

**SYMPOSIUM L**  
**Materials for Photovoltaics**

November 29 - December 2, 2004

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\* Invited paper

**8:30 AM \*L1.1**  
**Dye Sensitized Nanocrystalline Photovoltaic Cells.**  
Michael Graetzel, FSB, EPFL, Lausanne, Switzerland.

The dye sensitized nanocrystalline solar cell (DSC) employs organic dyes or transition metal complexes for spectral sensitization of oxide semiconductors, such as TiO<sub>2</sub>, ZnO, SnO<sub>2</sub>, Nb<sub>2</sub>O<sub>5</sub>. Mesoscopic films of these materials are contacted with redox electrolytes, ionic liquids, amorphous organic hole conductors or conducting polymers as well as inorganic semiconductors. Light harvesting occurs efficiently over the whole visible and near IR range due to the very large internal surface area of the films. Judicious molecular engineering allows the photoinduced charge separation to proceed quantitatively within femtoseconds. The overall power conversion efficiency of the new solar cell for standard AM 1.5 solar radiation stands presently at 11.2 percent. The lecture will highlight recent progress in the development of low cost solar cells for practical use. Major points to be covered concern the stability of operation of sealed cells under prolonged light soaking including UV-light exposure and the effects of thermal stress. Stable cell performance both under prolonged illumination and exposure to high temperature has recently been achieved through judicious engineering of the oxide interface using self assembled monolayers of sensitizers and amphiphilic coadsorbents. Advancement in the understanding of the factors that govern photovoltaic performance will be discussed. Recent improvements of cell components, in particular the sensitizer, the mesoporous oxide films and the hole transport materials will be communicated. Literature 1) M. Graetzel, Nature, London, 414, 338, 2001. 2) B. O'Regan and M. Graetzel, Nature, London, 353, 737 (1991). 3 a) A. Hagfeldt and M. Graetzel, Acc. Chem. Res. 33, 269 (2000) b) P.Wang, S. M. Zakeeruddin, J. E. Moser, M. K. Nazeeruddin, T. Sekiguchi and M. Graetzel Nature Mat. 2, 402 (2003),

**9:00 AM L1.2**  
**Progress in Producing Large Area Flexible Dye Sensitized Solar Cells.** Krishna C. Mandal, Michael Choi, Caleb C. Noblitt and R. David Rauh; Materials and Devices Research Division, EIC Laboratories, Inc., Norwood, Massachusetts.

Dye sensitized nanocrystalline TiO<sub>2</sub> solar cells are reported with over 11% efficiency and are extremely promising as very low cost and lightweight photovoltaic sources. However, most reports are for cells of low area fabricated on glass, which withstands processing temperatures of 450°C. In this paper, we describe the fabrication and performance of cells made on flexible ITO-coated polyethylene terephthalate substrates (60 ohms/sq) with 6 x 3 sq inches dimensions. The cells were made using a 150°C slow sintering process for the nano-TiO<sub>2</sub>, a plasticized PVDF-based polymer electrolyte, and a sputtered Pt on PET counter electrode. Initially, these cells showed up to two orders of magnitude lower efficiency than the smaller glass cells. The lower efficiency originates from 1) a reduced TiO<sub>2</sub> processing temperature, and 2) a higher sheet resistivity of ITO on plastic than on glass. To improve the efficiency in the large area cells, we enhanced the ITO current collection efficiency with metallization fingers. The fingers occluded <10% of the light collection area and resulted in a 5-10 fold increase in short circuit current under normal solar illumination compared to cells without metallization. Further improvements were realized by passivating the metallization fingers at the metal/electrolyte interface.

**9:15 AM L1.3**  
**Grafting of Polymers From Modified Titania Surfaces: Application to Dye-Sensitized Solar Cells.** Devon Shipp and Brian J. Lowes; Department of Chemistry, Clarkson University, Potsdam, New York.

Dye-sensitized solar cells (DSSCs) are photovoltaic devices that have attracted significant interest over the past decade or so because they offer a cheap alternative to conventional inorganic solar cells (e.g. see O'Regan and Gratzel, Nature (1991), vol. 353, p. 737). Although excellent conversion rates for solar-to-electricity of 10% have been achieved, one of the main problems facing wide usage of DSSCs is poor stability, particularly at higher temperatures. This paper will present a new approach in tackling this issue by incorporating the dye component of the cell into a polymer that is covalently attached to the titanium dioxide. The synthetic approach to surface modification with free radical initiators and polymerizable groups will be addressed, as will their subsequent polymerizations and modification with light absorbing moieties. Surface modifications of titania nanoparticles (Degussa P25, particle size 21 nm) have been achieved using organic acid chlorides that react with the titanol groups on the surface of the titania particles. These organic compounds include one with an azo

free radical initiator-containing group, another with an atom transfer radical polymerization (ATRP) initiating group (an alkyl halide), and a third that is a vinyl compound. While the density of grafting using this approach is relatively low (compared with what can be achieved using condensation of titanates on the surface), growth of polymer was observed, giving nanocomposite materials with approximately 5-30% organics. Two monomers have been used: styrene and 4-vinyl pyridine. The latter forms polymers that can be complexed with ruthenium salts in order to create a dye similar to that used in other DSSCs. Various spectroscopic methods, including IR and UV/visible, have been used to characterize these nanocomposites.

**9:30 AM L1.4**  
**Amphiphilic Dye for Solid State Dye Sensitized Solar Cells.** Lukas Schmidt-Mende, Shaik M. Zakeeruddin and Michael Graetzel; LPI, EPFL, Lausanne, Vaud, Switzerland.

We report a solid state solar cell with a record efficiency of 4% under simulated sunlight (AM1.5global, 100mW/cm<sup>2</sup>). This was made possible by using a new amphiphilic dye with hydrophobic spacers in combination with Spiro-OMeTAD. We attribute the significant improvement in performance to the self assembly of the dye to form a compact monolayer on the TiO<sub>2</sub> surface with hydrophobic chains working as blocking layer between Spiro-OMeTAD and TiO<sub>2</sub> reducing the back electron transfer. In addition, we studied the influence of nanoporous TiO<sub>2</sub> film thickness on the performance of the device. These results demonstrate the high potential for solid state dye sensitized solar cells to compete with amorphous silicon cells as low cost alternative.

**9:45 AM L1.5**  
**Solid State Dye Sensitized Solar Cells Incorporating Polyelectrolyte Multilayer Composites.** Geoffrey Marc Lowman, Hiroaki Tokuhisa, Jodie L. Lutkenhaus and Paula T. Hammond; Dept. of Chemical Engineering, MIT, Cambridge, Massachusetts.

Dye-sensitized solar cells (DSSCs) based on TiO<sub>2</sub> have generated tremendous attention due to their potential to replace Si solar cells with a material that is relatively cheap and simple to process. One hurdle for DSSC design remains their reliance on liquid or gel electrolytes that present problems in sealing and stability. We report on a DSSC system that combines a TiO<sub>2</sub> layer, sensitized by efficient Ru-based dyes, which incorporates a polyelectrolyte multilayer (PEO-PAA or LPEI-PAA) / oligoethylene glycol dicarboxylic acid composite as a solid-state electrolyte. This composite can be doped with I<sup>-</sup> and I<sup>-</sup> from LiI / I<sub>2</sub> or iodide based ionic liquids to form an I<sup>-</sup>/I<sub>3</sub><sup>-</sup> redox couple with ionic conductivities on the order of 1 x 10<sup>-4</sup> S / cm. Potential light trapping phenomena within a patterned TiO<sub>2</sub> layer, produced by liquid phase deposition and soft lithography techniques, and its impact on device performance will also be discussed.

**10:30 AM L1.6**  
**Low Temperature Deposition of Indium-Zinc-Oxide Thin Films For Polymer Based Photovoltaic Devices.** Matthew Taylor<sup>1</sup>, Dennis W. Readey<sup>1</sup>, Charles W. Teplin<sup>2</sup>, Maikel F.A.M. van Hest<sup>2</sup>, Jeff L. Alleman<sup>2</sup>, Matthew S. Dabney<sup>2</sup>, Lynn M. Gedvilas<sup>2</sup>, Brian M. Keyes<sup>2</sup>, Bobby To<sup>2</sup>, John D. Perkins<sup>2</sup> and David S. Ginley<sup>2</sup>; <sup>1</sup>Materials Science, Colorado School of Mines, Golden, Colorado; <sup>2</sup>National Renewable Energy Laboratory, Golden, Colorado.

Indium zinc oxide (IZO) is a promising family of materials for transparent electrode applications in photovoltaic and display devices. IZO can be sputtered at low temperature and still retain the desired properties of high electrical conductivity and optical transparency. The immediate benefits of low temperature deposition are that temperature-sensitive polymer materials can be utilized as substrates and that lower processing costs may be realized through energy savings. The use of IZO can also help reduce the raw material cost of the TCO layer if large quantities of indium (~20 atomic %) can be replaced with zinc, a more economical metal. To explore the potential of IZO as a "low temperature" TCO, we deposited compositionally graded libraries of indium zinc oxide from ceramic In<sub>2</sub>O<sub>3</sub> and ZnO targets by dc magnetron sputtering onto 2//x2// glass substrates which were heated to 100°C. Combinatorial mapping tools were utilized to determine the In:Zn metals ratio, the optical transmission and reflection characteristics (0.25 - 25 μm) and the structural and electrical properties. In addition, the carrier mobility, carrier concentration and surface roughness were measured on discrete samples cut from the larger 2//x2// libraries. The composition range investigated was 4 to 95 atomic % In for Zn. A maximum in conductivity of ~3000(ohm-cm)<sup>-1</sup> was found in an amorphous film with a composition of ~70 atomic %In for Zn. The amorphous region extended from ~45 to 75% In with crystalline regions at both lower and higher indium content. The mobility and carrier concentration for the amorphous films exceeded 30cm<sup>2</sup>/V-s and 8x10<sup>20</sup>/cm<sup>3</sup>, respectively. The rms roughness of the as-deposited amorphous films

was on the order of 2 Å. All films, regardless of crystallinity, showed optical transmission greater than 80% in the visible spectrum. The results of work function measurements and annealing experiments will also be presented. These results clearly demonstrate the potential for IZO as a TCO for next-generation thin film and polymer-based photovoltaics.

#### 10:45 AM L1.7

**Effect of Atmospheres on Photovoltaic Properties of Nanoporous TiO<sub>2</sub>/Semiconducting Polymer Heterojunction Solar Cell.** Akira Watanabe<sup>1</sup> and Atsuo Kasuya<sup>2</sup>; <sup>1</sup>Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai, Japan; <sup>2</sup>Center for Interdisciplinary Research, Tohoku University, Sendai, Japan.

Dye sensitized solar cells (DSSC) based on nanocrystalline TiO<sub>2</sub> have attracted considerable interest because of the excellent power conversion performance and the efficient low cost as an alternative to silicon solar cell. Recently, TiO<sub>2</sub>/semiconducting polymer solar cells have been studied, where the liquid electrolyte of DSSC is replaced with p-type semiconducting polymer as a hole conducting material. Although those solid-state photovoltaic devices are promising candidates, unfortunately, up to now none of these efforts has led to a power conversion efficiency above 1%. In comparison with silicon solar cell, the properties of the space charge layer of the TiO<sub>2</sub>/semiconducting polymer is very complicated owing to the nanoporous structure of TiO<sub>2</sub> and the heterojunction between inorganic and organic semiconductors. The conversion efficiency of the device often depends on the manufacturing process of the cell because the nature of the nanoporous heterojunction has not yet been completely elucidated. The atmospheres during the measurements also influence the device performance because the nanosurface of the heterojunction is exposed to the atmospheres due to the porosity of the TiO<sub>2</sub> layer. The aim of this study is to investigate the effect of atmosphere on the photovoltaic properties of a TiO<sub>2</sub>/semiconducting polymer cell. In this work, we focused on a bilayer-type cell consisting of TiO<sub>2</sub> and semiconducting polymer layers to simplify photovoltaic behavior. The poly(3-hexylthiophene) (P3HT) was adopted as a p-type semiconducting polymer. The photovoltaic properties of the nanoporous TiO<sub>2</sub>/P3HT heterojunction solar cells in vacuo were compared with those in air and O<sub>2</sub> atmosphere. Photovoltaic properties of the TiO<sub>2</sub>/P3HT heterojunction solar cell were studied by photovoltammetry under periodic photoirradiation, which is effective in examining the photo- and dark current-potential profiles simultaneously in the same experiment. The open-circuit voltage (V<sub>oc</sub>) of the TiO<sub>2</sub>/P3HT cell significantly depended on the atmosphere in the measurements. Accompanying the increase of the dark current, the photovoltammogram in vacuo showed the lower V<sub>oc</sub> than that in air. The stepwise increase of the dark current after pulse irradiation was observed in the transient current-time profile for the TiO<sub>2</sub>/P3HT cell in vacuo. The difference spectra of the TiO<sub>2</sub>/P3HT cell during photoirradiation in vacuo showed the increase of a broad absorption band attributed to trapped charge carriers in the near-IR region. In the case of the TiO<sub>2</sub>/P3HT heterojunction in vacuo, the trapped charge carrier is stable and long-lived after the photoirradiation, which induces the increase of the dark current.

#### 11:00 AM L1.8

**Synthesis and Temperature Stability of Pure Crystalline Titania Nanotubes.** B. Poudel<sup>1</sup>, W. Z. Wang<sup>1</sup>, Christopher Dames<sup>2</sup>, Jianyu Huang, S. Kunwar<sup>1</sup>, Dezhi Wang<sup>1</sup>, D. Banerjee<sup>1</sup> and Z. Ren<sup>1</sup>; <sup>1</sup>Physics, Boston College, Chestnut Hill, Massachusetts; <sup>2</sup>Department of Mechanical Engineering, MIT, Cambridge, Massachusetts.

Large quantity of pure titania nanotubes were synthesized from anatase nanopowder as well as micronpowder by chemical method, having average diameter about 9 nm, wall thickness about 2.5 nm, and average length about 600 nm. XRD, HRTEM, SEM, SAED and EDX were applied to characterize as-prepared nanotubes. Their crystallization, structural and phase stability at high temperatures were systematically studied. As-prepared nanotubes are usually contaminated with Na impurities and are not well crystallized but under certain optimized synthesis conditions those impurity phases could completely be removed and pure perfectly crystallized nanotubes were prepared. The volume filling fraction of the autoclave as well as the concentration of the acid wash, were found to be very important at controlling the crystallinity and purity of the resulting nanotubes. All other TiO<sub>2</sub>-derived nanotube phases reported by different groups were observed under different synthesis conditions and studied, which solves the contradiction among the different results. The effects of acidic treatment as well as the reaction temperature were also studied.

#### 11:15 AM L1.9

**Effect of Anodization Bath Chemistry on Photochemical Water Splitting Using Titania Nanotubes.** Craig A. Grimes<sup>2,1</sup>, Karthik Shankar<sup>2,1</sup>, Gopal K. Mor<sup>2,1</sup> and Qingyn Cai<sup>1,2</sup>; <sup>1</sup>Penn State

University, University Park, Pennsylvania; <sup>2</sup>Penn State University, University Park, Pennsylvania.

For sustainable generation of energy from photovoltaic and wind-energy systems the frequent mismatch between energy supply and energy demand is a significant impediment. The simultaneous collection and storage of energy promises greater efficiency and lower cost than strategies where collection and storage are done sequentially. This paper focuses on the development of a photochemical conversion system that uses UV Bandgap illumination of photoanodes comprised of titania nanotube arrays, oriented perpendicularly to the surface of the substrate, to drive water-splitting. The photoresponse of the titania nanotube array-based photoanodes was evaluated by measuring the rate of water-splitting reaction to hydrogen and oxygen, which is proportional to the photocurrent density. Gas evolves were sampled and analyzed by a gas chromatograph. Titania nanotubes are versatile nanoporous structures whose size, crystallinity, length, composition and optical absorption can be readily and precisely controlled during synthesis. The nanotubes are prepared by potentiostatic anodization in fluoride ion containing electrolytes. We find that for titania nanotubes of similar morphology and phase, the anodization bath chemistry has a large influence on the magnitudes of the resulting photocurrent densities. When the anodization bath contained sulfate ion species, maximum photocurrent densities of about 1 mA/cm<sup>2</sup> were obtained while baths containing carboxylate ions in similar concentrations resulted in nanotubes with photocurrent densities as high as 25 mA/cm<sup>2</sup>. The photoresponse of the titania nanotubes can be extended into the visible region by control of nanotube diameter and crystallinity.

#### 11:30 AM L1.10

**Noncovalent synthesis of multilayer films that generate photocurrent and that exhibit photoswitchable wettability.** John C. MacDonald, W. Grant McGimpsey, Ernesto Soto, Christopher C. Cooper and Kasim Biyikli; Department of Chemistry & Biochemistry, Worcester Polytechnic Institute, Worcester, Massachusetts.

We have developed a noncovalent strategy to fabricate ordered multilayer thin films that generate electric current upon irradiation. We have used a similar strategy to fabricate thin films whose wettability that can be varied in response to light. In these systems, multiple layers of organic ligands are assembled by complexation with layers of metal ions. We show that complexes between 2,6-dicarboxypyridines and transition or lanthanide metals generate persistent molecular scaffolds. These scaffolds provide a platform with which to control deposition of additional molecular layers. Our intention in undertaking this multilayer approach is to show that the construction of complex, multicomponent supramolecular devices on gold and silica can be achieved in considerably less time and with less effort than by traditional covalent methods. The structures and properties of these multilayer films will be discussed.

#### 11:45 AM L1.11

**Performance of a solid-state Photoelectrochromic window.** Ursula Opara Krasovec<sup>1</sup>, Anneke Georg<sup>2</sup>, Andreas Georg<sup>3</sup> and Marko Topic<sup>1</sup>; <sup>1</sup>Laboratory of semiconductor devices, Faculty of electrical engineering, University of Ljubljana, Ljubljana, Slovenia; <sup>2</sup>Freiburg Materials Research Centre, Freiburg, Germany; <sup>3</sup>Fraunhofer Institute for Solar Energy Systems, Freiburg, Germany.

Switchable windows are used to control daylighting and thermal conditions in modern buildings. The photoelectrochromic (PE) device reported in this paper is a new type of switchable window, which combines a dye-sensitized solar cell [1] with an additional electrochromic layer. The coloring is induced by illumination, so no external voltage is needed. An alternative PE configuration was first published by Bechinger et al. [2]. The coloring and the bleaching are competing processes, because the bleaching is possible only via loss reactions. Therefore, either fast coloring and bleaching with a small transmittance change [2], or a large transmittance change with slow bleaching are achievable. In our new PE device, the materials can be optimized for coloring and bleaching independently, so it simultaneously allows fast coloring and bleaching and high contrast [3]. For our PE device is characteristic a 6-segment design with glass substrates on both sides: glass/transparent conductive oxide (TCO)/WO<sub>3</sub>/TiO<sub>2</sub> (dye)/electrolyte/Pt/TCO/glass. A sol-gel route followed by dip-coating deposition is used for the preparation of photoactive (dye-sensitized TiO<sub>2</sub>) and the electrochromic (WO<sub>3</sub>) layers. Pt layer is sputtered on the opposite TCO electrode. Between both electrodes is an electrolyte containing Li<sup>+</sup> ions and redox couple (I<sup>-</sup> and I<sup>3-</sup>). The coloring process in the PE device takes place under open circuit conditions and illumination. A dye molecule is excited by light and injects electrons via the TiO<sub>2</sub> layer to the WO<sub>3</sub>. In parallel, Li<sup>+</sup> ions are incorporated into the WO<sub>3</sub> and I<sup>-</sup> is reduced to I<sup>3-</sup>. Because of the injection of electrons, the WO<sub>3</sub> changes its color from transparent to blue. Bleaching is achieved under short circuit conditions. The

electrons are transferred from the WO<sub>3</sub> to the Pt electrode, causing the regeneration of I<sup>-</sup> ions in the electrolyte. As a result WO<sub>3</sub> is oxidized and the system bleaches. Solid PE devices in a size 10x10 cm<sup>2</sup> employing a solid Li<sup>+</sup> ion conductor, based on organically modified silane network having incorporated I<sup>-</sup> and I<sub>3</sub><sup>-</sup>, were built and characterized. The visible transmittance of such solid PE device is 62 % in the bleached state and 1.6 % in the colored state. Time for coloring and bleaching is about 10 minutes. The performance of the PE devices aged at room temperature and exposed to different accelerated conditions (cycling, UV and visible illumination, elevated temperature: 65 and 85 degrees C) will be reported. Thicker layers of TiO<sub>2</sub> will lead to a window, which can be used as a solar cell as well as switched in its transmittance. Using the same layer configuration and a thick WO<sub>3</sub> layer it is possible to build a photovoltaically self-charging battery [4]. 1. B. O'Regan and M. Graetzel, *Nature*, 353, 737 (1991). 2. C. Becherer et al., *Nature*, 383, 608 (1996). 3. A. Hauch et al., *Electrochimica acta*, 46, 2131 (2001). 4. A. Hauch et al., *J. Electrochem. Soc.*, 149, A1208 (2002).

