7
Ghosh, N.: EN-ThP17, 28
Glazek, W.: EN-ThP12, 27
Goislard de Monsabert, T.: EN1+TF-WeA3, 17
Gokmen, T.: EN1+TF-WeA3, 17
Grandjean, S.: EN+AC-FrM7, 29
Gregorzcyk, K.E.: EN+NS-ThA11, **24**
Gregorkiewicz, T.: EN+PS-MoM6, 2
Gregory, C.: EN+EM+NS-MoA3, 4
Guglietta, G.W.: EN+EM+NS-WeM11, 14
Guha, S.: EN+TF-TuA7, 11
Gunawan, O.: EN1+TF-WeA3, 17
Gunning, B.: EN+TF-TuA11, **12**
Gunther, D.: EN-ThP15, **27**
Guo, T.: EN+TF-TuA9, 12

— H —

Haight, R.: EN1+TF-WeA3, 17
Haldar, P.: EN+MS+VT-ThA3, 22
Hamoudi, H.: EN+NS-TuM2, 6
Hanley, L.: EN+NS-WeM10, 16
HarLavan, R.: EN+NS-WeM11, 16
Harris, N.: EN+EM+NS-WeM12, 14

Haspert, L.C.: EN+NS-ThA4, **23**
Hemminger, J.C.: EN1+TF-WeA8, 17
Hersam, M.C.: EN+NS-WeM2, 14; EN+NS-WeM3, 15; EN+NS-WeM4, 15
Hill, I.: EN+NS-WeM1, 14
Hitchcock, A.P.: EN+NS-ThA8, **23**
Hla, S.-W.: EN+NS-TuM9, 6
Hnatush, S.O.: EN-ThP18, 28
Hogan, W.W.: EN-MoM1, **2**
Holloway, P.H.: EN+EM+NS-MoA8, 4
Holman, Z.: EN+EM+NS-WeM1, 13
Hong, S.: EN-ThP3, 25
Hu, X.: TF+EN-TuM10, 9
Huang, C.-H.: EN+EM+NS-MoA1, 4
Huang, J.Y.: EN+NS-ThM11, **21**
Hurst, K.E.: TF+EN-TuM2, 7
Hwang, D.: EN+PS-MoM9, 2
Hwang, J.: EN+EM+NS-MoA9, 5

— I —

Iagarashi, M.: EN+EM+NS-MoA1, 4

— J —

Jadhav, P.: EN+NS-WeM5, 15
Javey, A.: EN+EM+NS-WeM9, **13**
Jennings, G.K.: EN-ThP15, 27
Jeon, J.: EN-ThP9, **26**
Johnson, E.V.: EN+PS-MoM5, 1; EN+TF-TuA4, 11
Jones, J.: EN+NS-ThA10, **24**
Jones, K.: TF+EN-TuM2, 7
Juang, B.: EN+EM+NS-MoA9, 5
Jur, J.S.: TF+EN-TuM9, 8

— K —

Kalanyan, B.: TF+EN-TuM9, 8
Kang, W.P.: EN+NS-TuA12, 10; EN-ThP17, 28
Kao, P.: EN+NS-TuM2, 6
Karmel, H.J.: EN+NS-WeM3, 15
Kasouit, S.: EN+PS-MoM8, **2**
Kassakian, J.G.: EN-MoA3, **5**
Katayama, K.: EN-ThP1, 25; EN-ThP7, 26
Kaul, A.: EN1+TF-WeA1, **17**
Kessels, W.M.M.: EN+PS-MoM10, **2**
Khare, A.: EN1+TF-WeA11, 18; EN1+TF-WeA7, 17
Kim, D.: EN+PS-MoM9, 2; TF+EN-TuM9, **8**
Kim, N.: EN-ThP10, 26; EN-ThP9, 26
Kim, S.: EN+EM+NS-MoA9, 5; EN+EM+NS-WeM12, **14**
Kim, Y.-G.: EN+PS-MoM9, 2
Klem, E.J.D.: EN+EM+NS-MoA3, **4**
Klimov, V.I.: EN+NS-TuM3, **6**
Kobayashi, N.P.: EN+NS-TuA11, 10
Kocha, S.: TF+EN-TuM2, 7
Koeck, F.A.M.: EN-ThP2, 25
Kohl, P.A.: EN+NS-ThM10, 20
Koleske, D.: EN+TF-TuA11, 12
Kong, L.: EN+NS-ThA3, 23
Kongkanand, A.: TF+EN-TuM3, 7
Koo, H.J.: TF+EN-TuM9, 8
Kortshagen, U.: EN+EM+NS-WeM1, **13**
Kotru, S.: EN-ThP16, **27**
Kramer, N.J.: EN+PS-MoM6, 2
Kung, P.: EN+EM+NS-WeM12, 14