SESSION L2: Nanoparticle-Hybrid Solar Cells  
Chair: John Reynolds  
Monday Afternoon, November 29, 2004  
Back Bay A (Sheraton)

### 1:30 PM \*L2.1

**Advances in Materials for Photovoltaics.** A. Paul Alivisatos, Chemistry, University of California, Berkeley, Berkeley, California.

Inorganic nanocrystals can be blended with semiconductor polymers to provide new types of hybrid solar cells. The inorganic nanorods have high electron affinities and high electron mobilities, thus providing a good partner in blends with semiconductor polymers, such as polythiophenes. The present status of these cells will be reviewed, and potential new designs will also be described.

### 2:00 PM \*L2.2

**Conjugated Polymer / Nanostructured ZnO Semiconductor Composite Devices.** Dana C. Olson<sup>1,2</sup>, Sean E. Shaheen<sup>1</sup>, Alexander Miedaner<sup>1</sup>, Garry Rumbles<sup>1</sup>, Brian A. Gregg<sup>1</sup>, Reuben T. Collins<sup>2</sup> and David S. Ginley<sup>1</sup>; <sup>1</sup>National Renewable Energy Laboratory, Golden, Colorado; <sup>2</sup>Physics, Colorado School of Mines, Golden, Colorado.

Conjugated polymer / nanostructured oxide semiconductor composites are promising systems for use in low cost organic photovoltaic devices. Incorporation of a conjugated polymer into a porous oxide semiconductor can result in a bulk heterojunction device in which photogenerated charges have unimpeded transport pathways to the electrodes. ZnO is one of the most interesting candidate oxide semiconductors because of its unique growth behavior [1]. ZnO preferentially grows single crystal nanofibers that can provide a direct charge transport pathway to the electrode. Additionally, carrier mobilities in such structures can be orders of magnitude higher than in typical organic materials, with electron mobilities in single crystal ZnO measured at 100 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup>. Here we demonstrate low temperature growth of ZnO nanofibers from solution precursors resulting in nanofibers that are aligned normal to the substrate. We show that the fiber length can be controlled through a variety of changes in growth conditions including growth time, solution temperature, pH, and concentration. We will show how a simple nucleating layer allows increased growth control and growth on a variety of substrate materials. Control of the spacing between the fibers is demonstrated through changes in the nucleation layer processing parameters. The fiber diameter and orientation are found to be strongly dependant on the microstructure of the underlying nucleation layer. The nanofibers are essentially the same width as the crystallites in the substrate. Finally, intercalation of conjugated polymer into the empty volume of the ZnO nanofiber film and preliminary devices demonstrating photovoltaic behavior made using this architecture are discussed. [1] R.B. Peterson, C.L. Fields, B.A. Gregg, *Langmuir* 20, 5114 (2004)

### 2:30 PM L2.3

**Exciton and Charge Transport in Composite Solar Cells: Modeling and Experimental Studies.** Victor M. Burlakov<sup>1</sup>, K. Kawata<sup>1</sup>, C. Martin<sup>1</sup>, H. E. Assender<sup>1</sup>, G. A. D. Briggs<sup>1</sup>, A. Ruseckas<sup>2</sup> and I. D. W. Samuel<sup>2</sup>; <sup>1</sup>Department of Materials, University of Oxford, Oxford, United Kingdom; <sup>2</sup>School of Physics and Astronomy, University of St Andrews, St Andrews, United Kingdom.

We study the performance of organic-inorganic composite solar cells as a function of the parameters of exciton and charge transport, and the composite morphology. Exciton transport is described analytically within phenomenological model taking into account resonance energy transfer between inhomogeneously broadened exciton energy levels.

The model is parameterized using experimental data on time dependence of exciton photoluminescence quenching by TiO<sub>2</sub> substrate. The model is then used to predict a dependence of internal quantum efficiency of the MEH-PPV/TiO<sub>2</sub> solar cells upon the wavelength of incident monochromatic light. We found that internal quantum efficiency increases with decreasing the light wavelength, which is confirmed by experimental observations. Charge transport in the solar cells is modeled taking into account diffusion and drift of electrons and holes in the organic-inorganic composite with interpenetrating columnar morphology. We predict a pronounced peak in the short circuit current as a function of the column length, which suggests that the columnar structure can be optimized according to the charge transport parameters of the materials in the composite. Optimum scale-morphology relation based on our results on exciton and charge transport in the composite solar devices is discussed.

### 2:45 PM L2.4

**Properties and Performance of TiO<sub>2</sub>/Conjugated Polymer Solar Cells.** Zhibin Xie<sup>1</sup>, Bernard M. Henry<sup>1</sup>, Michelle J. Carey<sup>1</sup>, Kiril R. Kirov<sup>1</sup>, Christopher R.M. Grovenor<sup>1</sup>, Hazel E. Assender<sup>1</sup>, G. Andrew D. Briggs<sup>1</sup>, Mitsuru Kano<sup>2</sup> and Yusuke Tsukahara<sup>2</sup>; <sup>1</sup>Department of Materials, University of Oxford, Oxford, United Kingdom; <sup>2</sup>Technical Research Institute, Toppan Printing Co., Ltd., Sugito-machi, Kitakatsushika-gun, Japan.

Composite Solar Cells (CSC's) composed of titanium dioxide and a conjugated polymer sandwiched between anode and cathode electrodes have attracted considerable attention from a number of research groups due to the potential for the fabrication of low cost device. In CSC's, the titanium dioxide layer forms part of the interface for exciton dissociation and also provides an electron transport route to the electrodes. As a result, the microstructure, electronic and optical properties of the TiO<sub>2</sub> layer plays a crucial role in determining photovoltaic (PV) performance. In this presentation, we report results on the structure and properties of titanium dioxide layers fabricated by doctor blade casting, sol-gel deposition and reactive evaporation. The electronic and optical properties were characterised by photoconductivity (PC) measurements and UV-vis spectrometry, respectively, and the microstructures were characterised by SEM, TEM, XRD and AFM. The dependence of PC on illumination light intensity, temperature, wavelength, ambient atmosphere and fabrication methods was investigated. For instance, when the light intensity is reduced, PC takes a longer time to reach saturation but decays much faster after the illumination is switched off. PC in vacuum is higher than that in air, whereas the dark conductivity in vacuum is lower than that in air. A model will be presented to account for all these observations. The power efficiency of our CSC's based on titanium dioxide and MEH-PPV is reproducibly 0.2% under irradiation at 100mW/cm<sup>2</sup>, with I<sub>sc</sub> = 1.5mA/cm<sup>2</sup>, V<sub>oc</sub> = 0.47V and FF = 33%. We will speculate on how the TiO<sub>2</sub> fabrication parameters, nanostructure and photoconductivity performance may affect the overall device PV performance.

### 3:30 PM L2.5

**Fabrication and Testing of Nanorod Arrays for Organic Solar Cell Applications.** Susan Huang<sup>1</sup>, Pradeep Haldar<sup>1</sup>, Harry Efsthadiadis<sup>1</sup>, Hee-yeoun Lee<sup>2</sup>, Brian Landi<sup>3</sup> and Ryne Raffaele<sup>3</sup>; <sup>1</sup>College of Nanoscale Science and Engineering, University at Albany SUNY, Albany, New York; <sup>2</sup>Korean Polytechnic University, Siheung, South Korea; <sup>3</sup>Rochester Institute of Technology, Rochester, New York.

Research efforts devoted to the development of photovoltaic (PV) devices based on organic materials, for the conversion of sunlight to electricity have produced promising results in recent years. Although less efficient than corresponding inorganic (semiconductor based) devices, organic devices show promise as a cost-effective means of providing widespread application of the photovoltaic energy conversion. Novel nanomaterials in PV devices, by incorporating inorganic nanorods into polymer films, are processed from solution providing a low cost approach to increase conductivity of the films. The economic gain of reduced cost promises to outweigh the liability of reduced efficiency. We report on a novel use of nanorod arrays for organic based solar cell devices. A metal foil with copper nanorods attached to the surface was developed by electrodepositing copper from a copper sulfate solution into an anodic alumina oxide (AAO) template that had been coated with a metal on one side. The AAO membrane was dissolved in NaOH leaving behind the copper nanorods. This nanorod array was evaluated to explore the possibility of increasing the power conversion efficiency of organic solar cells. A solar cell device could be made by applying a polymer layer of poly(2-methoxy-5-(3',7'-dimethyloctyloxy)-1,4-phenylene-vinylene) (MDMO:PPV) onto the copper nanorod array and sandwiching it with a film of poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) applied onto a indium tin oxide coated glass substrate. Nanorod array characteristics were investigated by focus ion beam, scanning electron microscopy, and transmission electron microscopy.

3:45 PM [L2.6](#)

**Fabrication of Photovoltaic Devices Incorporated with Cadmium Sulfide Nanoparticles by a Multilayer Deposition Process.** [Wai Kin Chan](#)<sup>1</sup>, Kai Wing Cheng<sup>1</sup>, Ka Yan Kitty Man<sup>1</sup>, Chui Wan Tse<sup>1</sup> and Aleksandra B. Djuricic<sup>2</sup>; <sup>1</sup>Department of Chemistry, The University of Hong Kong, Hong Kong, Hong Kong; <sup>2</sup>Department of Physics, The University of Hong Kong, Hong Kong, Hong Kong.

A series of photovoltaic devices with p-i-n type structure was fabricated by the deposition of alternating layers of polycation and polyanion on ITO surface. A conjugated polymer functionalized with rhenium aromatic diimine complex was used as the polycationic photosensitizers and sulfonated polyaniline was used as the p-type polyanion. Cadmium sulfide nanoparticles were used as the n-type material in these devices. By treating CdS nanoparticles with an anionic surfactant, the surface of the nanoparticles became anionic in nature so that it can adsorb on the surface of the polycation by electrostatic attraction. This approach provides an easy and efficient method in fabricating photovoltaic devices with well-defined layer structures. The thickness of the p-type and n-type materials can be adjusted accurately by varying the number of bilayers deposited. Therefore, optimization of device performance can be easily achieved. When irradiated with AM 1.5 simulated solar light, the devices exhibited power conversion efficiencies in the order of 0.1 %, and the fill factors were in the range 0.2-0.4. By using a mixed metal containing polymers, devices with wide range of photosensitivity can also be fabricated.

4:00 PM [L2.7](#)

**Synthesis of nanostructured-MoS<sub>2</sub> / Ag<sub>2</sub>S multilayered coatings by sol-gel for solar energy storage applications.** [Phani Ratna Ayalasomayajula](#), Luca Lozzi, Maurizio Passacantando and Sandro Santucci; Department of Physics, University of L'Aquila and INFN-CASTI Regional Laboratory, Aquila, Abruzzo, Italy.

The optical and electrical properties of transition metal chalcogenides make these semiconductors promising candidate for efficient solar energy conversion. In recent years, considerable interest has been shown to synthesis of thin semiconductor films of MoS<sub>2</sub>, Ag<sub>2</sub>S by electrochemical and chemical deposition of colloidal semiconductors. By these methods the size of the particle can be limited to 15-20 nm. In the present work, in order to have quantum confinement effect, thin nanostructured single MoS<sub>2</sub> and Ag<sub>2</sub>S as well as multilayered films of MoS<sub>2</sub> / Ag<sub>2</sub>S have been synthesised by sol-gel dip coating technique. The films were deposited on to glass, quartz substrates at room temperature. The deposited nanostructured films were subjected to annealing treatment from 100°C to 400°C and the effect of annealing on structural, optical and electrical properties has been studied in detailed. X-ray diffraction and electron microscopy measurements indicated that the deposited films are nanocrystalline with uniform and smooth coatings. High-resolution transmission electron microscopy (HRTEM) and atomic force microscopy (AFM) techniques revealed the presence of monodispersed nanoparticles of MoS<sub>2</sub> (5-6nm) and Ag<sub>2</sub>S (5-8 nm) in the deposited films. UV-vis and Fourier transform infrared (FTIR) spectroscopies have been employed in order to study the optical absorption as well as band gap of the individual films and multilayered films and vibrational and stretching bands respectively. Film thickness and chemical composition was estimated by survey and depth profile analysis by X-ray photoelectron spectroscopy (XPS) respectively. Electrical resistivity of the films have been measured using four-probe sheet resistance technique. Thermoemf measurements indicated that the deposited films were p-type in case of MoS<sub>2</sub> and n-type in case of Ag<sub>2</sub>S.

4:15 PM [L2.8](#)

**Quantum Dot-Single Wall Carbon Nanotube Complexes for Polymeric Photovoltaics.** [Brian J. Landi](#)<sup>1</sup>, Stephanie L. Castro<sup>2</sup>, Chris M. Evans<sup>1</sup>, Herbert J. Ruf<sup>1</sup>, Sheila G. Bailey<sup>3</sup> and Ryne P. Raffaele<sup>1</sup>; <sup>1</sup>NanoPower Research Laboratories, Rochester Institute of Technology, Rochester, New York; <sup>2</sup>Ohio Aerospace Institute, Brookpark, Ohio; <sup>3</sup>NASA Glenn Research Center, Cleveland, Ohio.

The ability to dissociate the photo-generated excitons and transport the resulting charge carriers are the major impediments in improving the efficiency of polymeric solar cells. In order to simultaneously address both of these issues, we have investigated the use of quantum dot-single wall carbon nanotube (QD-SWNT) complexes as a suitable nanomaterial dopant in these devices. A major advantage of these nanomaterials is the potential for designed compositions which may also serve as photo-active materials. This is made possible by the synthetic control of nanomaterial diameters (which are directly related to their optical bandgaps), allowing for the capability to tune the spectral absorption of these devices. These complexes could provide a series of junctions in a properly structured polymeric device that would be analogous to a conventional triple-junction crystalline

solar cell. The SWNTs used in the complexes were synthesized by an Alexandrite pulsed laser vaporization reactor at standard conditions and purified with conventional nitric acid and thermal oxidation steps. The SWNTs were functionalized prior to covalent attachment with the semiconductor quantum dots using a 4:1 mixture of concentrated H<sub>2</sub>SO<sub>4</sub>:H<sub>2</sub>O<sub>2</sub>. The CdSe quantum dots were prepared using a colloidal synthesis method with CdO as the precursor and injection of Selenium-triethylphosphine at 280°C. The formation of CdSe-SWNT complexes occurred through covalent attachment of carboxylic acid-functionalized SWNTs with CdSe-aminoethanethiol (AET) quantum dots after ligand exchange of the triethylphosphine oxide (TOPO) with AET. We will review this work as well as noncovalent schemes using CdSe and CuInS<sub>2</sub> quantum dots. The corresponding microscopy (AFM and TEM) and spectroscopy (Raman, FT-IR, and UV-Vis) data from each of the synthesis strategies will be described. Results on the optoelectronic characterization of the polymer composite materials and associated photovoltaic devices containing the various complexes will be presented.

4:30 PM [L2.9](#)

**Aligning Conjugated Polymer Chains in Nanopores to Improve Bulk Heterojunction Photovoltaic Cells.**

[Chia Tzun Goh](#), Kevin M. Coakley, Yuxiang Liu and Michael D. McGehee; Department of Materials Science & Engineering, Stanford University, Stanford, California.

To make bulk heterojunction photovoltaic cells efficient, it is crucial for the charge carrier mobilities in both semiconductors to be high enough to allow the carriers to escape the device before back electron transfer occurs. Previously, we have made ordered bulk heterojunction PV cells by filling films of self assembled mesoporous titania with regioregular poly(3-hexylthiophene) (P3HT) by melt infiltration. An advantage of this structure is that there are no spots in the polymer more than 4 nm from a titania interface. Another is that there are no deadends in the polymer or titania that prevent charge carriers from reaching electrodes. Unfortunately, the mesoporous titania films consist of arrays of ellipsoidal pores with highly curved surfaces that cause the polymer chains to coil in a way that leads to extremely low charge carrier mobilities. To address this problem, we have used anodic alumina to make devices with straight pores. By measuring the reflectance and transmittance of films as a function of angle and polarization, we have found that P3HT chains align along the pore walls. Absorption and photoluminescence measurements show that they pi stack on each other. The charge carrier mobility of the P3HT in the straight pores, measured by modeling the space charge limited current in a diode, is almost 10-2 cm<sup>2</sup>/Vs, which is higher than the mobility in a diode with just P3HT between the electrodes. The procedures for making straight pores in semiconductors like titania and the performance of the photovoltaic cells will be presented.

4:45 PM [L2.10](#)

**Hybrid Solar Cells Based on Nanocomposites of Porous Si and Copper Phthalocyanine and its Derivatives.** W. B. Euler<sup>2</sup>, N. Tokranova<sup>3</sup>, B. Xu<sup>4</sup>, J. Castracane<sup>4</sup> and I. A. Levitsky<sup>1,2</sup>;

<sup>1</sup>Emitech, Inc., Fall River, Massachusetts; <sup>2</sup>Department of Chemistry, University of RI, Kingston, Rhode Island; <sup>3</sup>UAlbany Institute for Materials, University of Albany (SUNY), Albany, New York; <sup>4</sup>College of Nanoscale Science and Engineering, University of Albany (SUNY), Albany, New York.

Hybrid organic-inorganic solid solar cells have been the subject of increasing research interest for the past several years. Solid state dye-sensitized solar cells based on nanoporous titania has been the primary direction in this field, which recently demonstrated a conversion efficiency above 3% [1]. Meanwhile, hybrid photovoltaic composites fabricated from nanoporous n-type semiconductors (such as Si, III-V, IV-VI) and p-type organic materials have received little attention. We report novel composite photovoltaics fabricated from nanoporous Si filled with Copper Phthalocyanine (CuPC) and its derivatives, including discotic liquid crystal CuPC (LC-CuPC). Porous n-type Si (pSi) was prepared electrochemically (pore size 10-20 nm) and filled with CuPC solution by impregnation or spin casting (LC-CuPC) onto a porous surface followed by heating to the temperature of the mesophase transition. The top electrode was a thin layer of sputtered gold (20-30 nm) or ITO (80-100 nm). The reference samples fabricated by the same method without organic fillers showed a diminished PV effect (conversion efficiency was less than 0.01%). For the CuPC-pSi composite the cell performance depends significantly on the pores' depth, size, structure, and density. Shallow (depth less than 300-400 nm) and/or poorly developed pore structure exhibits low PV response and the I-V characteristics show "kink" behavior [2] that can be explained by high reflectivity and slow hole transport through the CuPC network. For straight pores with a depth of more than 1500-2000 nm, the conversion efficiency was up to 2-3% using a tungsten lamp with solar filters (30 mW/cm<sup>2</sup>). The porous structure and pore filling were examined by SEM and XPS techniques. Photocurrent spectra of the CuPC-pSi cell demonstrate

two bands that correspond to the absorbance of the protonated form of CuPC (CuPC was dissolved in sulfuric acid for deposition into the pores). A comparative analysis between CuPC, CuPC(R1)8 (R1 = -O-C8H17, no LC mesophase) and LC-CuPC(R2)8 (R2 = O-C12H25, LC mesophase exists in the range of 67-250 °C) has been made and conclusions about possible mechanisms of charge transfer and transport are drawn. The solar cell optimization is discussed as well. References: [1] M. Gratzel, J. Photochem. Photobiol. C: Photochem. Rev., 2003, 4, 143; [2] J. Nelson, J. Kirkpatrick, and P. Ravirajan, Phys. Rev. B, 2004, 69, 035337.

SESSION L3: Polymer-Based Devices  
Chair: Stephen Forrest  
Tuesday Morning, November 30, 2004  
Back Bay A (Sheraton)

### 8:30 AM \*L3.1

#### Conjugated Polymeric Photovoltaic Devices.

N. Serdar Sariciftci, Linzer Institut für Organische Solarzellen (LIOS), Physikalische Chemie, Johannes Kepler Universität Linz, Linz, Austria.

Recent developments on "plastic" photovoltaic elements are reviewed. Semiconducting conjugated polymers as well as nanocrystalline inorganic semiconductors are used in composite thin films. The photophysics of such photoactive devices is based on the photoinduced charge transfer from donor type semiconducting conjugated polymers onto acceptor type conjugated polymers or acceptor molecules such as Buckminsterfullerene, C<sub>60</sub> or nanoparticles. This photoinduced charge transfer can be reversible, ultrafast (within 40 femtoseconds) with a quantum efficiency approaching unity, and the charge separated state may reach metastable state (up to milliseconds at 80K). Similar to the first steps in natural photosynthesis, this photoinduced electron transfer leads to a number of potentially interesting applications which include sensitization of the photoconductivity and photovoltaic phenomena. Examples of photovoltaic architectures are discussed with their potential in terrestrial solar energy conversion. Several materials are introduced and discussed for their photovoltaic activities. Furthermore, nanomorphology has been investigated with AFM, SEM and TEM. The morphology/property relationship for a given photoactive system is found to be a major effect. The mobilities of photoinduced charges as well as electro absorption studies for determining the built-in-potential of the photovoltaic devices will be reported.

### 9:00 AM L3.2

**Temperature and Time Dependence of Heat Treatment on P3HT/PCBM Polymer 3- Hexalthiophine - soluble C60 Solar Cells.** Anvar A. Zakhidov, Kanzan Inoue, Sergey Lee, Mike Sampson, Chandra Pallavi and Ross Ulbrich; Physics, University of Texas at Dallas, Richardson, Texas.

The temperature and time dependence of postproduction heat treatment on organic solar cells was intensively studied. Organic devices were fabricated on PEDOT-PSS coated ITO substrates from a solution of P3HT/PCBM dissolved in Toluene by spin-casting. An aluminum electrode was thermally deposited in a vacuum chamber. The efficiency of the devices was significantly improved by heat treatment and both optimal temperature and time dependencies were determined. The device performance was maximized after 20 minutes of postproduction heat treatment at 90 °C. On the other hand only 20-40 sec of annealing is enough for samples at T=150 °C. After optimizing temperature and time, a LiF layer was added to achieve even greater device performance. The final device performance using optimized temperature / time and the LiF layer was found to be 3%. The spectral changes are carefully studied and the role of nano-morphology is analysed

### 9:15 AM L3.3

**Solar Power for Defense Applications: Towards Spectral Response Broadening and Nanoscale Morphological Control.** Michael Durstock<sup>1</sup>, Adam P. Smith<sup>1</sup>, Cristin Moran<sup>1</sup>, John B.

Ferguson<sup>1</sup>, Rachel R. Smith<sup>2</sup> and Barney E. Taylor<sup>2</sup>; <sup>1</sup>Air Force Research Lab, Wright-Patterson Air Force Base, Ohio; <sup>2</sup>University of Dayton Research Institute, Dayton, Ohio.

The development of flexible, low-cost, and light-weight photovoltaic devices are an enabling technology for a variety of defense-related applications including airbase military shelters, space vehicles, special operations forces, and next-generation surveillance capabilities. Devices based on organic as well as dye-sensitized materials offer the potential for low-cost manufacturability, however the challenge has been to improve device efficiencies. One approach that we have been pursuing towards this goal of improving efficiency has been the utilization of variable bandgap conjugated polymers to broaden the

spectral response of the devices. Functionalized poly(arylene vinylene)s are one such system that we have been investigating due to the ability to tune this response by changing the nature of the arylene group or the substituents on the chain. Another approach is through control over the nanoscale morphology of the film which should lead to improvements in the charge transport characteristics of the film and thereby enhance the overall performance of the devices. Towards this end, we have been examining a variety of different fabrication and processing schemes, such as layer-by-layer assembly and templating techniques, geared towards the ability to manipulate and control the thin film morphology. The specifics of these two approaches will be outlined and recent progress will be discussed.

### 9:30 AM L3.4

**Negative Electric Field Dependence of Charge Carrier Mobility in Regioregular Poly(3-hexylthiophene) Probed by Transient Conductivity Techniques.** Attila Janos Mozer and Niyazi Serdar Sariciftci; Linz Institute for Organic Solar Cells (LIOS), Physical Chemistry, Johannes Kepler University, Linz, Austria.

The temperature and electric field dependence of mobility in chemically purified, low dark conductivity samples of regioregular poly(3-hexylthiophene) (P3HT) using time of flight (ToF) technique is studied. Subsequently, the mobility of doping induced charge carriers in samples with increased dark conductivity exposed to air is probed by the application of a novel method: charge carrier extraction by linearly increasing voltage technique (CELIV). At lower temperatures, the electric field dependence of mobility follows the typical Poole-Frenkel type  $\log \mu \propto \beta E^{1/2}$ ,  $\beta > 0$  electric field dependence. However, as the temperature is raised, the electric field dependence measured by both experimental techniques diminishes around 250 K, and  $\beta$  turns to negative at higher temperatures. Such negative electric field dependence of mobility has been observed in several amorphous charge transport materials, including molecularly doped polymers and molecular glasses, but first time reported in a conjugated semiconducting polymer. The overall agreement between the experiments shows that the two different experimental techniques are mutually consistent. Moreover, this comparative study proves that the negative electric field dependence is an intrinsic property of the samples studied, and not related to the peculiar features of the experimental technique applied. The temperature and electric field dependence of the mobility is analyzed in the framework of disorder formalism developed by Bässler and coworkers. The temperature dependence of the photogenerated charge carriers probed by the time of flight technique tends to yield higher mobility values at the lowest temperatures, indicating that more mobile charge carriers in the absence of quasi-equilibrium being probed. The temperature dependence of the CELIV technique, in which the doping induced charge carriers occupy the deepest energy states of the density of states distribution without further energetic relaxation, follows the  $\log \mu(E=0) \propto T^{-2}$  dependence at all measured temperatures. The energetic disorder parameter ( $\sigma$ ) of disorder formalism has been calculated by fitting the experimental data, and the very similar value of  $\sigma=70$  meV and  $\sigma=64$  meV has been determined by the ToF technique and the CELIV technique, respectively, which indicates that the mode of charge generation has little effect on the charge transport properties of the regioregular P3HT. Finally, large degree of positional disorder equivalent to the large spread of intersite coupling matrix elements are proposed to be responsible for this negative electric field dependence of mobility as suggested by the disorder model.

### 9:45 AM L3.5

**Photovoltaic Devices from Poly(3-hexylthiophene) Doped by Fluorinated Perylene Diimides.** Hongzheng Chen<sup>1,2</sup>, Minmin Shi<sup>1</sup>, Mang Wang<sup>1</sup> and Paul Heremans<sup>2</sup>; <sup>1</sup>Department of Polymer Science & Engineering, Zhejiang University, Hangzhou, China; <sup>2</sup>IMEC, Leuven, Belgium.

Recently, photovoltaic devices based on conjugated semiconducting polymers have attracted much attention due to their low-cost, flexibility, and easy process for large-area. However, their practical uses are limited because of their poor energy conversion efficiency. One solution is to fabricate bulk donor-acceptor (p-n) heterojunctions through blending a semiconducting polymer, which is generally an electron donor (p-type semiconducting material), with an electron acceptor (n-type semiconducting material) with a high electron affinity [1-3]. In this paper, we synthesized two kinds of fluorinated perylene diimides as electron acceptors, one was fluorinated aryl substituted perylene diimide: N, N'-diperfluorophenyl-3,4,9,10-perylenetetracarboxylic diimide (DFPP), another was fluorinated alkyl substituted perylene diimide: N, N'-di(1H, 1H-perfluorooctyl)-3,4,9,10-perylenetetracarboxylic diimide (DFOP). From cyclic voltammetry (CV) measurements, the LUMO energy levels of DFPP and DFOP were estimated to be -4.37 and -4.26 eV, respectively, which were 0.14 and 0.07 eV lower than those of the corresponding non-fluorinated perylene diimides, respectively. Organic photovoltaic devices from spin-coated

poly(3-hexylthiophene) (P3HT) films doped with 1 wt% DFPP or DFOP were prepared (ITO/PEDOT-PSS/P3HT-DFPP/LiF/Al or ITO/PEDOT-PSS/P3HT-DFOP/LiF/Al). Their current-voltage ( $I - V$ ) characteristics were compared with that of the photovoltaic device made from the pristine P3HT film (ITO/PEDOT-PSS/P3HT/LiF/Al). It was found that the doping resulted in the increasing of the short circuit current ( $I_{SC}$ ) of the photovoltaic device through the efficient photoinduced charge transfer from P3HT to fluorinated perylene diimide, which was confirmed by the fluorescence quenching of the doped P3HT film. However, the doping also caused the decreasing of the open circuit voltage ( $V_{OC}$ ), suggesting the disruption of Schottky junction between P3HT and cathode electrode. Acknowledgments This work was supported by the National Natural Science Foundation of China (Nos. 50173021, 50225312) and by the fund for the century scholar-training project from the Education Department of China. It was also partly supported by the Flemish Government under the Bilateral Research Agreement BIL01/75. References [1] G. Yu, J. Gan, J. C. Hummelen, F. Wudl, A. J. Heeger, Science, 1995, 270, 1789. [2] J. J. M. Halls, C. A. Walsh, N. C. Greenham, E. A. Marsegla, R. H. Friend, S. C. Moratti, A. B. Holmes, Nature, 1995, 376, 498. [3] J. Breeze, A. Salomon, D. S. Ginley, B. A. Gregg, H. Tillmann, H.-H. H?rhold, Appl. Phys. Lett., 2002, 81, 3085.

#### 10:15 AM \*L3.6

**Variable Gap Conjugated Polymers for Photovoltaic Devices.** John R. Reynolds, Barry C. Thompson, Young-Gi Kim, Emilie Galand and Nisha Ananthakrishnan; Chemistry, University of Florida, Gainesville, Florida.

We have developed a family of soluble conjugated polymers with band gaps ranging from 2.4 to 1.5 eV and evaluated the utility of this family for applications in photovoltaic devices. Considering the absorption spectra of all the polymers, a thorough overlap of the solar spectrum is achieved. Of special interest are the narrow gap conjugated polymers that can absorb solar energy most strongly at the peak of solar photon flux near 1.8 eV. These narrow gap polymers are synthesized using the donor-acceptor approach, which relies on the interaction between electron rich donors and electron poor acceptors to achieve a compressed band gap. Our use of 3,4-alkylenedioxythiophene (XDOT) donors and cyanovinylene acceptors has led to the development of a representative class of soluble narrow gap polymers. In order to blanket the solar spectrum, higher band gap polymers based on thiophene and dialkoxybenzene or XDOT and dialkoxybenzene such as poly(thiophene-didodecyloxybenzene) (LPTB) with a band gap of 2.4 eV and poly(bis-thienyl-dihexyloxybenzene) (PBTB) with a band gap of 2.1 eV, (as well as commercial polymers such as MEH-PPV or P3HT), have been used in addition to the narrow band gap polymers. Specifically we have fabricated devices based on MEH-PPV/PCBM blends that have efficiencies of 1.5%. Initial results with tricomponent blend devices based on LPTB/MEH-PPV/PCBM show efficiencies of 1.0%. Here we present fundamental optical and electrochemical data in order to establish the band structure of the newly synthesized polymers. Additionally, results will be presented on a variety of photovoltaic devices, primarily based on the bulk heterojunction methodology with a combination of conjugated polymer donors and PCBM or other soluble fullerene derivatives as acceptors.

#### 10:45 AM L3.7

**Plasticized Conjugated Polymers: A Possible Route to Higher Voltage Solar Cells.** Aurelien Du Pasquier and Paul Wentzel; Ceramic and Materials Engineering, Rutgers University, Piscataway, New Jersey.

The increase of voltage in solar cells is a major challenge since current single cell systems, either based on silicon [1], Dye sensitized TiO<sub>2</sub> [2] or conjugated polymers [3], have output potentials comprised between 0.4 and 0.9 Volts. We report the effect of adding limited amounts of propylene carbonate (PC hereafter) on the thermal and photochemical properties of undoped regioregular poly(3-octylthiophene) (P3OT hereafter). Differential scanning calorimetry of PC plasticized P3OT films cast from a 10g/L solution in chloroform reveals a decrease in P3OT melting temperature from 200°C to 85°C, with a minimum at 50 Wt.% PC content. When such films are used in a Schottky diode configuration PET-ITO/P3OT+x%PC/Al, the rectification ratio in the dark increases with an increase in PC content. Under constant white illumination of 165 mW/cm<sup>2</sup>, the open-circuit voltage increases from 610 to 800 mV with an increase in PC from 22 to 54 Wt.%. At the same time, short-circuit currents increase from 1.3 to 2.4 μA/cm<sup>2</sup>. When the aluminum contact is replaced by a magnesium contact, the open circuit voltage increases up to 1.8 Volts and the short-circuit current up to 5 μA/cm<sup>2</sup> for a 60 Wt.% PC content in P3OT (Table I). The study of short-circuit current dependency to light intensity indicates a linear relationship  $I_{sc} \propto I_a$  with a passing through a maximum when the melting temperature of P3OT is lowest. When a magnesium contact is used, the values for  $I_a$  are higher than with an

Al contact, with a maximum observed of 0.73. In order to increase short-circuit currents by avoiding charge recombination, a fullerene-based electron acceptor was mixed with the poly(3-octylthiophene). Latest results using this approach will be presented. References [1] R.Rizzoli, E.Centurioni, J. Pla, C.Summonte, A.Migliori, A.Desalvo, F.Zignani, Journal of Non-Crystalline Solids 299-302 (2002) 1203-1207 [2] Michael Gratzel, Journal of Photochemistry and Photobiology C: Photochemistry Reviews 4 (2003) 145-153 [3] Christoph J. Brabec, Antonio Cravino, Dieter Meissner, N. Serdar Sariciftci, Thomas Fromherz, Minze T. Rispsen, Luis Sanchez, and Jan C. Hummelen, Adv. Funct. Mater., 11, No.5, (2001) 374-380

#### 11:00 AM L3.8

**Integrated Electrical and Optical Models of High Performance Polyfluorene/Fullerene Solar Cells.** Sasa Lasic<sup>1,2</sup>, Nilskrister Persson<sup>1</sup> and Olle W. Inganäs<sup>1,2</sup>; <sup>1</sup>Biomolecular and Organic Electronics, IFM, Linköping University, Linköping, Sweden; <sup>2</sup>Center of Organic Electronics, Linköping University, Linköping, Sweden.

The development of polymer solar cells requires advances in our understanding of device physics in organics. Simulation of the optical and electrical properties of devices is therefore an important target and tool, to allow optimization of device geometry. The ever present trade off between optical absorption in the thin organic layers, and the poor charge transport of photogenerated charges makes this optimization quite crucial. The thicker films allow more optical absorption, which is strongly influenced by internal reflection and interference in the planar polymer solar cell devices. We have developed optical models of the excitation density profile in multilayer organic/polymer solar cells, starting with the dielectric functions of the layer materials as determined using spectroscopic ellipsometry. These calculations predict the optical excitation profile, the distribution of dissipated light energy in the multilayer device, and the reflectance of the device, as a function of wavelength. By combining these data with simulated light sources of AM 1.5, 100 mW/cm<sup>2</sup>, we can predict the optical excitation profiles for solar light. This is a source term for the electrical transport models, which use mathematical models of charge injection at anode and cathode, charge transport in a bulk material characterized in a continuum model with field and temperature dependent mobility for holes and electrons, and optical generation of free holes and electrons by photoinduced charge transfer in the polymer based donor-acceptor solar cells. The model requires input parameters describing the mobility of charge carriers in blends, data which are not always experimentally accessible. Most of the data can however be obtained from electrical studies of polymer or organic diodes (field and temperature dependence of charge carriers), by electrochemical determination of HOMO and LUMO of donor and acceptor, and by spectroscopic ellipsometry to determine the dielectric constant of the materials used. One parameter remains adjustable, namely the recombination rate, which can be chosen to make models match experimental behaviour, at least qualitatively. The model has been evaluated with respect to the behaviour of devices based on alternating copolyfluorene of dioctyl-fluorene and di-thienyl-benzothiadiazole (DiO-PFDTBT)/[6,6]-phenyl-C61-butryric acid methylester (PCBM) materials. Such devices generate power conversion efficiencies (AM1.5, 100mW/cm<sup>2</sup>) close to 3% at room temperature. With the recombination parameter set from experiments, a number which we consider to reflect both the morphology of donor-acceptor networks and the real recombination kinetics, we can explore the model with numerical simulation. From these simulations we conclude a resounding necessity of increasing the hole mobility in the donor-acceptor material in order to enhance power conversion efficiencies.

#### 11:15 AM L3.9

**Polymer solar cells: screen printing as a novel deposition technique.** Tom Aernouts, Peter Vanlaeke, Jef Poortmans and Paul Heremans; IMEC, Leuven, Belgium.

Recently, there has been a growing interest for polymer solar cells. One of the most promising concepts in this field is that of the bulk donor/acceptor heterojunction. Here, the active layer consists of a mixture of two different semiconducting organic materials sandwiched between two metallic electrodes. Energy conversion efficiencies exceeding 3% have already been obtained with such devices. In this work, the processing of the active layer is studied. One of the important advantages of the applied materials is that they can be easily processed from solution. This leads to easy-to-use and low-cost deposition techniques like spin coating or screen-printing. Whereas spin coating provides easily a homogeneous film on large substrates, no direct patterning of the deposited layer is possible. This latter can however be achieved by screen-printing. By developing suitable masks, one can obtain very different kinds of layer patterns. Therefore, screen-printing offers many possibilities for the preparation of low-cost organic solar cell modules. Solution viscosity, mesh size or deposition speed are important deposition parameters that have to be controlled

very well in the screen-printing process. In a first step, we have produced single layer devices with poly(2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylene vinylene) (MEH-PPV). Optimisation of the printing conditions resulted in light-emitting devices with high brightness. Secondly, blends of MEH-PPV and (6,6)-phenyl C61-butyric acid methyl ester (PCBM) have been printed in a similar way to produce photovoltaic devices. These devices have been characterised by dark and illuminated IV-measurements, e.g. AM1.5 simulated solar illumination, showing very promising results. These technical achievements show that screen-printing can be a suitable deposition technique for the active layer of organic solar cells. This technology will be suitable for the realisation of fully flexible organic solar cell modules.

#### 11:30 AM L3.10

**Electrostatic Self-assembly and Photovoltaic Properties of Multilayer Films based on Polythiophenes Deposited on Flexible Substrates.** M. Joseph Roberts and David J. Irvin; NAVAIR NAWCWD, China Lake, California.

Aggregates of organic and inorganic (hybrid) materials enable new material functionality. The advantages hybrid material aggregates include functional flexibility, processibility, and low weight. Such hybrid material aggregates may be assembled on the nanometer scale using layer-by-layer electrostatic deposition (LBL ESD). LBL ESD allows the incorporation of multiple materials and thus film properties may be tuned with nanometer precision in the direction of film growth. In this study, LBL ESD was used to fabricate photovoltaic devices incorporating titania nanoparticles, polythiophenes polyelectrolytes, and dye-functionalized carbon nanotubes. We have fabricated both ionic liquid-junction and solid-junction cells. We will present results of our latest photovoltaic device performance measurements.

#### 11:45 AM L3.11

**Photoelectron spectroscopy of surfaces and interfaces in plastic solar cells: the benefit of LiF/Al as opposed to Al electrodes.** Stina Karin Maria Jonsson<sup>1</sup>, Elin Carlegrim<sup>1</sup>, Fengling Zhang<sup>2</sup>, Olle Inganäs<sup>2</sup>, William R. Salaneck<sup>2</sup> and Mats Fahlman<sup>1</sup>; <sup>1</sup>Department of Science and Technology, Linköping University, Norrköping, Sweden; <sup>2</sup>Department of Physics and Measurement Technology, Linköping University, Linköping, Sweden.