— L —

Lach, P.: EN-ThP12, 27
Langreth, D.C.: EN+NS-ThA3, 23
Larson, B.C.: EN+AC-FrM8, 29
Law, M.: EN1+TF-WeA8, 17
Le Tarte, L.: EN-ThP19, **28**
Le, T.P.: EN+EM+NS-WeM11, 14
Lee, C.: EN-ThP3, **25**
Lee, D.J.: EN-ThP13, **27**
Lee, H.-J.: EN+PS-MoM9, 2
Lee, J.H.: EN-ThP3, 25

Lee, K.: TF+EN-TuM9, 8
Lee, M.: EN-ThP3, 25
Lee, S.: EN+TF-TuA11, 12
Lee, S.B.: EN+NS-ThA4, 23
Lee, W.: EN-ThP10, 26; EN-ThP9, 26
Leever, B.J.: EN+NS-WeM2, 14; EN+NS-WeM4, 15
Lei, Z.: EN+TF-TuA9, 12
Leick, N.: TF+EN-TuM2, 7
Leighton, C.: EN1+TF-WeA11, 18
Lewis, J.: EN+EM+NS-MoA3, 4
Li, H.: EN+TF-TuA9, 12
Li, J.: EN+NS-ThA3, 23
Li, L.: EN+TF-TuA9, 12
Li, Q.: EN+TF-TuA11, 12
Li, W.: EN+TF-TuA9, 12
Li, Y.: EN1+TF-WeA7, 17
Lima, L.P.B.: EN-ThP5, 25
Lin, S.-H.: EN+EM+NS-MoA1, 4
Liu, C.Y.: EN+EM+NS-WeM1, 13
Liu, Y.: EN1+TF-WeA8, 17
Liu, Z.: EN1+TF-WeA8, 17
Lohn, A.J.: EN+NS-TuA11, 10
Lowder, J.E.: EN+TF-TuA11, 12
Lozzi, L.: EN2+TF-WeA11, 19
Lu, J.: EN+NS-ThM3, 20
Lu, Y.C.: EN+NS-ThA2, 22
Luttrell, T.: EN2+TF-WeA7, 18
Lyding, J.W.: EN1+TF-WeA10, 18

— M —

MacElroy, J.M.D.: EN2+TF-WeA8, 19
Majidi, H.: EN+EM+NS-WeM11, 14
Malko, A.V.: EN+NS-TuM1, 6
Maness, Jr., L.V.: EN+MS+VT-ThA1, 22
Manno, M.: EN1+TF-WeA11, 18
Mansour, A.N.: EN+NS-ThA2, 22
Margarella, A.: EN1+TF-WeA8, 17
Marks, T.J.: EN+NS-WeM2, 14; EN+NS-WeM3, 15; EN+NS-WeM4, 15
Masters, A.E.: TF+EN-TuM10, 9
McFarlane, H.F.: EN-MoA1, 5
Meisner, G.P.: EN-TuM5, 7
Melendez-Lira, M.A.: EN1+TF-WeA9, 18
Membreno, D.: TF+EN-TuM4, 8
Meng, Y.: EN+TF-TuA9, 12
Minami, T.: EN-ThP4, 25
Mitzi, D.B.: EN1+TF-WeA3, 17
Miyata, T.: EN-ThP4, 25
Miyoshi, J.: EN-ThP5, 25
Mohanty, A.: EN+NS-WeM5, 15
Morris-Cohen, A.: EN+NS-TuM11, 7
Morrish, R.: EN2+TF-WeA8, 19
Moseley, M.W.: EN+TF-TuA11, 12
Moutinho, H.R.: EN1+TF-WeA1, 17
Mu, R.: EN+NS-ThA10, 24
Murayama, A.: EN+EM+NS-MoA1, 4
Murray, I.P.: EN+NS-WeM2, 14
Musho, T.D.: EN+NS-TuM10, 6
Musin, I.R.: EN+EM+NS-WeM3, 13
Myung, K.: EN-ThP10, 26

— N —

Nagpal, P.: EN+EM+NS-MoA6, 4
Nahor, A.: EN+EM+NS-WeM6, 13
Naito, K.: EN-ThP1, 25; EN-ThP7, 26
Nakata, K.: EN-ThP1, 25; EN-ThP7, 26
Nalamasu, O.: EN-MoM10, 3
Nampoori, H.V.: EN-ThP16, 27
Nemanic, V.: EN-ThP2, 25
Nemanich, R.J.: EN-ThP2, 25
Neppel, S.: EN+NS-TuM2, 6
Neria-Gonzalez, M.I.: EN1+TF-WeA9, 18
Nguyen, H.M.: EN+NS-TuM1, 6
Nijem, N.: EN+NS-ThA3, 23
Nishi, Y.: EN-ThP4, 25
Nomoto, J.: EN-ThP4, 25
Norris, D.J.: EN+NS-TuA1, 10; EN1+TF-WeA7, 17

— O —

Ohno, Y.: EN+EM+NS-MoA1, 4
Olalde-Velasco, P.: EN+AC-FrM4, 29
Ortiz, C.: EN2+TF-WeA12, 19
Otaño, W.: EN2+TF-WeA12, 19
Ozimek, P.: EN-ThP12, 27

— P —

Palomaki, P.K.B.: EN-ThP8, 26
Pan, X.: EN+EM+NS-MoA9, 5
Pantojas, V.: EN2+TF-WeA12, 19
Park, H.: EN+NS-ThA10, 24
Parsons, G.N.: TF+EN-TuM9, 8
Patrinós, A.A.N.: EN-MoM8, 3
Paxton, W.F.: EN+NS-TuA12, 10
Peña Martin, P.: EN1+TF-WeA10, 18
Pereira, N.: EN+NS-ThM2, 20
Perera, U.G.E.: EN+NS-TuM9, 6
Perng, Y.-C.: TF+EN-TuM4, 8
Petkovich, N.: EN+NS-ThM5, 20
Phillips, J.: EN+EM+NS-MoA9, 5
Phillip, S.R.: EN+NS-WeM10, 16
Piao, H.: EN-ThP19, 28
Plaisant, M.: EN+EM+NS-MoA8, 4
Pleticha, F.D.: EN+NS-WeM10, 16
Ponduri, S.: EN+PS-MoM3, 1
Pouliquen, S.: EN+PS-MoM5, 1; EN+TF-TuA4, 11

Predith, A.: EN-ThP14, 27
Prinz, F.: EN+NS-ThA6, 23

— Q —

Qian, Y.: EN+NS-ThM5, 20
Quinlan, R.A.: EN+NS-ThA2, 22

— R —

Rahman, M.: EN2+TF-WeA8, 19
Rangan, S.: EN+NS-ThM2, 20
Rangel-Chavez, L.G.: EN1+TF-WeA9, 18
Rentsch, J.: EN+PS-MoM4, 1
Reutt-Robey, J.E.: EN+NS-ThA1, 22
Rivenet, M.: EN+AC-FrM7, 29
Robey, S.W.: EN+NS-WeM9, 15
Roca i Cabarrocas, P.: EN+PS-MoM8, 2
Rockett, A.: EN1+TF-WeA10, 18
Rodil, S.E.: EN+NS-ThA9, 24
Rodríguez-Vindas, D.: EN2+TF-WeA12, 19
Rozanski, P.: EN-ThP12, 27
Rubloff, G.W.: EN+NS-ThA11, 24; EN+NS-ThA4, 23; TF+EN-TuM5, 8
Rudisill, S.: EN+NS-ThM5, 20
Ruggieri, F.: EN2+TF-WeA11, 19
Rusli, F.: EN+NS-ThM10, 20

— S —

Sa'ar, A.: EN+EM+NS-WeM6, 13
Sakai, M.: EN-ThP1, 25; EN-ThP7, 26
Samukawa, S.: EN+EM+NS-MoA1, 4
Santucci, S.: EN2+TF-WeA11, 19
Scarel, G.: TF+EN-TuM10, 9
Schneller, E.: EN1+TF-WeA1, 17
Schüpbach, B.: EN+NS-TuM2, 6
Segalman, R.A.: EN+NS-TuA9, 10
Seitz, O.: EN+NS-TuM1, 6
Shao-Horn, Y.: EN+NS-ThA2, 22
Sharma, K.: EN+TF-TuA3, 11
Sharma, S.: EN+AC-FrM4, 29
Shen, G.: EN+EM+NS-WeM12, 14
Shin, N.: EN+EM+NS-WeM3, 13
Siekhaus, W.J.: EN+AC-FrM4, 29
Sigmon, G.: EN+AC-FrM2, 29
Silva, A.R.: EN-ThP5, 25
Silva-Bermudez, P.: EN+NS-ThA9, 24
Sinnott, S.B.: EN+NS-WeM10, 16
Sivaram, S.: EN+EM+NS-MoA7, 4; EN+EM+NS-WeM3, 13
Sivula, K.: EN2+TF-WeA9, 19
Smith, N.J.: EN+EM+NS-WeM5, 13
Song, W.: EN+NS-ThA1, 22
Souren, F.M.M.: EN+PS-MoM4, 1
Stein, A.: EN+NS-ThM5, 20

Steinfeld, E.: EN-MoM3, 3
Stocks, G.M.: EN+AC-FrM8, 29
Stumper, J.: EN+NS-ThA8, 23
Susac, D.: EN+NS-ThA8, 23
Sussman, J.: EN+NS-WeM5, 15
Swanson, S.A.: EN-TuM3, 7