The surfaces and electrode interfaces of a particular polymer blend used in prototype solar cells have been characterized with photoelectron spectroscopy. The polymer blend in question is a one to four mixture of LBPF5 (a low band gap copolymer based on alternating fluorene and donor-acceptor-donor units) to PCBM (soluble C60 derivative). The surfaces of pure LBPF5 and PCBM are studied separately in order to determine surface features, possible segregation and difference in interface formation with the electrode materials. Based on surface analysis of the pristine film we can conclude that the surface of the blend is dominated by LBPF5. The electrode materials studied are Al and Al/LiF since these are widely used in devices. According to literature, device characteristics are in general improved by insertion of a thin LiF layer and its beneficial effect has been observed from 1 Å up to >20 Å thicknesses. We have studied Al/LiF/organic structures in which the LiF layer thickness has been varied within this range. This has enabled us to determine thickness dependant effects of the LiF layer seen in the Al/LiF/organic structure as opposed to the Al/organic case. LiF has a protective effect for all thicknesses preventing formation of Al-organic complexes that destroy the  $\pi$ -conjugation. In addition to this, there are two other beneficial effects (depending on LiF thickness). Decomposition of LiF occurs for thin enough layers in which the LiF species are in contact with both the organic film and the aluminum atoms. For thicker layers there is an interfacial dipole forming at the LiF/organic interface and an interfacial dipole at the Al/LiF interface. According to our data, both situations result in a more favorable energy level matching with regard to electron extraction at the interfaces compared to the Al/organic case.

SESSION L4: Small Molecule-Based Devices

Chair: M. Durstock

Tuesday Afternoon, November 30, 2004

Back Bay A (Sheraton)

#### 1:30 PM \*L4.1

**Tandem, Planar, Bulk and Mixed Heterojunction Solar Cells: Achieving High Efficiencies Using Small Molecular Weight Organic Semiconductors.** Stephen Forrest, J. Xue, S. Uchida and B. Rand; Center for Photonics and Optoelectronic Materials (POEM), Princeton University, Princeton, New Jersey.

We discuss the fundamental limitations to solar cell efficiencies employing organic thin films. To support our analysis, several

strategies for optimizing the power conversion efficiency of small molecular weight organic PV cells. Conversion efficiencies approaching 6% at 1 sun, AM1.5G simulated illumination are observed employing thin film cells consisting of CuPc and C60 as the active region materials. The influence of structural morphology in high efficiency bulk heterojunction and mixed molecular heterojunction cells is considered, as well as that of surface plasmons in tandem cell architectures containing metallic nanoparticle layers separating each sub-cell in a multilayer stack. Surface plasmons are shown to increase the efficiency by a significant fraction in these tandem cells, suggesting that this particular approach has the highest potential for resulting in solar power conversion efficiencies >10%.

#### 2:00 PM L4.2

**High Efficiency Co-Evaporated C60:Pentacene Bulk-Heterojunction Photovoltaics.** Matthew Thomas Lloyd, Alex Mayer and George Malliaras; Materials Science and Engineering, Cornell University, Ithaca, New York.

Pentacene is a high mobility, narrow bandgap small molecule that when blended with fullerenes has the greatest potential to improve the 5% power conversion efficiency benchmark of organic photovoltaic cells. We studied the optimum blending concentration of pentacene:C60 in cells made via co-evaporation. We investigated absorption and charge separation of the devices with UV-Vis spectroscopy, IPCE measurements, and illumination intensity dependence, and characterized the micro phase segregation and charge extraction pathways with surface and bulk microscopy. To facilitate metal-organic charge injection we inserted neat under/overlayers of pentacene and C60. To further improve performance characteristics we maximized the optical field within the blended layer using conductive photo-passive spacers under the metal cathode.

#### 2:15 PM L4.3

**Novel approaches to raise Voc in small molecule-based photovoltaic cells.** Alex Christopher Mayer<sup>1</sup>, Matthew Lloyd<sup>1</sup>, Daniel Bernards<sup>1</sup>, John Anthony<sup>2</sup> and George Malliaras<sup>1</sup>; <sup>1</sup>Cornell University, Ithaca, New York; <sup>2</sup>Department of Chemistry, University of Kentucky, Lexington, Kentucky.

Vacuum deposited small molecules, like pentacene, are known to have higher charge-carrier mobilities than their polymer counterparts as well as equivalent optical properties. However, photovoltaic (PV) sandwich structure cells made entirely from small molecules have a much lower Voc due to shunting problems and a rough interface with the top electrode, which leads to local defects in the electric field across the device that lowers Vbi and hence Voc. In this report, we focus on two complimentary methods to eliminate this problem. The first involves using soluble pentacene and C60 derivatives that form smoother films and have equivalent optical and electrical properties to reduce local defects and prevent shorting. The second approach uses laminated top electrodes that allow novel device structure to be explored and eliminate the damage caused by the high kinetic energy metal atoms that impinge on the surface of the active layer.

#### 2:30 PM L4.4

**High-efficiency Bulk Heterojunction Photovoltaic Cells Grown by Organic Vapor Phase Deposition.** Fan Yang<sup>1,2</sup>, Max Shtein<sup>1,2</sup> and Stephen Forrest<sup>1,2</sup>; <sup>1</sup>Electrical Engineering, Princeton University, Princeton, New Jersey; <sup>2</sup>Princeton Institute for the Science and Technology of Materials (PRISM), Princeton University, Princeton, New Jersey.

Organic vapor phase deposition (OVPD) has been introduced as a method for the growth of small molecular weight organic semiconductor thin films. OVPD employs a carrier gas in a hot walled reactor to transport organic source materials to a cooled substrate, where the organic molecules are physisorbed. By controlling the carrier gas flow rate, OVPD has exhibited a high control over film growth and morphology beyond that achievable by conventional vacuum thermal evaporation. This technique has successfully been used to grow organic light emitting diodes and lasers [1], and pentacene thin-film transistors [2]. However, all materials so far grown by OVPD have been limited to sublimation temperatures < 300 °C. On the other hand, organic photovoltaic (PV) devices require materials that typically sublime at > 400 °C. In this work, we discuss a high-temperature compatible OVPD system for the fabrication of organic PV devices consisting of high sublimation temperature compounds of copper phthalocyanine (CuPc) and 3,4,9,10-perylenetetracarboxylic bis-benzimidazole (PTCBI). Using the unique film morphologies obtained by OVPD, we grow bulk heterojunction (BHJ) PV cells with a controllable (i.e. "deterministic") surface area of the donor/acceptor interface. PV devices based on BHJ's grown by OVPD have high fill factors of 0.56, open circuit voltages of 0.50 V, and short circuit current densities of 105 mA/cm<sup>2</sup> under 1 sun simulated AM1.5G illumination. As a result, the PV devices have the power conversion efficiencies of  $\eta_p =$

2.7±0.1%, which is significantly larger than planar heterojunction devices based on this same materials combination, where  $\eta_p = 1.0\%$  [3], and uncontrolled BHJ devices achieved by annealing, where  $\eta_p = 1.5\%$  [4]. This work opens several new avenues for controlling the thin film morphology of organic heterojunction devices, and has already resulted in a significant improvement in organic BHJ solar cell performance. [1] M. Baldo, M. Deutsch, P. Burrows, H. Gossenberger, M. Gerstenberg, V. Ban, and S. Forrest, *Adv. Mater.* 10, 1505(1998) [2] M. Shtein, J. Mapel, J. B. Benziger, and S. R. Forrest, *Appl. Phys. Lett.* 81, 268 (2002) [3] C. W. Tang, *Appl. Phys. Lett.* 48, 183 (1986) [4] P. Peumans, S. Uchida and S. R. Forrest, *Nature* 425, 158 (2003)

#### 2:45 PM L4.5

**Hybrid Planar-Mixed Molecular Donor-Acceptor Heterojunctions for Photovoltaic Applications.** Jiangeng Xue<sup>1,2</sup>, Barry P. Rand<sup>1,2</sup>, Soichi Uchida<sup>1,2</sup> and Stephen R. Forrest<sup>1,2</sup>; <sup>1</sup>Dept of Electrical Engineering, Princeton Univ, Princeton, New Jersey; <sup>2</sup>Princeton Institute for the Science and Technology of Materials (PRISM), Princeton Univ, Princeton, New Jersey.

The power conversion efficiency of molecular organic photovoltaic cells has steadily improved over the last several years, reaching 4.2% under intense simulated AM1.5G solar illumination [1]. Similar to a polymer bulk heterojunction [2], a mixed layer of donor-acceptor (D-A) molecules provides a spatially distributed D-A interface accessible from most exciton generation sites, leading to a high exciton diffusion efficiency. However, collection of photogenerated charge carriers in mixed molecular layers critically depends on their charge transport properties. An as-deposited, mixed layer of copper phthalocyanine (CuPc):C60 has been found to result in efficient photovoltaic action [3]. Here, we study the optical and structural properties of mixed CuPc:C60 films, and model their charge transport properties based on the carrier drift length in the mixture. By fitting the current-voltage characteristics of organic photovoltaic cells incorporating a 1:1 mixed CuPc:C60 layer, we obtain a carrier collection length of approximately 400 Å, suggesting the existence of percolating paths for charge transport. Furthermore, we propose the hybrid planar-mixed molecular heterojunction structure, or a thin mixed D-A layer sandwiched between homogeneous donor and acceptor layers, for photovoltaic applications. Such a structure combines the high exciton diffusion efficiency of a mixed heterojunction and the low resistance to charge transport of a planar heterojunction between homogeneous D-A layers. With the structure of indium-tin-oxide/150 Å CuPc/100 Å CuPc:C60 (1:1 by weight)/350 Å C60/100 Å bathocuproine/1000 Å Ag, we obtain a power conversion efficiency of (5.0 ± 0.3)% under 1 to 4 suns simulated AM1.5G solar illumination. [1] J. Xue, S. Uchida, B. P. Rand, and S. R. Forrest, *Appl. Phys. Lett.* 84, 3013 (2004). [2] G. Yu, J. Gao, J. C. Hummelen, F. Wudl, and A. J. Heeger, *Science* 270, 1789 (1995). [3] S. Uchida, J. Xue, B. P. Rand, and S. R. Forrest, *Appl. Phys. Lett.* 84, 4218 (2004).

#### 3:30 PM L4.6

**Star-shaped Heptamers of Discotic Dyes as New Materials for Photovoltaic Devices.** Stephan Holger Eichhorn, Nicholas Fox and Bryan Bornais; Chemistry, University of Windsor, Windsor, Ontario, Canada.

Potentially n-type and p-type semi-conducting discotic liquid crystal dyes are linked together to star-shaped heptamers which self-organize into super-columns of separated p-type and n-type columnar stacks. Their synthesis, mesomorphism, and electronic properties will be discussed along with their potential use in photovoltaic devices.

#### 3:45 PM L4.7

**Control and Influence of Molecular Interfaces in Photovoltaics from Discotic Liquid Crystalline Materials.**

Johanna P. Schmidtke<sup>1</sup>, Klaus Mullen<sup>2</sup> and Richard H. Friend<sup>1</sup>; <sup>1</sup>Cavendish Laboratories, University of Cambridge, Cambridge, United Kingdom; <sup>2</sup>Max-Planck-Institut für Polymerforschung, Mainz, Germany.

Discotic liquid crystalline materials are promising hole-conductors for thin-film, organic photovoltaic diodes because of their potential for self-assembly, high charge-transport mobility, and high solubility in common solvents. The importance of molecular interfaces for the charge transport and optical properties of these systems is well recognized, yet is not fully understood. Here we present spectroscopic studies of spin-cast films of hexabenzocoronene derivatives blended with a perylene dye. We find that the blended films have an optical absorption not directly correlated to either of the individual components. We present steady-state and time-resolved photoluminescence studies and absorption spectra, which indicate that the short-range packing of the perylene dye is altered by the presence of the discotic component and so gives rise to an additional ground-state absorption. Furthermore, we show that the additional absorption is directly influenced by the (meso)phase of the hexabenzocoronene derivative. The significance of molecular interfaces

in hexabenzocoronene / perylene blend photovoltaics is further explored by demonstration of a top-surface modification technique on the device active layer. We show that annealing the thin film while under molecular-scale contact with a flat elastomeric surface induces 50% improvement in the external quantum efficiency of the photovoltaic diodes. The influence of the surface energy of the elastomer and morphological changes within the thin film during the technique is discussed. In addition, the effectiveness of the technique for hexabenzocoronene derivatives with various side-chain structures is examined.

#### 4:00 PM L4.8

**High Electron Mobility Liquid Crystals.** Junsheng Yu<sup>1,2</sup>, Zesheng An<sup>1,3</sup>, Seunghyup Yoo<sup>1,2</sup>, Benoit Domerq<sup>1,2</sup>, Stephen Barlow<sup>1,3</sup>, Bernard Kippelen<sup>1,2</sup> and Seth R. Marder<sup>1,3</sup>; <sup>1</sup>Center for Organic Photonics and Electronics (COPE), Georgia Institute of Technology, Atlanta, Georgia; <sup>2</sup>School of ECE, Georgia Institute of Technology, Atlanta, Georgia; <sup>3</sup>Department of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, Georgia.

Organic semiconductors with high charge mobility play a critical role in organic light-emitting diodes (OLED), photovoltaic cells, organic field-effect transistors (OFET), xerography, and photorefractive systems. Charge mobility in organic semiconductors can be measured using various techniques, including the time-of-flight (TOF) method, the pulse-radiolysis time-resolved microwave conductivity (PR-TRMC) technique, the space-charge limited current method (SCLC), and the field-effect transistor method. For most of these applications we are interested in the bulk drift mobility in thin films and therefore, TOF and SCLC are often the methods of choice. We have developed a new and more accurate expression for the space-charge limited current measured in organic thin films. We are currently applying this technique to measure charge mobility in organic films that form injecting contacts with electrodes. Amorphous organic molecular materials and polymers have relatively low electron mobility. Discotic liquid crystals based materials have been studied as electron transport materials. Several different cores have been used and materials based on perylene core have been identified as promising materials. We have measured an electron mobility of 0.2 cm<sup>2</sup>/Vs in 5 μm-thick films in air at room temperature using the space-charge limited current method.

#### 4:15 PM L4.9

**Highly Efficient Thin-Film Organic Solar Cell : Modeling of Light Intensity Dependence and Spectral Response.**

Seunghyup Yoo<sup>1,2</sup>, Benoit Domerq<sup>1,2</sup> and Bernard Kippelen<sup>1,2</sup>; <sup>1</sup>Center for Organic Photonics and Electronics, Georgia Institute of Technology, Atlanta, Georgia; <sup>2</sup>School of ECE, Georgia Institute of Technology, Atlanta, Georgia.

We present the photovoltaic properties of multilayer thin-film solar cells based on organic small molecules, which exhibit power conversion efficiencies over 2.7% under white light illumination (100 mW/cm<sup>2</sup>, 350-900 nm). The electrical characteristics under illumination with varying intensities are measured and analyzed using an equivalent circuit model. The external quantum efficiency is measured as a function of wavelength, and analyzed using the exciton diffusion model that takes into account the distribution of the electric field in the multilayer thin films with the reflecting electrode.[1] The analysis indicates that large exciton diffusion lengths in the active layers are responsible for high internal quantum efficiency. Design considerations for optimizing this kind of solar cells and the loss mechanism that limits the photovoltaic performance will also be discussed. References [1] L. A. A. Pettersson, L. S. Roman, and O. Inganäs, *J. Appl. Phys.* 86, 487 (1999).

#### 4:30 PM L4.10

**Molecular Scale Disorder in Organic Semiconductors- A Limiting Factor in Solar Cell Operation.**

Mathew Koruthu Mathai<sup>1,2</sup>, Magesh Nandagopal<sup>2</sup>, Marcel Utz<sup>2,4</sup> and Fotios Papadimitrakopoulos<sup>1,2,3</sup>; <sup>1</sup>Nanomaterials Opto-Electronics Laboratory, University of Connecticut, Storrs, Connecticut; <sup>2</sup>Polymer Program, Institute of Materials Science, University of Connecticut, Storrs, Connecticut; <sup>3</sup>Department of Chemistry, University of Connecticut, Storrs, Connecticut; <sup>4</sup>Department of Physics, University of Connecticut, Storrs, Connecticut.

Organic semiconductor based solar cells constitute an upcoming technology whose full potential is yet to be realized. One of the factors limiting the enhanced performance of these devices is the transport of charge carriers after exciton dissociation to the respective electrodes. Unlike organic light emitting diodes, in photovoltaics it is important to realize that the measured currents in typical thin film devices arise from the transport of *intrinsic* charge carriers as opposed to *injected* charge carriers. Our studies on metalorganic molecules have indicated that molecular scale disorder plays a major role in determining single

layer device current-voltage ( $J - V$ ) characteristics. Here, molecular scale disorder is the term used to describe disorder in the spatial arrangement of organic moieties around a metal ion in a single molecule. The effect of this disorder is most evident in the ohmic regime of the charge transport manifold, where intrinsic charge carriers dominate measured currents. One of the factors affecting this disorder is the film growth rate while depositing metalorganic molecules onto substrates under high vacuum. In this study, we choose Aluminum *tris* (8-hydroxyquinoline) ( $Alq_3$ ) as a typical charge transporter and report the results for unipolar thin film devices of the same on varying the film growth rate. While X-ray diffraction suggests improved long-range ordering on lowering the film growth rate, the trends in the device currents measured in the ohmic regime do not agree with a simple model based on long-range disorder. However, the use of  $^{27}Al$  solid state magic angle spinning NMR enables an enhanced understanding of the extent of disorder at the length scale of *single* molecules, which is an additional factor governing charge transport in these devices. Based on an understanding of the contribution of molecular scale disorder and dipolar disorder, charge transport in the ohmic regime for  $Alq_3$  is explained. Thus solid state NMR provides an excellent tool to quantify short range disorder and explain the physical origin of the same, which is the main limiting factor in the charge hopping mechanism governing electron/hole transport in small molecule organic thin films.

SESSION L5: Poster Session  
 Chairs: M. Durstock and Daniel Friedman  
 Tuesday Evening, November 30, 2004  
 8:00 PM  
 Exhibition Hall D (Hynes)

**L5.1**  
**Synthesis and Photophysical Properties of Novel Ruthenium Complexes and Their Application in Dye Sensitized Solar Cells.** Cedric Klein, Md. Khaja Nazeeruddin, Paul Liska and Michael Graetzel, Laboratory for Photonics & Interfaces, EPFL, Lausanne, Switzerland.

A new molecular photovoltaic system based on the spectral sensitization of a nanocrystalline semiconductor film by transition metal complexes for conversion of solar light to electricity has been developed in our laboratory [1]. In this system, dye is one of the key components for high power conversion efficiencies. The pioneering studies on dye sensitized nanocrystalline  $TiO_2$  films using *cis*-dithiocyanatobis(4,4'-dicarboxylic acid-2,2'-bipyridine)Ruthenium(II) is a paradigm in this field [2]. In spite this, the main drawback of this sensitizer is the lack of absorption in the red region of the visible spectrum and also relatively low molar extinction coefficient. Several groups have tried to overcome these shortcomings without significant success. It is because, molecular engineering of ruthenium complexes that can absorb all the visible light and act as an efficient charge transfer sensitizer for  $TiO_2$  based solar cells presents a challenging task as several stringent requirements have to be fulfilled by the sensitizer which are very difficult to be met simultaneously. For example, the lowest unoccupied molecular orbitals (LUMO) and the highest occupied molecular orbitals (HOMO) have to be maintained at levels where photo-induced electron transfer into the  $TiO_2$  conduction band and regeneration of the dye by a redox couple can take place at practically 100% yield. The present work discusses the ways to tune the spectral and photo-physical properties of ruthenium polypyridyl complexes while maintaining these conditions. [1] M. Graetzel, Nature 2001, 414, 338. [2] M. K. Nazeeruddin, A. Kay, I. Rodicio, R. Humphry-Baker, E. Muller, P. Liska, N. Vlachopoulos, M. Graetzel, J. Am. Chem. Soc. 1993, 115, 6382.

**L5.2**  
**Abstract Withdrawn**

**L5.3**  
**Increased Efficiency of Dye Sensitized Solar Cells Through the Localization of Light.** Neal Abrams<sup>1</sup>, Lara I. Halaoui<sup>2,1</sup> and Thomas E. Mallouk<sup>1</sup>; <sup>1</sup>Chemistry, Penn State University, University Park, Pennsylvania; <sup>2</sup>Chemistry, American University of Beirut, Beirut, Lebanon.

The effects of tuning and scattering on the enhancement of conventional nanocrystalline  $TiO_2$  dye sensitized solar cells (DSSCs) were investigated when coupled to an inverse opal photonic crystal or disordered macroporous  $TiO_2$  film. Multiple scattering events and localization between the nanocrystalline  $TiO_2$  film and the coupled films have led to an increase in the molar absorption to the red edge of the stop band for the Ruthenium535 dye as compared to a standard Grätzel cell. This enhancement has shown an improvement up to 26% over conventional DSSCs. Both Bragg diffraction and diffuse

scattering events have been attributed to this efficiency enhancement. The effect of introducing scattering centers, tuning the bilayer structure, and novel cell designs will be presented.

**L5.4**  
**Preparation of  $TiO_2$  Nanocrystalline Films For Dye-Sensitized Solid-State Solar Cells.** Boateng Onwona-Agyeman, Shoji Kaneko, Asoka Kumara, Masayuki Okuya and Kenji Murakami; Materials Science and Technology, Shizuoka University, Hamamatsu, Japan.

A promising and cheaper alternative to the silicon solar cell is the dye-sensitized photoelectrochemical cell made from nano-porous  $TiO_2$ . In these cells semiconductor crystallites are covered with the dye at monolayer concentrations. When the dye is excited by the incident light, the electrons are injected into the semiconductor. The oxidized dye is subsequently reduced back to its native state by external donor present in the electrolyte. Unfortunately, the liquid electrolyte (which enables migration of the charge carriers from the dye anchored  $TiO_2$  electrode to the metal counter electrode) in these cells, leads to several technological problems such as; dye desorption, solvent evaporation and degradation, seal imperfection etc. An alternative to this wet cell is the dye-sensitized solid-state cell where the electrolyte is replaced by a solid hole collector. It has been found that  $TiO_2$  films prepared for wet cell use do not function when adopted in solid-state cells. This difference results from the nature of recombination occurring at the exposed conducting glass (i.e., the substrate on which  $TiO_2$  film is deposited) surface in the two cases. Recombination of electrons in the conducting glass surface with acceptors in the electrolyte become negligible in a photoelectrochemical cell, whereas in the solid cell the contact between the conducting glass surface and the solid hole collector short-circuits the cell. We have succeeded in fabricating nanocrystalline  $TiO_2$  films suitable for use in dye-sensitized solid-state cells by several methods. All the  $TiO_2$  films are deposited on conducting tin oxide glass substrates (10ohms/sq) and are sintered at 450°C. The sintered  $TiO_2$  films were immersed in dye solution (Ru-535 bis TBA in a mixture of acetonitrile, tert-butanol and ethanol) at 80°C for 3 hrs. The surface morphologies of the  $TiO_2$  films prepared by the different methods are examined by Scanning Electron Microscope as well as their thickness. The quantum and energy conversion efficiencies are measured for each type film with CuI as the hole collector by using a solar cell evaluation system. Different film morphologies are obtained and how the short-circuiting is prevented is explained.

**L5.5**  
**Temperature effects on photocurrent generation in polymer hetero-junction photovoltaic devices.** Mi Yeon Song<sup>1,2</sup>, Kang-Jin Kim<sup>1</sup> and Dong Young Kim<sup>1</sup>; <sup>1</sup>Optoelectronic Materials Research Center, Korea Institute of Science and Technology, Seoul, South Korea; <sup>2</sup>Department of Chemistry and Molecular Engineering, Korea University, Seoul, South Korea.

In a photovoltaic device of ITO/ $TiO_2$ /poly(3-alkyl thiophene)(PAT)/Au, the charge separation occurs at the interface between  $TiO_2$  after generating photoexcitation in conjugated polymers. The excited electrons under irradiation are injected to  $TiO_2$  due to the difference in a quasi-Fermi level of  $TiO_2$  and LUMO level of conjugated polymer. The photocurrent is delivered to a load by draining the hole carriers to back contact. Conjugated polymer in a photovoltaic device has both functions of light sensitizing and hole carrier transporting. In this study, regio-random poly(3-hexylthiophene)(P3HT), regio-regular poly(3-hexylthiophene)(RP3HT) and regio-regular poly(3-dodecylthiophene)(RP3DT) were used as hole conductors to investigate the structure-property relationships on photocurrent generation at different temperatures. Photovoltaic cells were fabricated with a multi-layered structure using hetero junctions of inorganic  $TiO_2$  and polymers.  $TiO_2$  layer was prepared using the sol-gel method. Spin-coated  $TiO_2$  film on ITO glass substrate was treated at 450 °C for 30 min to obtain anatase crystalline form. Conjugated polymers were spin-coated from monochlorobenzene solution. Au layer as a back contact electrode was evaporated thermally on polymer film at the pressure below  $10^{-5}$  torr. The short-circuit current decreased gradually with lowering temperature. On the other hand, the open circuit voltage increased slightly. The critical temperature ( $T_c$ ) was defined as a temperature at which the  $J_{sc}$  shows a fast decrease. The  $T_c$  related to the drift charge mobility calculated from the space-charge limited current (SCLC) theory using dark J-V characteristics. The  $T_c$  was observed at 273, 223 and 233K for P3HT, RP3HT and RP3DT under 50 mW/cm<sup>2</sup> illumination, respectively, and the drift mobility was  $1.8 \times 10^{-5}$ ,  $5.4 \times 10^{-5}$ , and  $4.8 \times 10^{-5}$  cm<sup>2</sup>/V.s. In photocurrent spectrum, the contributions of PAT in visible range showed a larger effects on temperatures than those of  $TiO_2$  layer near 340 nm.

**L5.6**  
**New application of electrospun  $TiO_2$  nanofibers as an**

**electrode for dye-sensitized solar cell.** Mi Yeon Song<sup>1</sup>, Seong Mu Jo<sup>2</sup> and Dong Young Kim<sup>1</sup>; <sup>1</sup>Optoelectronic Materials Research Center, Korea Institute of Science and Technology, Seoul, South Korea; <sup>2</sup>Polymer Hybrid Research Center, Korea Institute of Science and Technology, Seoul, South Korea.

One-dimensional (1-D) nanostructured metal oxides have attracted much attention because of their unique properties and potential applications such as electronics, photonics and other related areas. In order to prepare 1-D structured metal oxides, several different methods have been suggested including the sol-gel template synthesis for TiO<sub>2</sub> nanowires, the template- and catalyst-free direct synthesis of TiO<sub>2</sub> or ZnO nanorods using MOCVD, the alkali-treatment method for TiO<sub>2</sub> nanotubes and the solution phase synthesis of CdSe nanorods. Recently, the electrospinning technique has been also a simple and cost-effective approach forming polymeric nanofibers within a broad range of diameters from tens of nanometers to few micrometers by proper selection of the processing parameters. In the present work, we employ an electrospinning method to generate the TiO<sub>2</sub> nanofiber web which is applied to an electrode for a photoelectrochemical device so called as a dye-sensitized solar cell (DSSC). TiO<sub>2</sub> nanofiber electrode was electrospun directly onto a SnO<sub>2</sub>:F coated glass substrate from the mixture of titanium propoxide and poly(vinyl acetate) (PVAc) in dimethyl formamide. TiO<sub>2</sub> nanofibers were composed of one-dimensionally aligned fibrils in ca. 20-nm thick as an islands-in-a-sea morphology, which were formed from the phase separation of TiO<sub>2</sub> gel and PVAc during the solidification process. The pretreatment of electrospun web formed the stable DSSC electrode by exposing to solvent vapor prior to the calcination at 450 °C in air. The electrospun TiO<sub>2</sub> electrode could be penetrated efficiently by viscous polymer gel electrolyte because of its porous structure. In order to improve the short-circuit photocurrent, we treated the electrospun TiO<sub>2</sub> electrode with TiCl<sub>4</sub> aq. solution. The rutile crystal was grown epitaxially on anatase TiO<sub>2</sub> fibers. An additional TiO<sub>2</sub> layer increased the volume fraction of active materials resulting in an increase of sensitizer adsorption. The overall IPCE of TiCl<sub>4</sub>-treated electrode was higher than the untreated. In particular, the contribution from TiO<sub>2</sub> increases after the surface treatment due to an increase in packing density. The photocurrent of the DSSC with electrospun TiO<sub>2</sub> electrode was enhanced more than 30% after TiCl<sub>4</sub> treatment. The DSSC with electrospun TiO<sub>2</sub> electrode with gel electrolyte based on PVDF-HFP reveals the conversion efficiency of 4.6 % with the global AM 1.5 illumination of 100 mW/cm<sup>2</sup>. The overall performance of gel electrolyte system is over 90 % of the liquid system.

#### **L5.7**

#### **Patterning Nanoparticles in Self-assembled Conducting/**

**Insulating Block Copolymers.** Chi-Jen Kao<sup>3</sup>, Chi-An Dai<sup>1,3</sup>, Chun-Chih Ho<sup>2</sup> and Wei-Fang Su<sup>2,3</sup>; <sup>1</sup>Department of Chemical Engineering, National Taiwan University, Taipei, Taiwan; <sup>2</sup>Department of Materials Science and Engineering, National Taiwan University, Taipei, Taiwan; <sup>3</sup>Institute of Polymer Science and Engineering, National Taiwan University, Taipei, Taiwan.

Nanoparticle/polymer hybrid materials have been found useful in the fabrication of devices such as light emitting diode, photovoltaic, etc. In order to achieve high device efficiency, it is desired to have nanoparticles well organized and well dispersed in the polymer matrix. We are proposing to pattern nanoparticles in self-assembled conducting/insulating block copolymers to achieve the goal. The conducting/insulating block copolymers of poly (para-phenylene)-b-Poly (2-vinyl pyridine) (PPP-PVP) were synthesized by using sequential anionic polymerization to produce a precursor of PPP-PVP, poly (1,3 cyclohexadiene)-b-poly (2-vinyl pyridine) (PCHD-PVP). PCHD-PVP copolymers were subsequently derivatized through an aromatization reaction and reduced to PPP-PVP. Block copolymers that can be self-assembled to different morphologies e.g. lamellae, cylinders and spheres were synthesized. Semiconducting nanoparticles of cadmium sulfate (CdS) was incorporated into PPP-PVP nanostructure using in-situ synthesis of CdS in the PVP domain. The structure of the nanoparticle/copolymer hybrid was determined by AFM and TEM. Optoelectronic property of the hybrid material was measured by UV-Vis absorption and photoluminescence. The structure-property relationship of the patterned nanoparticle/copolymer hybrid will be discussed.

#### **L5.8**

#### **Photoresponse of sol-gel-synthesized ZnO nanorods.**

Seung-eon Ahn, Jong Soo Lee, Hyunsuk Kim, Kang Hyun Kim and Gyu Tae Kim; Electrical engineering, Korea university, Seoul, South Korea.

ZnO nanorods were grown on SiO<sub>2</sub>/Si substrates by a sol-gel method at low temperatures of T=95°C. The diameters and the lengths of ZnO nanorods increased at high concentrations of zinc nitrate hexahydrate and methenamine solution. Similar photoresponses were

recorded in a single ZnO nanorod and a network of ZnO nanorods below λ=400 nm in air. Current-voltage characteristics followed a typical nonlinear behavior with noticeable temperature dependence and the conductance was enhanced in vacuum with negligible photoresponses. In photoluminescence (PL) and photocurrent (PC) spectra, the PL peak (λ= 380 nm, 3.26 eV) did not match the PC edge (λ= 400 nm, 3.1 eV), indicating a nondirect band-gap origin of the photocurrent. In this presentation, the origin of the photocurrent in ZnO nanorods will be discussed from the point of the influence of the desorption of adsorbed water molecules on the surface or inside of ZnO nanorods.

#### **L5.9**

#### **Synthesis and Characterization of Cu<sub>x</sub>(In<sub>y</sub>Ga<sub>1-y</sub>)Se<sub>2-z</sub>**

**Nanoparticles by Colloidal Route.** Ki-Hyun Kim<sup>1,2</sup>, Young-Gab Chun<sup>1</sup>, Byung-Ok Park<sup>2</sup> and Kyung-Hoon Yoon<sup>1</sup>; <sup>1</sup>New & Renewable Energy Research Center, Korea Institute of Energy Research, Deajeon, South Korea; <sup>2</sup>Dept. of Inorganic Materials Engineering, Kyungpook National University, Daegu, South Korea.

CuInGaSe<sub>2</sub> (CIGS) is one such material which is attractive as it allows tailoring of the band gap and other material properties. In this work, we synthesized the quaternary CIGS nanoparticles with various mole ratios for absorber layer of solar cells by colloidal route. The CIGS nanoparticles were prepared by reacting CuI, InI<sub>3</sub>, GaI<sub>3</sub> in pyridine with Na<sub>2</sub>Se in methanol at 0°C under inert atmosphere. The reaction products of dark red and yellow colors were turned out to be NaI and CIGS nanoparticles, respectively, by inductively coupled plasma emission spectroscopy (ICPAES) and scanning electron microscopy energy dispersive spectroscopy (SEM-EDS) analyses. Chalcopyrite structure of the CIGS nanoparticles was confirmed by x-ray diffraction (XRD) and transmission electron microscopy (TEM) diffraction patterns. For Cu<sub>0.9</sub>In<sub>0.7</sub>Ga<sub>0.4</sub>Se<sub>2</sub> stoichiometric ratio, tube-type particles were obtained from reaction at 0°C for 20 min. The CIGS tube-type particles were measured to be with the widths in the range of 100-450 nm and lengths of 1-5 μm by high-resolution scanning electron microscopy (HRSEM). For Cu<sub>1.1</sub>In<sub>0.68</sub>Ga<sub>0.23</sub>Se<sub>1.91</sub>, and Cu<sub>0.9</sub>In<sub>0.8</sub>Ga<sub>0.3</sub>Se<sub>2</sub> ratios spherical nanoparticles were obtained from the same reaction condition of Cu<sub>0.9</sub>In<sub>0.7</sub>Ga<sub>0.4</sub>Se<sub>2</sub> tube-type particles. As the reaction time increased, the shapes of CIGS nanoparticles changed from flat to spherical types. As compared to particles from Cu<sub>0.9</sub>In<sub>0.8</sub>Ga<sub>0.3</sub>Se<sub>2</sub> ratio, more uniform and smaller nanoparticles with diameter in the range of 5-15 nm were obtained from the Cu<sub>1.1</sub>In<sub>0.68</sub>Ga<sub>0.23</sub>Se<sub>1.91</sub> stoichiometric ratio. The morphology change of the CIGS particles has been discussed in terms of the ratio of Cu/(In,Ga).

#### **L5.10**

#### **Preparation of CuInGaSe<sub>2</sub> Solar Cells by Nanoparticles-**

**Based Spray Deposition.** Ki-Hyun Kim<sup>1,2</sup>, Young-Gab Chun<sup>2</sup>,

Byung-Ok Park<sup>1</sup> and Kyung-Hoon Yoon<sup>2</sup>; <sup>1</sup>Dept. of Inorganic Materials Engineering, Kyungpook National University, Daegu, South Korea; <sup>2</sup>New & Renewable Energy Research Dept., Korea Institute of Energy Research, Daegu, South Korea.

Chalcopyrite material CuInGaSe<sub>2</sub> (CIGS) is known to be a very prominent absorber layer for high efficiency thin film solar cells. Current interest in the photovoltaic industry is to identify and develop more suitable materials and processes for the fabrication of efficient and cost-effective solar cells. Various processes have been tried for making a low cost CIGS absorber layer. Spray deposition process has been employed using CIGS nanoparticles in low temperature processes for solar cells. We synthesized CIGS nanoparticles for the CIGS absorber layer by low temperature colloidal and solvothermal routes. The CIGS absorber layers for solar cells were prepared by spray deposition of nanoparticle precursors in glove box under inert atmosphere. An automatic air atomizing nozzle spray system with computer controlled X-Y step motor system was used to spray. The nanoparticle precursor CIGS film was deposited onto molybdenum-coated soda-lime glass substrates (2.5 cm x 5.0 cm) heated to 160°C. The film thickness in the range of 2 μm ± 0.3 μm was attained by spraying of 10 M colloidal over an area of 12.5 cm<sup>2</sup>. The CIGS nanoparticles-based films were deposited under various deposition conditions such as the deposition temperature and time, Cu/(In,Ga)/Se stoichiometric ratios and flow rate of carrier gas in the spray system. CdS buffer layer was deposited on the CIGS/Mo/soda-lime glass substrate by chemical bath deposition. Then ZnO layer and Al electrode were successively deposited on the layer by rf-sputtering and evaporation, respectively. The CIGS nanoparticles-based absorber layers were characterized by using energy dispersive spectroscopy (EDS), x-ray diffraction (XRD) and high-resolution scanning electron microscopy (HRSEM). The efficiency of solar cells at active area of 0.25 cm<sup>2</sup> was measured under illumination of 100 mW/cm<sup>2</sup>.

### L5.11

**Controlling the Nanoscale Architecture of Dye-Sensitized Solar Cells.** Cristin Moran<sup>1</sup>, Adam Smith<sup>1</sup>, Dan Li<sup>2</sup>, Younan Xia<sup>2</sup>, Barney Taylor<sup>3</sup> and Michael Durstock<sup>1</sup>; <sup>1</sup>Air Force Research Laboratory, Dayton, Ohio; <sup>2</sup>Department of Chemistry, University of Washington, Seattle, Washington; <sup>3</sup>University of Dayton Research Institute, Dayton, Ohio.

One challenge to widespread use of dye-sensitized photovoltaic devices is improving the conversion efficiency of solar to electrical power to be more comparable to traditional silicon devices. Recent studies suggest that the morphology of the active layers of a PV device greatly affects the efficiency. In order to obtain reasonable efficiencies, the size and spacing of the charge transport materials must be on the order of the exciton diffusion length scale. Typical dye-sensitized solar cells are composed of a polycrystalline mesoporous titania layer which functions to transport electrons from a photoexcited dye molecule to the electrode. We have investigated two different types of nanostructured titania, nanotemplated titania rods and electrospun titania nanofibers. Anodic aluminum oxide membranes are used to fabricate arrays of titania nanotubes of controlled length and diameter perpendicular to the electrode surface. The aligned titania nanotubes provide a direct pathway for charge transport, and have a highly controlled surface area. Additionally, electrospinning was used to fabricate disordered titania nanowires on the surface of a counter electrode. The effects of the two titania architectures on device fabrication and performance is discussed.

### L5.12

**Spatially-Defined Arrays of Cu<sub>2</sub>O Quantum Dots on SrTiO<sub>3</sub> (100).** Yingge Du<sup>1</sup>, James Groves<sup>1</sup>, Igor Lyubintsev<sup>2</sup> and Suntharampillai Thevuthasan<sup>2</sup>; <sup>1</sup>University of Virginia, Charlottesville, Virginia; <sup>2</sup>Pacific Northwest National Laboratory, Richland, Washington.

Numerous lattice mismatched material systems form self-assembled quantum dots during epitaxial thin film growth. To most effectively harness this phenomenon into engineered devices, the quantum dot size, size distribution, inter-dot spacing and properties must be precisely controlled. This talk will report the results of efforts to grow arrays of Cu<sub>2</sub>O quantum dots on SrTiO<sub>3</sub> (100) substrates. In this work, a focused ion beam tool has been used to define the growth location of individual quantum dots by injecting gallium ions into each selected growth site on the single crystal surface. Following subsequent surface annealing and cleaning, oxygen plasma assisted molecular beam epitaxy has been used to grow arrays of Cu<sub>2</sub>O quantum dots. Single-phased Cu<sub>2</sub>O nanodots were obtained under carefully controlled temperature and oxygen partial pressure. Under selected conditions, islands form first in the FIB-generated surface topography and grow in size before reaching a critical limit, and then, with continuous deposition, islands begin to form elsewhere on the unmodified surface. Island size, shape and relation to local FIB modifications are studied. In-situ X-ray photoelectron spectroscopy and Auger electron spectroscopy analysis demonstrated that the final phase of the nanodots was Cu<sub>2</sub>O; x-ray diffraction was performed to confirm quantum dot epitaxy. This paper will report upon the extent to which quantum dot size, size distribution, and inter-dot spacing has been controlled. It will also describe differences in quantum dot growth motivated by changes to the specific focused ion beam surface patterning parameters employed. The photocatalytic decomposition of water on Cu<sub>2</sub>O under visible light irradiation has been reported. Well defined Cu<sub>2</sub>O island arrays on the SrTiO<sub>3</sub> substrate could be an efficient, clean means of producing hydrogen for fuel cells. The ability to control quantum dot growth as reported here also has broad implications for nanoscale electronics, magnetics, and related fields of use.