— T —

Takagi, K.: EN-ThP1, 25; EN-ThP7, 26
Takei, H.: EN-ThP1, 25; EN-ThP7, 26
Talapin, D.V.: EN+NS-TuA3, 10
Tamaín, C.: EN+AC-FrM7, 29
Tang, B.: EN+TF-TuA9, 12
Taylor, P.C.: EN+TF-TuA1, 11
Temple, D.: EN+EM+NS-MoA3, 4
Terfort, A.: EN+NS-TuM2, 6
Thiruvengadam, S.: EN1+TF-WeA3, 17
Thorpe, R.: EN+NS-ThM2, 20
Tisdale, W.A.: EN+NS-TuM5, 6
Tobin, J.G.: EN+AC-FrM1, 29; EN+AC-FrM4, 29
Todorov, T.K.: EN1+TF-WeA3, 17
Toker, G.: EN+EM+NS-WeM6, 13
Tolk, N.H.: EN+NS-ThA10, 24; EN-ThP17, 28
Tomba, G.S.: EN+NS-TuA11, 10
Tosun, B.S.: EN1+TF-WeA2, 17; EN1+TF-WeA7, 17
Tseng, C.T.: EN+NS-WeM12, 16
Tseng, W.H.: EN+NS-WeM12, 16
Tyler, T.P.: EN+NS-WeM3, 15

— U —

Unocic, K.: EN-ThP17, 28
Urban, J.: EN+NS-TuA9, 10

— V —

Valone, S.M.: EN+AC-FrM6, 29
van de Sanden, M.C.M.: EN+PS-MoM3, 1; EN+PS-MoM4, 1; EN+PS-MoM6, 2; EN+TF-TuA3, 11
Vanhart, D.: EN1+TF-WeA12, 18
Vasekar, P.: EN1+TF-WeA12, 18
Vasquez, K.A.: TF+EN-TuM10, 9
Vasylyv, O.M.: EN-ThP18, 28
Venstrom, L.: EN+NS-ThM5, 20
Verheijen, M.A.: EN+PS-MoM6, 2
Vincent-Johnson, A.J.: TF+EN-TuM10, 9
Vu, A.: EN+NS-ThM5, 20

— W —

Wade, T.C.: EN-ThP17, 28
Wagner, F.T.: TF+EN-TuM3, 7
Walker, D.G.: EN+NS-TuM10, 6
Wang, J.Y.: EN+NS-WeM12, 16
Wang, M.: EN+NS-WeM1, 14
Wang, X.-Y.: EN+EM+NS-MoA1, 4
Wang, Z.: EN-ThP3, 25
Weiss, E.A.: EN+NS-TuM11, 7
Welzel, S.: EN+PS-MoM3, 1
Westgate, C.R.: EN1+TF-WeA12, 18
Wi, S.-S.: EN+PS-MoM9, 2
Wierer, J.: EN+TF-TuA11, 12
Wilbert, S.: EN+EM+NS-WeM12, 14
Williams, E.D.: EN-MoM5, 3
Wills, A.W.: EN1+TF-WeA7, 17
Wittig, J.E.: EN-ThP17, 28
Wolden, C.A.: EN2+TF-WeA8, 19
Woodroof, M.: TF+EN-TuM9, 8
Wu, C.L.: EN+NS-WeM12, 16
Wu, H.: EN+NS-ThA3, 23
Wu, W.: EN+NS-ThM3, 20

— X —

Xu, Z.: EN+TF-TuA9, 12

— Y —

Yaffe, O.: EN+NS-WeM11, 16
Yan, B.: EN+TF-TuA7, 11
Yang, J.: EN+EM+NS-WeM1, 13; EN+TF-TuA7, 11
Yang, W.L.: EN+AC-FrM4, 29
Yang, Z.G.: EN-MoA6, 5
Yee, S.: EN+NS-TuA9, 10

Yitzchaik, S.: EN+EM+NS-WeM6, 13
Yoo, S.J.: EN+PS-MoM1, **1**
Yu, S.W.: EN+AC-FrM1, 29; EN+AC-FrM4, **29**
— **Z** —
Zajec, B.: EN-ThP2, 25

Zavadil, K.R.: EN+NS-ThA1, 22
Zelechowski, M.: EN-ThP12, 27
Zhang, F.: EN+TF-TuA9, 12
Zhang, Y.: EN+NS-TuM9, **6**
Zhang, Z.: EN+NS-ThM3, 20
Zhao, Y.: EN+NS-ThA3, 23

Zharnikov, M.: EN+NS-TuM2, **6**
Zhou, D.: EN+TF-TuA9, 12
Zhu, L.: EN+NS-ThA10, 24
Zumer, M.: EN-ThP2, **25**