### L5.13

**Dye Sensitized Solar Cells Using Nanostructured Thin Films of Titanium Dioxide.** D. A. Gish, G. K. Kiema, M. O. Jensen and M. J. Brett; Electrical and Computer Engineering, University of Alberta, Edmonton, Alberta, Canada.

Dye sensitized solar cells (DSSC's) are an attractive alternative to solid state solar cells due to their high conversion efficiency, low fabrication cost, and simple cell technology. DSSC devices typically include a porous dye sensitized TiO<sub>2</sub> electrode. We have developed a single-step deposition process, utilizing e-beam evaporation and advanced substrate motion, which is capable of fabricating highly porous TiO<sub>2</sub> thin films consisting of tightly woven nanoscale fibres [1]. These nanofibres have diameters as small as 20 nm, and maintain a consistent fibre width throughout the entire thickness of the film (up to 4 µm). This new process is an extension of the glancing angle deposition (GLAD) technique, which exploits the accentuated self-shadowing effects which arise when the vapour flux arrives at highly oblique angles to the substrate surface [2]. The morphology of GLAD films, which have nominal porosities of 70%, can be engineered

into slanted columns, polygonal spirals, zigzags, or vertical posts. While the standard GLAD technique (with a fibre size of 300 nm) has been utilized to fabricate TiO<sub>2</sub> electron collecting layers for DSSC's [3], this new nanofibre process affords an additional degree of control of the nanoscale morphology of the TiO<sub>2</sub> GLAD films, with control of both the quantity and size scale of the porosity now possible. We present here results of the performance of our DSSC's based on the nanofibrous films and compare these results with our earlier DSSC work and with conventional DSSC's based on colloidal TiO<sub>2</sub> films. [1] M. O. Jensen, M. J. Brett, Appl. Phys. A, In press (2004). [2] K. Robbie, M. J. Brett, U. S. Pat. 5,866,204, (1999). [3] G. K. Kiema, M. J. Colgan, M. J. Brett, Solar Energy Materials & Solar Cells, In press (2004).

### L5.14

**Electrospun Mesoporous Metal Oxide Nanofibers.** Minedys Macias<sup>1</sup>, John P. Ferraris<sup>1</sup> and Kenneth J. Balkus, Jr.<sup>1</sup>; <sup>1</sup>Chemistry, University of Texas at Dallas, Richardson, Texas; <sup>2</sup>The Nanotech Institute, University of Texas at Dallas, Richardson, Texas.

Electrospinning has been used extensively to produce fibers of various polymers. We have used this technique in a novel way to produce mesoporous molecular sieve fibers of various metal oxides including TiO<sub>2</sub>, Ta<sub>2</sub>O<sub>5</sub>, SnO<sub>2</sub>, and mixed metal oxides such as ITO, VxTixOx, and NbTaO<sub>5</sub>. These mesoporous materials are made by the liquid crystal templating mechanism using surfactants. Pluronic P-123 (EO20PO70EO20) and Brij-76 (C18H37(OCH2CH2)20 - OH) have been used as structure directing agents. The mesoporous metal oxide fibers exhibit the advantage of high surface area, high density and thermal stability. Furthermore, we have used some of the metal oxide fibers as supports for Carbon nanofibers in order to improve some of their properties such as electrical conductivity.

### L5.15

**Surface Modification and Enhanced Electron Transfer at Sputter Deposited ITO Thin Films For Greater Organic Photovoltaic Efficiency.** Michael Brumbach<sup>1</sup>, Adam Simmonds<sup>1</sup>, Chet Carter<sup>1</sup>, Carrie Donley<sup>2,1</sup>, Saneeha Marikkar<sup>1</sup> and Neal Armstrong<sup>1</sup>; <sup>1</sup>Chemistry, University of Arizona, Tucson, Arizona; <sup>2</sup>Physics, University of Cambridge, Cambridge, United Kingdom.

Small molecule chemisorption can be used as a modification strategy for transparent conducting oxides, such as ITO, to enhance their physical and chemical compatibility with organic thin films, their effective work functions, and to enhance rates of charge injection. Such modifications dramatically improve the performance of both organic light emitting diodes and organic photovoltaic devices. This talk will focus on new small-molecule modification strategies developed for ITO films which have been freshly sputter-deposited, affecting modification within seconds of cessation of the deposition process. Freshly deposited ITO films hydrolyze quickly upon exposure to ambient atmosphere, which has been shown to partially insulate the ITO surface, slowing electron transfer rates and creating electrical dead spots. New modifiers will be presented which contain multiple heteroatoms, in an aromatic framework, which block hydrolysis, and impact on both wettability and solution electron transfer to probe molecules. Preliminary studies of vacuum-deposited organic photovoltaic devices will be presented to show how enhanced rates of solution electron transfer correlate with changes in overall device efficiency.

### L5.16

**Bulk Heterojunction Photovoltaic Cells from Polymer Mixtures and Copolymers with Soluble Oxadiazole and Quinoline Polymers as Electron Acceptors.** Vasilis Gregoriou<sup>1</sup>, Christos L. Chochos<sup>1</sup>, Giannis Govaris<sup>1</sup>, Panagiotis Yiannoulis<sup>2</sup> and Joannis Kallitsis<sup>2</sup>; <sup>1</sup>FORTH-ICEHT, Patras, Greece; <sup>2</sup>University of Patras, Patras, Greece.

The interplay between phase separation in polymer blend consisting of electron donating poly(3-hexylthiophene), P3HT, with an electron accepting polyquinoline and the subsequent photovoltaic performance has been examined. Observed quenching of the photoluminescence of the polythiophene in the blend and a 100-fold photocurrent enhancement of the bulk heterojunction device compared with the single layer P3HT device suggested photoinduced electron transfer from the polythiophene to the polyquinoline phase. The structure of the blend film was investigated using atomic force microscopy and scanning electron microscopy. The phase separated morphology of P3HT:polyquinoline blend consisted of SDPQ spherical domains (500nm) dispersed in a P3HT matrix. In addition, new copoly(aryl ether)s containing substituted triphenyl, quinquiphenyl, anthracene and fluorene segments with aromatic 1,3,4-oxadiazole moiety and a copolymer containing fluorene and 1,3,4-oxadiazole unit were prepared by nucleophilic polycondensation and Suzuki coupling reaction respectively. These polymers are extremely soluble in common organic solvents such as tetrahydrofuran (THF), trichloromethane (CHCl<sub>3</sub>)

and *o*-dichlorobenzene (ODCB) and their absorption and emission properties were investigated and revealed that they emit blue light both in solution and in solid state except from the copolyethers with the anthracene segment which are yellow emitters. Furthermore, due to their high electron affinity caused from the oxadiazole ring, their photovoltaic response was investigated as blends P3HT as electron donor. The power conversion efficiencies of the devices were low but higher than that of a monolayer device consisted of P3HT. Moreover, morphological characterization of the blends surface was performed using AFM. Finally, the anthracene-oxadiazole copolymer was also examined in a monolayer photovoltaic device and gave one of the highest open circuit voltages reported in the literature (Voc) 0.89V.

#### **L5.17**

#### **Study of Hole Transport in Diodes Made from Low Bandgap Polyfluorene Copolymers.** Abay Gadisa Dinku<sup>1</sup>, Deepak Sharma<sup>2</sup>,

Fengling Zhang<sup>1</sup>, Mattias Svensson<sup>3</sup>, Mats R. Andersson<sup>3</sup> and Olle Inganäs<sup>1</sup>, <sup>1</sup>Applied Physics, Center of Organic Electronics, Linköping University, Linköping, Sweden; <sup>2</sup>Department of Electrical Engineering, Indian Institute of Technology Kanpur, Kanpur, India; <sup>3</sup>Department of Organic Chemistry and Polymer Technology, Chalmers University of Technology, Goteborg, Sweden.

Polyfluorene polymers have emerged as a new class of semiconductor materials due to their high charge carrier mobility and good processability. Moreover, several polyfluorenes and their copolymers incorporate liquid crystallinity. We have investigated the charge (holes) transport characteristics of polyfluorene copolymers that have the same aromatic backbone structure and differ only by the length of their alkyl side chain. The synthesis of the copolymers was performed through careful molecular engineering so that they achieve the desired quality for use in solar cells. At moderately low fields, the hole transport in the bulk of all the copolymers is space charge limited with a field and temperature dependent mobility. The experimental data was fitted by numerical calculation of the Poisson's equation considering a Poole-Frenkel type of field and temperature dependent mobility. Important microscopic transport parameters are extracted and discussed based on the spatially correlated Gaussian disorder model (GDM) that treats carrier transport as hopping among sites subject to energetic and positional disorder. In all the devices studied, it was observed that the hole mobility is governed by both thermal and field activation. However, the degree of the disorder seems to vary with the polymer type.

#### **L5.18**

#### **Electronic Structure of Novel Low Band Gap Conjugated Polymers.** Stina Karin Maria Jonsson<sup>1</sup>, Helena Sodergren<sup>2</sup>, Patrick Norman<sup>2</sup>, Erik Perzon<sup>3</sup>, Mats R. Andersson<sup>3</sup>, Miaxiang Chen<sup>1</sup>, Magnus Berggren<sup>1</sup> and Mats Fahlman<sup>2</sup>; <sup>1</sup>Department of Science and Technology, Linköping University, Norrköping, Sweden; <sup>2</sup>Department of Physics and Measurement Technology, Linköping University, Linköping, Sweden; <sup>3</sup>Materials and Surface Chemistry, Chalmers University of Technology, Goteborg, Sweden.

The electronic structure of two novel low band gap conjugated polymers, hereafter denoted LBPF5 and EP37, have been studied. Both materials are alternating conjugated polymers based on fluorene units and low band gap donor-acceptor-donor units. These materials have successfully been synthesized with the aim of achieving materials that absorb well in the solar spectral region and emit in the infrared region. Thus LBPF5 and EP37 are potential candidates as electron donors in plastic solar cells. It is also important that the materials can conduct holes fairly well in order for the devices to function. Hence, the emphasis in this study has been to study the valence and the conduction bands. In particular the degree of localization or delocalization along the polymers and the symmetry of these states have been studied, since these features can be related to their transport properties. The main experimental part of this work is photoelectron spectroscopy, near-edge x-ray photon absorption and resonant photoemission. These techniques have been used to probe the frontier orbitals of these systems. The experimental results are interpreted with the help of density functional theory calculations. The valence bands are dispersed while the conduction bands are more flat. This means that the transport of electrons in the valence bands should be easy, due its delocalized states, in contrast to limited electron transport in the conduction band, due its more localized states. Indeed, device characteristics of prototype devices based on these materials indicate that the hole conduction (electron transport in the valence band) is good while the electron conduction (electron transport in the conduction band) is poor.

#### **L5.19**

#### **Efficient Bulk Heterojunction Photovoltaic Cells using Sublimable Transition Metal Complex as Photosensitizers.** Wai Kin Chan<sup>1</sup>, Hei Ling Wong<sup>1</sup>, Lillian Sze Man Lam<sup>1</sup>, Kai Wing Cheng<sup>1</sup>, Ka Yan Kitty Man<sup>1</sup>, Chung Yin Kwong<sup>3</sup> and Aleksandra B. Djuricic<sup>2</sup>; <sup>1</sup>Chemistry, The University of Hong Kong, Hong Kong,

Hong Kong; <sup>2</sup>Physics, The University of Hong Kong, Hong Kong, Hong Kong; <sup>3</sup>Electrical and Electronic Engineering, The University of Hong Kong, Hong Kong, Hong Kong.

A series of chlorotricarbonyl rhenium(I) bis(phenylimino)acenaphthene (Re-DIAN) complexes were used as the photosensitizers to fabricate photovoltaic cells. The structures of some of these complexes were confirmed by X-ray crystallography. Unlike other transition-metal-based photovoltaic sensitizers, these complexes are sublimable. Compared to other rhenium diimine complexes based on bipyridine or 1,4-diaza-1,3-butadiene ligands, these complexes have lower band gaps, which can be adjusted easily by changing the structure of the ligand. The complex also exhibits bipolar charge transport character with relatively high charge carrier mobilities in the order of  $10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ . Multilayer heterojunction and bulk heterojunction devices with fullerene as the electron accepting molecule were prepared. For the bulk heterojunction devices, the fill factor and power conversion efficiency under AM 1.5 simulated solar light illumination were 0.51 and 1.29 %, respectively. The amount of photosensitizer and electron transport molecules may strongly influence the balance between the exciton formation, dissociation, and charge transport processes. The effect of changing the Re-DIAN/C<sub>60</sub> ratio was studied. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels of the Re-DIAN series were estimated by cyclic voltammetry using ferrocene as the internal standard. Optical functions of Re-DIAN in the spectral range between 1.55 and 3.10 eV (400 - 800 nm) were determined by spectroscopic ellipsometry. Atomic force microscopic images showed that the complex dispersed evenly with fullerene molecules in solid state.

#### **L5.20**

#### **Mobility Measurements on Donor-Acceptor-Donor co-Polyfluorenes.** Mattias Andersson<sup>1,4</sup>, Miaoxiang Chen<sup>2,4</sup>, Erik Perzon<sup>3,4</sup>, Mats R Andersson<sup>3,4</sup>, Magnus Berggren<sup>2,4</sup> and Olle Inganäs<sup>1,4</sup>; <sup>1</sup>Department of Physics and Measurement Technology, Linköping University, Linköping, Sweden; <sup>2</sup>Department of Science and Technology, Linköping University, Norrköping, Sweden; <sup>3</sup>Department of Materials and Surface Chemistry, Chalmers University of Technology, Goteborg, Sweden; <sup>4</sup>Center for Organic Electronics, Linköping, Sweden.

Conjugated polymers of alternating fluorene and donor-acceptor-donor units can be tuned for band gap and, due to the existence of liquid crystalline phases, thin film structure. Low band gap polymers are of use in polymer photovoltaics and can also give rise to electroluminescence at 1  $\mu\text{m}$ . We report here studies of electronic transport in these polymers, using mainly field effect transistors as tools. Novel phenomena complicate measurements, in particular light activation and short relaxation times. Some of the polymers go from being more or less insulating at all biases if kept in the dark, to fairly good transistor operation under illumination. When transistor operation is achieved, it is well behaved but relaxing and show high mobility of holes. Other members of this class of polymer show less pronounced light activation and mobilities in the  $10^{-2} \text{ cm}^2/\text{Vs}$  range can be reached. The liquid crystalline state is easily accessible and somewhat modifies the transport properties.

#### **L5.21**

#### **Synthesis of thiophene-tetrafluorophenylene copolymers for FETs.** David James Crouch<sup>1</sup>, Simon Coles<sup>2</sup>, Martin Heeney<sup>3</sup>, Michael Hursthouse<sup>2</sup>, Iain McCulloch<sup>3</sup> and Peter Skabara<sup>1</sup>; <sup>1</sup>Chemistry, University of Manchester, Manchester, United Kingdom; <sup>2</sup>Chemistry, University of Southampton, Southampton, United Kingdom; <sup>3</sup>MERCK Chemicals Ltd, Southampton, United Kingdom.

Compared with organic p-type semiconductors (hole transport materials), organic n-type semi-conductors for practical use are few and rather difficult to develop. The incorporation of fluorine groups, attached directly to the conjugated chain, is an effective way to raise the ionisation potential of an organic semi-conductor and therefore increase the oxidative stability of the material. To date, very few fluorinated examples have appeared in the literature and often include complicated synthetic strategies. The synthetic route to fluorinated monomers described in this work makes use of inexpensive hexafluorobenzene leading directly to 1,4-bis(2-thienyl)-2,3,5,6-tetrafluorobenzene derivatives. Extension of the thiophene framework via bromination of (1) yields analogues (2) and subsequent coupling with organo-tin reagents leads to a range of pi-extended fluorinated n-type phenylene-thiophene monomers such as the symmetrical tetrahexyl derivative (3). Synthetic manipulation of the phenylene backbone within the monomer affords a range of phenylene and difluorophenylene derivatives (2 and 3), therefore enabling comparative studies on the effects of fluorination has on the molecular properties of the monomers, and subsequent polymeric materials. X-Ray crystallographic studies indicate significant intramolecular H...F and S...F contacts within the molecular

framework of these pi-extended monomers resulting in increased planarity within the molecular architecture. These interactions are expected to persist in the corresponding polymer, leading to a high number of extensive pi-pi co-facial interactions and efficient packing in the solid state. Accordingly, polymerisation of (3) occurs readily under chemical and electrochemical conditions affording polymeric materials (4). For example FeCl<sub>3</sub> oxidative coupling can be achieved using traditional methods or via microwave assisted reactions utilising propagation times as low as 600 seconds. Thiophene and selenophene spaced containing polymers can also be prepared using Stille-type conditions in reactions involving dibromo analogues 2 with the corresponding distannyl reagent, affording polymeric materials 5. This molecular architecture, combined with such ease of synthesis, combined with the molecular architecture generated within these systems makes these pi-extended polymers attractive candidates for field effect transistor (FET) applications. P-type transistor devices were fabricated and the electrical properties of the polymers are reported.

#### L5.22

**Role of exciton transport in the internal quantum efficiency of composite solar cells.** K. Kawata<sup>1</sup>, Victor M. Burlakov<sup>1</sup>, H. E. Assender<sup>1</sup>, G. A. D. Briggs<sup>1</sup>, A. Ruseckas<sup>2</sup> and I. D. W. Samuel<sup>2</sup>; <sup>1</sup>Department of Materials, University of Oxford, Oxford, United Kingdom; <sup>2</sup>School of Physics and Astronomy, University of St Andrews, St Andrews, United Kingdom.

We carried out modeling and experimental studies of exciton transport in conjugate polymer MEH-PPV. Description of exciton transport is performed within analytically solvable model taking into account resonance energy transfer between inhomogeneously broadened exciton energy levels. The model parameters are extracted from experimental data on time dependence of exciton photoluminescence of MEH-PPV films deposited on quartz and on TiO<sub>2</sub> substrates. Using the parameterized model we predict an increase in the internal quantum efficiency (absorbed photon - to conduction electron conversion coefficient) of the MEH-PPV/TiO<sub>2</sub> solar cells upon decreasing wavelength of incident monochromatic light, which is confirmed by experimental observations.

#### L5.23

**Modeling of ambipolar charge transport in composite solar cells.** C. Martin, Victor M. Burlakov, H. E. Assender and G. A. D. Briggs; Department of Materials, University of Oxford, Oxford, United Kingdom.

We performed continuous modeling of ambipolar charge transport in composite solar cells with interpenetrating columnar morphology. Both diffusion and drift of electrons and holes, and their injection and bimolecular recombination at the interfaces between electron- and hole-conducting columns were taken into account. We predict a pronounced peak in the short circuit current as a function of the column length, which suggests that the columnar structure can be optimized according to the charge transport parameters of the composite materials. The peak was also observed in the composite with triangular shape of the columns. The results were checked against static and dynamic disorder in the composite materials. The peak origin and implementation of the results to real photovoltaic devices are discussed.

#### L5.24

**Photovoltaic Devices Incorporating Multiple Electron Donor Polymers for Efficient Solar Light Harvesting.** Young-Gi Kim, Barry C. Thompson, Emilie Galand and John R. Reynolds; Department of Chemistry, Center for Macromolecular Science and Engineering, University of Florida, Gainesville, Florida.

A family of variable gap conjugated polymers in which 2,5-thienylene, 2,5-(3,4-alkylenedioxythiophene), 1,4-phenylene, and cyanovinylene linkages are utilized along the polymer backbone has been designed and synthesized in order to achieve variable spectral absorption polymers with band gaps (E<sub>g</sub>) ranging from 1.5 to 2.6 eV, while also modulating the HOMO/LUMO electronic energy levels as desired for bulk heterojunction organic solar cells. As an initial result, linear poly[2,5-thienylene-1,4-(2,5-didodecyloxyphenylene)] (LPTB) shows the ability to transfer photoinduced charge into the electron acceptor PCBM after sensitization with incident light in an LPTB/PCBM based solar cell. Photovoltaic devices incorporating LPTB, MEH-PPV, and PCBM have been constructed with AM1.5 efficiencies of 1%, comparable to values observed for MEH-PPV/PCBM devices. These results indicate that the multi-component blends can serve as efficient photoactive layers in the photovoltaic devices. Similar results have been achieved upon blending narrow band gap cyanovinylene polymers with MEH-PPV and PCBM. In order to reveal the relationship between the photoinduced charge transport phenomena and the electronic energy levels in this family of variable band gap conjugated polymers, optoelectronic, electrochemical and

spectroscopic results will be presented.

#### L5.25

**Regioselective fullerene-based acceptors for bulk-heterojunction solar cells.** Yusuke Tajima, Yasuo Shigemitsu, Yoshitaka Ito and Kazuo Takeuchi, RIKEN, Wako, Japan.

Bulk-heterojunction (BHJ) solar cells based on conjugated polymer/fullerene blends showed power conversion efficiency over 3%. However, it is still quite modest for practical use. Essential parameters which determine the power conversion efficiency of photovoltaic devices are the short-circuit current (J<sub>sc</sub>), the open circuit voltage (V<sub>oc</sub>), and the fill factor. Among them, the V<sub>oc</sub> in BHJ solar cells is directly related to the first reduction potential (E1<sub>red</sub>) of the fullerenes as an electron acceptor because the electronic structure of the acceptor contributes to improvement of the open circuit potentials in a BHJ solar cell. The use of fullerene derivatives to the BHJ solar cell guarantees processability and small reorganization energy for intermolecular electron transfer. In order to increase the V<sub>oc</sub>, it is required that the fullerene derivative as an acceptor has lower reduction potential than that of [6,6]-phenyl C61-butyric acid methyl ester (PCBM). While the tuning of the reduction potential of fullerene-based materials has also been attempted by other research groups, most studies have not succeeded in the preparation of the fullerene derivative which surpasses PCBM at first reduction potential. The regioselective multi-functionalization to fullerene core is effective to improve the electronic properties of fullerene derivative, but it was impossible to control positions of addition reaction sites. Recently, we have developed a novel method for converting fullerene epoxides, C60On, into 1,3-dioxolane compounds. It made regioselective synthesis of fullerene derivative possible by using isolated C60On isomers. Using this method, we synthesized some fullerene-1,3-dioxolanes regioselectively to examine acceptability in the BHJ solar cell. The first reduction potentials of them obtained by differential pulse voltammetry (DPV) were compared with LUMO energy obtained from the semiempirical molecular orbital calculation (PM3). The E1<sub>red</sub> of bis-dioxolane 2b was nearly equal to that of PCBM as shown in Table 1. In the same way, other poly-dioxolane compounds are expected to be acceptors which are superior to PCBM. These fullerene derivatives were also applied to the acceptor in BHJ solar cell devices. The details of undergoing the device characterization will be discussed at the meeting.

#### L5.26

**Photovoltaic devices based on polymer-polyelectrolyte carbon nanotube composites.** Marisol Reyes-Reyes, Benjamin S. Harrison, Kyungkon Kim, Richard Czerw and David L. Carroll; Center for Nanotechnology, Wake Forest University, Winston-Salem, North Carolina.

We have fabricated photovoltaic devices using electroactive polymers and undoped and nitrogen doped multiwalled carbon nanotubes (MWNTs). The results indicate that conjugated polymer-MWNT composites represent an improvement in the performance of organic devices. Alternative device designs were examined in order to make the best use of composite properties. Polyelectrolytes were electro-statically absorbed onto the nanotubes and concentration effects were characterized. The results of the synthesis and characterization are shown, and first results are discussed.

#### L5.27

**An Investigation of Substituted Poly(Arylene Vinylene)s in Organic Photovoltaic Devices.** Adam P. Smith<sup>1</sup>, Michael F. Durstock<sup>1</sup>, John B. Ferguson<sup>1</sup>, Rachel R. Smith<sup>2</sup> and Barney E. Taylor<sup>2</sup>; <sup>1</sup>Polymer Branch, Air Force Research Laboratory, WPAFB, Ohio; <sup>2</sup>University of Dayton Research Institute, Dayton, Ohio.

One approach for improving the power conversion efficiency of bulk heterojunction organic photovoltaic devices is to increase the number of incident photons that are absorbed. This can be done by broadening the spectral response of the photoactive layer. State-of-the-art systems with either MDMO-PPV or P3HT as electron donor and PCBM as acceptor absorb only a small portion of the solar irradiance. By incorporating conjugated polymers that exhibit absorbance in other regions of the spectrum, more of the incident radiation can be harnessed and converted to electrical energy. Of particular utility are poly(arylene vinylene)s because the band gaps of these materials can be tuned over several electron volts by changing the nature of the arylene (i.e. phenyl or thienyl) and its substituents (i.e. alkyl or alkoxy). Results of our investigations involving the incorporation of such polymers into bulk heterojunction devices will be presented.

#### L5.28

**Optical and metal contact properties of chemically synthesized poly3-octylthiophene.** Hailin Hu<sup>1</sup>, Cecilia Lopez Mata<sup>1,3</sup>, Oscar Salinas<sup>1</sup> and Maria Elena Nicho Diaz<sup>2</sup>; <sup>1</sup>Solar Materials, Centro de Investigacion en Energia, UNAM, Temixco,

Morelos, Mexico; <sup>2</sup>Centro de Investigacion en Ingenieria y Ciencias Aplicadas, UAEM, Cuernavaca, Morelos, Mexico; <sup>3</sup>Instituto Tecnologico de Zacatepec, Zacatepec, Morelos, Mexico.

Poly(3-octylthiophene (P3OT) is a very promoting conducting polymer because of its chemical stability in air and solubility in common organic solvents. In this work the polymer was chemically synthesized in chloroform by using FeCl<sub>3</sub> as the oxidant and washed with methanol, acetone and 10% HCl. The obtained undoped P3OT powder was dissolved in toluene and cast on glass or on conducting glass (ITO) substrates. XRD spectrum of the polymeric film showed a semicrystalline P3OT. The doped P3OT product was obtained by dissolving FeCl<sub>3</sub> in the undoped polymer solution and then casting on the same substrates. Band gap and ionization potential values of the P3OT films obtained from the optical spectra and electrochemical voltammograms were close to those reported in the literature. Gold as well as aluminum were used as metal contacts on P3OT films. Rectification behavior has been showed in the I-V curves of the ITO/undoped-P3OT/Al as well as ITO/doped-P3OT/Au arrangements, whereas an ohmic contact was found in ITO/undoped-P3OT/Au. A Schottky barrier was proposed for the former contacts.

#### L5.29

**Modification of Interfacial Interactions within Organic Photovoltaic Devices by Electrostatic Self-Assembly of PEDOT:PSS.** Rachel R. Smith<sup>1</sup>, Barney E. Taylor<sup>1</sup>, Michael F. Durstock<sup>2</sup>, John B. Ferguson<sup>2</sup> and Adam P. Smith<sup>2</sup>; <sup>1</sup>University of Dayton Research Institute, Dayton, Ohio; <sup>2</sup>Air Force Research Laboratory, Wright-Patterson Air Force Base, Ohio.

It is common practice in the fabrication of donor/acceptor organic photovoltaic devices to insert a conductive layer, composed of materials such as poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS), between the ITO electrode and the photoactive layer. The interface between the PEDOT:PSS layer and the photoactive layer has proven to be a crucial factor influencing both the topography and performance of organic photovoltaic devices. Thus, it is necessary to develop methods which provide better control of interfacial interactions. One such method involves the use of electrostatic self-assembly whereby a film is deposited by alternately dipping a substrate into dilute solutions of a polycation or polyanion. This technique affords control of surface interactions as evidenced by the fact that hydrophobicity can easily be manipulated by solution conditions. While the PEDOT:PSS is an aqueous suspension, the sulfonic acid functional groups on the PSS polymer allow it to be used as the anionic component in this application. By alternating the PEDOT:PSS with various polycations, we have been able to assemble ultra-thin conductive layers and have been investigating their use in organic photovoltaic devices. Preliminary results have shown that the conductivity is maintained even for very thin films, which could result in a decrease in the amount of incident light absorbed by the PEDOT:PSS layer.

#### L5.30

**Asymmetric Derivatives of Bathophenanthroline as Thermally Stable Materials for Organic Electronics.** Jian Li<sup>1</sup>, Biwu Ma<sup>1</sup>, Chad Tao<sup>1</sup>, Raymond Kwong<sup>2</sup>, Barry Rand<sup>3</sup>, Stephen R. Forrest<sup>3</sup> and Mark E. Thompson<sup>1</sup>; <sup>1</sup>Department of Chemistry, University of Southern California, Los Angeles, California; <sup>2</sup>Universal Display Corporation, Ewing, New Jersey; <sup>3</sup>Department of Electrical Engineering, Princeton University, Princeton, New Jersey.

Bathophenanthroline (BPhen) and its derivative BCP have been utilized widely for organic solar cells and organic light emitting diodes (OLEDs) as charge-blockers, host materials and electron transporting materials. However, BCP is a crystalline material and has no measurable glass transition temperature (T<sub>g</sub>) between room temperature and its melting point. It is believed that the crystallization of BCP at room temperature possibly hinders its further application for organic electronics. The synthesis of a series of asymmetric bathophenanthroline derivatives has provided a number of amorphous materials, e.g. T<sub>g</sub> ranges from 50 to 100 °C. The asymmetry inherent in these compounds prevents these low molecular mass compounds from crystallizing, thus yielding higher thermal stability over the symmetric derivatives. The photophysical and electrochemical properties of BPhen can be modified in a certain range by adding different functional groups to BPhen. We will also report and discuss the preliminary results on the incorporation of different BPhen derivatives into organic solar cells and organic light emitting devices as hole-blocking materials.

#### L5.31

Abstract Withdrawn

#### L5.32

**Anomalous Temperature Dependence of Reverse Saturation Currents in GaAsN.** Joseph Matthew Luther<sup>1,2</sup>, Steven W.

Johnston<sup>1</sup>, Sarah R. Kurtz<sup>1</sup>, Daniel J. Friedman<sup>1</sup>, Aaron J. Ptak<sup>1</sup> and Richard K. Ahrenkiel<sup>1</sup>; <sup>1</sup>NREL, Golden, Colorado; <sup>2</sup>Applied Physics, Colorado School of Mines, Golden, Colorado.

We have measured the temperature-dependence of the reverse-saturation or leakage currents in dilute nitrogen alloys of composition GaAs(1-x)N(x) (x = 0.01% to 1%). The alloy GaAs(1-x)N(x) (also referred to here as GaAsN) has an anomalously large bowing coefficient with bandgap shifts of approximately 0.1 eV/N% for N less than 3%. Our test devices were p-n junctions with the structure n-GaAs / p-GaAs(1-x)N(x) that were grown by MOCVD. Current-voltage (I-V) measurements as a function of temperature indicate a large step of reverse-bias leakage current when warming from liquid helium temperatures to room temperature. In addition to the expected exponential thermal current component, a sharp onset occurs at approximately 90 K in GaAsN p-n junctions. No such current increases were seen in a control sample of pure GaAs. We will propose physical mechanisms responsible for this sharp increase in saturation current. Deep Level Transient Spectroscopy (DLTS) measurements, also performed on these samples, indicate an electron trap in p-type GaAsN with similar thermal activation energy as the current step. In other words, our I-V-T activation energy agrees well with a trap activation energy measured by DLTS. Because of this agreement, we believe that the current step is related to the detected electron trap. These data, as well as, data on MBE-grown p-type GaAsN schottky diodes with similar alloy concentrations will be shown and compared. These new data provide some important clues to explaining the unusual electron transport effects in p-GaAs(1-x)N(x).

#### L5.33

**Modelling grain boundary diffusion and its affect on solar cell efficiency.** Michael A. Cousins, David Lane and Keith D. Rogers; Centre for Materials Science and Engineering, Cranfield University, Swindon, United Kingdom.

In our recent work [1,2] we have examined sulphur diffusion in polycrystalline CdTe thin films, and in particular diffusion from a sulphur source of finite size as found in many thin film photovoltaic solar cells. Here we present an expansion of this work to include the effects of sulphur diffusion on the opto-electronic properties of CdTe/CdS based solar cells. Two-dimensional concentration (x) profiles for CdTe<sub>x</sub>S<sub>1-x</sub> within single columnar grains of CdTe were converted into a series of electronic property profiles and a finite difference algorithm was used to solve the co-dependent Poisson and continuity equations for this system. This has, in effect, allowed us to model the current-voltage characteristics and spectral response of an individual mini solar cell that consisted of a single CdTe grain and its associated CdS layer that was assumed to be homogeneous. Our previous observations on the effects of different fabrication processes on sulphur diffusion are updated to include those on the resulting device parameters. Some observations on scaling these results to larger areas through observed statistical distributions of grain sizes are also discussed. 1. D W Lane, J D Painter, M A Cousins, G J Conibeer, K D Rogers, Cadmium telluride thin films (part 1): "The grain boundary diffusion coefficient", Thin Solid Films, 431-432 (2003) 73-77. 2. M A Cousins, D W Lane, J D Painter, G J Conibeer, K D Rogers, "Sulphur diffusion in cadmium telluride thin films (part 2): Modelling grain boundary diffusion", Thin Solid Films, (2003), 431- 432, 78-83.

#### L5.34

**Dendritic CuIn Films Grown by Electroless Deposition.** Jonathan D. Painter<sup>1</sup>, David Lane<sup>1</sup>, Keith D. Rogers<sup>1</sup>, Ian Forbes<sup>2</sup>, Robert W. Miles<sup>2</sup> and Kathleen M. Hynes<sup>2</sup>; <sup>1</sup>Centre for Materials Science and Engineering, Cranfield University, Swindon, United Kingdom; <sup>2</sup>Northumbria Photovoltaics Applications Centre, Northumbria University, Newcastle, United Kingdom.

CuInS<sub>2</sub> films are often grown in a two step process with the deposition of a CuIn alloy followed by a sulphurisation process. Numerous techniques exist for the deposition of CuIn. In this work CuIn films have been deposited on tin oxide coated glass using the electroless deposition technique, a low cost low temperature approach. The films were found to consist of a two layered structure. Initially, Cu islands grew forming a compact layer on the substrate. The deposition process subsequently produced dendritic Cu-In alloys from the tops of the Cu islands. Various CuIn phases were observed, namely Cu<sub>9</sub>In<sub>4</sub>, Cu<sub>11</sub>In<sub>3</sub> and CuIn, the presence of which was related to the solution pH. The solution pH also affected the growth of the two layers, varying the thickness of the Cu/CuIn layers.

#### L5.35

**Bath pH Dependence on the Structural and Optical Properties of Chemical Bath Deposited CdS Thin Films.** Udaya Ketipearachchi, David Lane, Keith D. Rogers, Jonathan D.

Painter and Michael A. Cousins; Centre for Materials Science and Engineering, Cranfield University, Swindon, United Kingdom.

High quality CdS thin films made with ultrasonic agitation during chemical bath deposition were investigated. The change in band gap and variation of atomic stacking during the film growth was observed as a function of bath pH. The band gap of as-deposited thin films of CdS was found to be between 2.42 eV and 2.52 eV, the highest being observed when the pH was 9.0. The transition from predominantly cubic ( $\beta$ -CdS) to hexagonal ( $\alpha$ -CdS) was observed with decreasing pH. The lattice parameters of CdCl<sub>2</sub> treated CdS were found to be  $a = 0.414$  nm and  $c = 0.672$  nm. The calculations based on Sherrer formula showed significant grain growth after annealing with CdCl<sub>2</sub>. No apparent effect of ultrasonication on crystalline structure of CdS was seen in this method, although ultrasonication was noted to produce films with a higher quality optical surface. A maximum bath temperature was fixed at 70 °C in order to suppress the rate of homogeneous reaction and minimise the evaporation of ammonia from the chemical bath.

#### L5.36

**Growth Of Photovoltaic Thin Film Of CdTe By Polymeric Precursors.** Claudio Luiz Carvalho, Victor Ciro Solano Reynoso, Raphael Otavio Peruzzi and Paulo Roberto Pesquero; Physics and Chemistry, Universidade Estadual Paulista, Ilha Solteira, SP, Brazil.

Nowadays, the carefulness with our environment has increased meaningfully. Thus, source of energy ecologically sustainable has been researched more and more. As we know some materials that use a photovoltaic (PV) process can transform luminous energy into electric energy, however the efficiency is still lower. Then, using the combination between some chemical elements of periodic table in the composition of such materials, as CdS, GaAs / GaAlAs, CdTe, InP and others, and together an special deposition process it is possible to obtain PV films with interesting technological applications, however such materials are regarding expensive. In this work, we considered the cost/benefit relationship of these photovoltaic materials looking for cheaper process. Therefore, following this reasoning, we obtained CdTe film using polymeric precursor solution deposited on glass substrate by dip coating technique. The films were submitted to heat treatment around 400°C-760°C during 5 minutes in resistive furnace with controlled atmosphere. Fitting of normalized transmittance using normal incidence and considering the thickness infinite substrate (Swanepol) it was possible to determine the thickness and refractive index that were around 50 nm and 1.6, respectively. Band gap 1.9 eV was also estimated using the data above and Tauc method. XRD showed some characteristics peaks of CdTe and spurious phases too. A quick study using optical microscopy showed a smooth and uniform surface. Chemical and efficiency measurements are still carrying out.

#### L5.37

**Absorber Films of Antimony Chalcogenides via Chemical Deposition for Photovoltaic Applications.**

M. T. Santhamma Nair, Yamilet Rodriguez, Yolanda Pena, Sarah Messina, Jose Campos and P. Karunakaran Nair; CIE - Solar Energy Materials, Univ. Nacional Autonoma de Mexico, Temixco, Morelos, Mexico.

Antimony sulfide thin films of thickness up to 400 nm have been deposited on glass substrates at 1-10 °C from chemical bath, with deposition yield of up to 30%. When these films and Sb<sub>2</sub>S<sub>3</sub>-CuS are heated in nitrogen at 300 °C, crystalline, photoconductive-intrinsic Sb<sub>2</sub>S<sub>3</sub> or p-type CuSbS<sub>2</sub> are formed with optical band gap of 1.4-1.7 eV. By controlling the deposition and heating condition, (i)Sb<sub>2</sub>S<sub>3</sub>-(p)CuSbS<sub>2</sub> layer is formed, which is utilized in a photovoltaic structure, (n)CdS:In-(i)Sb<sub>2</sub>S<sub>3</sub>-(p)CuSbS<sub>2</sub>, which demonstrated an open circuit voltage of 350 mV. The effort to obtain antimony selenide thin films from solution mixture containing SbCl<sub>3</sub> and sodium selenosulfate results in mixed phase Sb<sub>2</sub>O<sub>3</sub>/Sb<sub>2</sub>Se<sub>3</sub> film, which when heated in the presence of Se-vapor converts to single phase Sb<sub>2</sub>Se<sub>3</sub> film with optical band gap of 1.1 eV. Such films possess dark resistivity of 10<sup>-8</sup> Ω<sup>-1</sup>cm<sup>-1</sup> and shows photosensitivity of two orders. The possible formation of CuSbSe<sub>2</sub> or CuSbS/Se thin films, when a CuS or Cu<sub>2</sub>Se thin film deposited and heated at 300-400 °C, is investigated for their use in photovoltaic structures.

#### L5.38

**Ag<sub>2</sub>Se and AgSbSe<sub>2</sub> Thin Films for Photovoltaic Structures Produced Through Reaction of Chemically Deposited Selenium Thin Films with Ag and Sb<sub>2</sub>S<sub>3</sub>.** Bindu Krishnan, M. T. Santhamma Nair and P. Karunakaran Nair; CIE, Department of Solar Energy Materials, Universidad Nacional Autonoma de Mexico, Temixco, Morelos, Mexico.

We report the use of selenium thin films of thickness 100-300 nm, deposited from a 0.013 M solution of Na<sub>2</sub>SeSO<sub>3</sub> of pH 4.5 maintained at 10 °C for 13 h, as a source of selenium in vapour phase or solid

state reaction with vacuum deposited Ag thin film or chemically deposited Sb<sub>2</sub>S<sub>3</sub> thin film over which a Ag-film has been deposited. Ag<sub>2</sub>Se thin film of n-type conductivity, 10 ohm<sup>-1</sup>cm<sup>-1</sup> is formed when the Ag-film and Se-film are maintained in close contact at 80 °C for 1 h. When Ag film is deposited over Se- film and heated at 150 °C, photoconductive Ag<sub>2</sub>Se films are formed with dark conductivity 10<sup>-8</sup> ohm<sup>-1</sup>cm<sup>-1</sup>. The optical band gap of the material formed is nearly 1 eV. When a stack of Sb<sub>2</sub>S<sub>3</sub> film and Ag film are heated in contact with Se film, formation of AgSbSe<sub>2</sub> has been observed due to the solid state reaction of Sb<sub>2</sub>S<sub>3</sub> and Ag<sub>2</sub>Se. This AgSbSe<sub>2</sub> thin film is photoconductive and p-type. The optical band gap is nearly 1 eV and the dark conductivity is 10<sup>-3</sup> ohm<sup>-1</sup>cm<sup>-1</sup>. The materials developed have been utilized to fabricate a photovoltaic structure SnO<sub>2</sub>-(n)CdS:In-(i)Sb<sub>2</sub>S<sub>3</sub>-(p)AgSbSe<sub>2</sub>/Ag<sub>2</sub>Se, with an open circuit voltage of 400 mV under an illumination intensity of 1 kWcm<sup>-2</sup>. Further studies on characterization and device characteristics will be presented.

#### L5.39

**Optical studies on chloride-treated RF sputtered CdMnTe films.** Shanli Wang, Sunghyun Lee, Akhlesh Gupta and Alvin D.

Compaan; Department of Physics & Astronomy, University of Toledo, Toledo, Ohio.

Recently a goal of 25% conversion efficiency at air mass 1.5 has been established for polycrystalline film tandem cells. The optimum band gaps for a two-junction tandem cell are 1.14eV and 1.72eV.[1] CdTe - based wide-band-gap materials, such as CdZnTe and CdMnTe, are attractive for their flexibility in changing the band gap and are considered as attractive wide-band-gap candidates in such tandem cells.[2, 3] CdMnTe has been studied for several decades as a dilute magnetic semiconductor; however, there are few reports of this material for photovoltaic applications.[3, 4] An important step in fabricating high performance CdTe-based solar cells is the CdCl<sub>2</sub> activation treatment. Various explanations of the CdCl<sub>2</sub> treatment invoke the formation of shallow acceptor complexes, improvements of the microstructure, and interdiffusion. The improvement demonstrated for CdTe cell performance often exceeds a factor of two. It is expected that chloride treatments may improve the performance of cells fabricated from CdMnTe ternary alloys as well. All CdMnTe films in this report were deposited by RF sputtering with a cold pressed target composed of the mixed binary compounds. To exploit CdCl<sub>2</sub> treatments on the CdMnTe alloy, some efforts were made on vapor chloride thermal treatment in which the samples were annealed with either CdCl<sub>2</sub> or CdCl<sub>2</sub> + MnCl<sub>2</sub> ambients. The annealing condition usually was 380oC for 30mins in dry air. However, under these conditions, the sample band gap shifts to low energy and large disruptive changes occur in the surface morphology. Therefore, vapor chloride treatments on CdMnTe films were investigated with various conditions of ambients, temperatures and durations. In order to understand such treatments, scanning electron microscopy (SEM), x-ray diffraction (XRD), atomic force microscopy (AFM), and Raman spectroscopy were carried out before and after chloride treatments on CdMnTe films. Raman spectra indicate there are no elemental Te-related peaks for the as-deposited sample and after high temperature annealing without chloride vapors. However, Te-related peaks are usually observed after Cl treatment. Best PV results on these films have been obtained for a 500 oC annealing in a reducing atmosphere without chloride followed by vapor chloride treatment at 385 oC. This work supported by NREL High Performance PV project. Reference: [1] T. J. Coutts, K. A. Emery, and S. Ward, Prog. Photovolt: Res. Appl. 10 (2002) 195 [2] S.A.Ringel, R.Sudharsanan, A.Rohatgi, and W.B.Carter, J.Electron.Mater. 19 (3) (1990) 259 [3] S.H.Lee, A.Gupta, and A.D.Compaan, phy.stat.sol. (c) 1(4), (2004) 1042, [4] A.Rohatgi, S.A.Ringel, R.Sudharsanan, P.V.Meyers, C.H.Liu, and V. Ramanathan, Solar Cells, 27 (1989), 219

#### L5.40

**Direct Power Conversion from Neutrons, Photons and Alpha Particles.** Anthony Nicholas Caruso<sup>1</sup>, Petru Lunca-Popa<sup>1</sup>, Jennifer I.

Brand<sup>2</sup> and Peter A. Dowben<sup>1</sup>; <sup>1</sup>Physics & Astronomy, University of Nebraska, Lincoln, Nebraska; <sup>2</sup>College of Engineering, University of Nebraska, Lincoln, Nebraska.

While the direct conversion of radiation to power, with a solid state device, has been known since the invention of the photodiode in 1954, conversion of radiation other than visible light to electrical power, using a solid state device, has remained elusive. Using a novel all boron carbide solid state diode, we have established that neutron and alpha particle (helium nucleus) capture (absorption) can be directly converted to electrical energy. For small activated radiological sources, piles and reactors, direct electrical power generation with a boron rich semiconductor (like boron carbide) provides the added advantage of the neutron shielding through <sup>10</sup>B isotope absorption, and the potentials that arise due to a compact power source that is the result of direct power conversion. We have been able to fabricate this all boron carbide p-n junction diode by decomposing two different

icosahedral closo-carborane source compounds (metacarborane for the n-type layer and orthocarborane for the p-type layer). In this talk, we shall present raw data, showing neutron, photons in the visible and alpha particle incidence, resulting in current production with no voltage applied (zero bias). These boron carbide devices are insensitive to gamma and beta radiation. The neutron and alpha particle electrical energy conversion process is different from photon conversion in that greater than one billion charge-hole pairs are created per converted alpha particle or low kinetic energy (thermal) neutron versus the single charge-hole pair created per converted photon. The implications for remote power sources are outstanding. Using, for example, a milligram of  $^{210}\text{Po}$  with 5 curie strength or a microgram of moderated  $^{252}\text{Cf}$  with  $10^6$  neutrons/cm<sup>2</sup>/sec we may be able to obtain power on the scale of Watts. Fossil fuel and traditional nuclear power generation require a thermodynamic intermediary, and are thus always inefficient, as demonstrated by Carnot. In light of the widely used indirect conversion methods for power generation, this direct current generation from neutrons, alphas and photons is a key development for energy conversion from radiation. The conversion capabilities of these boron carbide diodes are also a giant step toward increased safety, decreased pollution and greater efficiency in many contexts. Because boron carbides are resistant to mechanical wear, are rather chemically inert and stable in harsh radiological and temperature environments, direct electrical power from a number of sources in extreme conditions is now possible.

#### L5.41

#### TeO<sub>2</sub> Based Thin Film pn-junction Devices for Solar Cells

**Applications.** Khalil Ibrahim Arshak, John Harris, Gerald O'Dwyer and Olga Korostynska; Computer and Electronic Engineering, University of Limerick, Limerick, Limerick, Ireland.

To date thin semiconducting films have been deposited under vacuum using pure elements such as Silicon (Si) and compounds such as Cadmium Telluride (CdTe), Cadmium Sulphide (CdS), Copper Indium Diselenide (CuGaSe<sub>2</sub>), etc [1]. Although oxides have been used in nanocrystalline dye cells [1], no evidence was found in the literature on the evaporation of oxides to fabricate pn-junction devices. The objective of this work was to explore the possibility of achieving an inexpensive solar cell by depositing a p-type oxide material on an n-type silicon wafer. In this study Tellurium Dioxide (TeO<sub>2</sub>) powder was thermally evaporated in various thicknesses to form a thin-film p-type layer on suitably prepared n-type silicon wafers to fabricate pn heterojunctions for solar cell applications. TeO<sub>2</sub> layers of 245nm and 1000nm thickness were evaporated at a deposition rate of 2-3 nm/s under an initial vacuum pressure of  $2 \times 10^{-6}$  mbars. Aluminium electrodes were evaporated on the TeO<sub>2</sub> at a pressure of  $4 \times 10^{-6}$  mbar to provide an electrical connection to the devices. Contact wires were then affixed using quick-drying silver paint. Current-voltage (I/V) characteristics were examined in darkness and under illumination using an AM1.5 Solar Simulator. Parameters such as Short Circuit Current (I<sub>sc</sub>), Open Circuit Voltage (V<sub>oc</sub>), Fill Factor (FF) and efficiency were measured. All samples exhibited diode behaviour and all performed as photocells. Devices with a TeO<sub>2</sub> layer thickness of 240nm yielded a V<sub>oc</sub> of 240mV with an I<sub>sc</sub> of 4.6mA, leading to an efficiency of 0.73% with a FF of 0.158. Devices with a TeO<sub>2</sub> layer thickness of 1mm yielded a V<sub>oc</sub> of 290mV with an I<sub>sc</sub> of 5.32mA, leading to an efficiency of 1.31% with a FF of 0.178. This indicated that the efficiency increased with an increasing TeO<sub>2</sub> layer thickness. 1. Green, M.A., Photovoltaics: technology overview. Energy Policy, 2000. 28(14): p. 989-998.

#### L5.42

#### Experimental Investigations of the Dynamic Behavior of Poly-Crystal and Amorphous Solar Cell Panels.

Michael Abraham Slonim<sup>1</sup> and Alexander A. Slonim<sup>2</sup>; <sup>1</sup>Electrical and Computer Engineering, Ben Gurion University of the Negev, Beer Sheva, Israel; <sup>2</sup>Department of Electrical and Electronic Engineering, Negev Academic College of Engineering, Beer Sheva, Israel.

Three photo-voltaic commercial panels based on poly-crystal (two panels) and amorphous (one panel) solar cells are analyzed. The dynamic behavior of the panels under transients, arising due to instantaneous load changes, is investigated. Two types of transients are observed: the first one is an instantaneous short-circuiting from an open circuit condition and the second one is an instantaneous open-circuiting from a short circuit condition. These transients are chosen because only the solar cell panel parameters themselves determine the developed processes. The solar cell panels behave differently under transients arising due to their short-circuiting and open-circuiting. The transients arising due to instantaneous short-circuiting from an open circuit condition have a character of damped oscillations for all analyzed solar cell panels. Such processes are observed in second order circuits. The transients arising due to instantaneous open-circuiting from a short circuit condition have a character of exponential growth for all analyzed solar cell panels. Such processes are observed in first order circuits. The processes developed

under above transients are determined by the solar cell panel parameters only, therefore the results obtained cannot be explained by the currently used equivalent diagrams. Solar cell equivalent diagrams used to date contain only resistance and capacitance, i.e. these are first order circuits where damped oscillations cannot arise. To explain these results it is necessary to propose a new equivalent diagram for solar cell panels, containing inductance during short-circuiting. Such an equivalent diagram will correspond to the experiments.

#### L5.43

**Current Matching and Operation Properties of a-Si/ $\mu\text{c-Si}$ /Thin-film Tandem Solar Cells.** Jeong Chul Lee, Keun Sik Lim, Jae Ho Yun, Seok Ki Kim, Jinsoo Song and Kyung Hoon Yoon; Korea Institute of Energy Research, Daejeon, South Korea.

Silicon based thin-film solar cells have been considered to be a promising candidate for low cost and high efficiency PV. Especially a-Si:H/ $\mu\text{c-Si}$  stacked cells are getting more attentions both for ideal bandgap combination of top and bottom cells and for high stability of  $\mu\text{c-Si}$  bottom-cell. In order to improve conversion efficiency of tandem solar cells, it is required to get an insight on current matching and operation properties of stacked solar cells. In this paper, the pin a-Si:H/ $\mu\text{c-Si}$ :H thin-film tandem solar cells are prepared by multi-chamber cluster tool systems. The intermediate ZnO thin-layer between top and bottom cells are very advantageous for preventing formation of reverse diode. The kink effect of pin/pin solar cells are totally removed by inserting thin (less than 10nm) ZnO between top and bottom cells. The effective current matching between two cells could be obtained both by enhancing light trapping and by changing thickness of a-Si:H top cell. The open circuit voltage (V<sub>oc</sub>) of a-Si:H single pin and tandem solar cells are strongly affected by front TCO. SnO<sub>2</sub>:F(AU-glass) and chemically etched ZnO:Al TCOs are used for solar cell deposition. The textured ZnO:Al TCO was advantageous for improving V<sub>oc</sub> as well as jsc of single and tandem solar cells. More detailed current matching and operation properties with front TCO, thickness of top and bottom cells and different light trapping schemes are presented in this paper.

#### L5.44

**Crystal Growth of Photovoltaic Polycrystalline Si<sub>1-x</sub>Ge<sub>x</sub> by Die-Casting Growth Technique.** Hisashi Hirahara<sup>1</sup>, T. Iida<sup>1</sup>, Y. Sugiyama<sup>1</sup>, Y. Takanashi<sup>1</sup> and S. Sakuragi<sup>2</sup>; <sup>1</sup>Department of Material Science, Tokyo University of Science, Noda, Japan; <sup>2</sup>Union Material, Inc., Kitasouma, Japan.

Alloys of Si and Ge (Si<sub>1-x</sub>Ge<sub>x</sub>) are important materials not only for microelectronic devices but also for solid-state power generator such as solar cells and thermoelectric devices. Chemical stability, mechanical strength at elevated temperatures, and a close match of the n-/p-type alloys in terms of their thermal and electrical characteristics enable better device operation with no noticeable variation in efficiency. Si<sub>1-x</sub>Ge<sub>x</sub> has been studied as possible high conversion efficiency photovoltaic material. Such alloys can have a conversion efficiency of 43 % when the Ge amount is about 60 %. This is because of the carrier-multiplication mechanism that comes from the Auger generation. However, because Si-Ge system shows a complete series of solid solutions in their phase relationship, it is difficult to precipitate crystals possessing a certain composition of Si or Ge selectively using conventional Bridgman and Czochralski methods. In the case of Zone melting method, the precipitating crystals at a certain composition may be available with a slight compositional change, but the grown ingot includes many defects that degrade the photovoltaic properties. We have applied a die-casting growth process combined with advanced version of the Bridgman method as a growth technique for Si<sub>1-x</sub>Ge<sub>x</sub> polycrystalline crystals 25 mm in diameter and 2 mm thick. Crystallization began with the initial melt composition of Si : Ge = 15 : 85 in atom.% which gives the composition of the precipitating Si<sub>0.4</sub>Ge<sub>0.6</sub> crystals on the Si-Ge phase diagram. Subsequent changes in the growth parameters, including the temperature gradient of the growth furnace and the growth rate, resulted in the solidification process forming coin-shaped sheet samples composed of a slight compositional fraction. Post annealing processes allow to form polycrystalline Si<sub>0.4</sub>Ge<sub>0.6</sub> samples with homogeneous x=0.6 composition. By changing the initial melt composition, various samples of Si<sub>1-x</sub>Ge<sub>x</sub> in the composition range between x=0.5 and 1.0 were obtained. We report here on the preparation of those crystals by the die-casting growth process and the effects of the post-annealing heat treatment in terms of changes in the compositional fraction in the sample and electrical and optical properties. The microstructure of the samples was analyzed by using an optical microscope, and their composition was determined by electron-probe microanalysis. Room temperature absorption measurement and low-temperature photoluminescence measurement were carried out. Hall effect measurement was also performed as a function of the sample temperature.

#### L5.45

##### Characterization of Polycrystalline Si Sheet Grown by Die-casting Growth Process Combined with the Bridgman Technique. Kenichi Saito<sup>1</sup>, T. Iida<sup>1</sup>, D. Akimoto<sup>1</sup>, A. Nose<sup>1</sup>, Y. Takanashi<sup>1</sup>, S. Sakuragi<sup>2</sup>, H. Namba<sup>2</sup> and T. Shimazaki<sup>2</sup>;

<sup>1</sup>Department of Materials Science and Technology, Tokyo University of Science, Noda, Japan; <sup>2</sup>Union Material Inc., Ibaraki, Japan.

A new growth technique of preparing polycrystalline silicon (Si) sheets of 100 mm x 150 mm x 0.5 mm by die-casting molten Si has been developed. This is an advanced version of the Bridgman crystal growth method and is based on g-shaped crystal technology that gives crystal growth technology enabling us to prepare crystals of various shapes in a crucible. Since the molten Si is one of the most reactive elements, it reacts with almost all elements and compounds resulting in stable ceramics, alloys, and many kinds of compounds. An important aspect of the die-casting growth method is to obtain non-wetting (non-reactive) chemical condition of molten silicon during growth, which is just like mercury droplets, at elevated growth temperature. We report here on the structural, electrical and chemical results obtained from polycrystalline sheet Si by die-casting growth method. Unintentional impurity incorporation during growth process was analyzed by glow discharge mass spectroscopy (GDMS). Transition metal impurities such as iron (Fe), cobalt (Co), and chromium (Cr), which degrade the solar cell performance, were order of  $10^{13-14} \text{ cm}^{-3}$ , depending on the growth parameters. The results of minority carrier lifetime measurements by the microwave photoconductivity decay (m-PCD) method are also discussed in terms of variation of the growth conditions and position in the sheet wafer. Post annealing was performed at temperature ranging from 1373 to 1650 K in argon (Ar), nitrogen (N<sub>2</sub>) and hydrogen (H<sub>2</sub>) containing forming gases such as Ar+H<sub>2</sub> and N<sub>2</sub>+H<sub>2</sub>. Subsequent hydrogen passivation of the die-cast Si sheet was also carried out at temperature ranging from 673 to 823 K. The effects of the post-annealing heat treatment and hydrogen passivation in terms of changes in the minority carrier lifetime and grown-in defects were investigated.

#### L5.46

##### Theoretical models and experimental results on the temperature dependence of high performance polyfluorene solar cells. Fengling Zhang<sup>1,3</sup>, Sasa Lasic<sup>1,3</sup>, Mikael Svensson<sup>2</sup>, Mats R. Andersson<sup>2,3</sup> and Olle W. Inganäs<sup>1,3</sup>;

<sup>1</sup>Biomolecular and organic electronics, IFM, Linköping University, Linköping, Sweden; <sup>2</sup>Department of Materials and Surface Chemistry /, Chalmers University of Technology, Gothenburg, Sweden; <sup>3</sup>Center of Organic Electronics, Linköping University, Linköping, Sweden.

The development of polymer solar cells requires both advances in materials and in our understanding of device physics in organics. Therefore simulation of devices is an important tool. We have developed a mathematical model of charge injection, charge transport and optical generation in donor-acceptor solar cells, integrating thin film optics as present in the thin film devices as well as models of injection from electrodes. The model has been evaluated with respect to the behaviour of devices based on alternating copolyfluorene incorporating dioctyl-fluorene and di-thienyl-benzothiadiazole (DiO-PFDTBT)/[6,6]-phenyl-C61-butyric acid methylester (PCBM) materials, in particular with the variation of temperature. Such devices generate power conversion efficiencies (AM1.5, 100 mW/cm<sup>2</sup>) close to 3% at room temperature. We find agreement between simulation and experimental results as pertains to the temperature dependence of photovoltage and fill factor. Polymer solar cells were fabricated by spin-coated DiO-PFDTBT mixed with PCBM from organic solutions on top of polymer anode PEDOT:PSS (40 nm) coated on indium-tin-oxide (ITO) substrates. LiF and Al as top electrode was vapor deposited in vacuum. These solar cells with different active areas were characterized under various temperatures. The temperature dependences of these polymer solar cells show that the short-circuit photocurrent densities (J<sub>sc</sub>) first increase with temperature from RT to 80 - 90 °C more than 20%, then decrease. The open-circuit voltages monotonically decrease and the fill factors slightly increase, resulting in the same tendency of power conversion efficiency (PCE) as J<sub>sc</sub>. The highest PCE was achieved at 80 - 90 °C. The temperature dependences also vary with the thickness of the active layers. Results show that J<sub>sc</sub> saturates at higher temperature in thick active layer. These results can be explained by taking into account the temperature dependence of the mobility, and the thermal activation of the injection current from the electrodes. The increase of PCE with temperature is a distinguishing feature of polymer solar cells.

#### L5.47

Current Transport in Schottky and P-N Junction Solar Cells using Metal-Induced Grown Poly-Si Thin Films. Chunhai Ji and Wayne A. Anderson; Electrical Engineering, SUNY at Buffalo, Amherst, New York.

Poly-Si thin films deposited at relative low temperature by using the metal-induced growth (MIG) method have the advantages of less metal impurity contamination and relative large grains with preferred crystal orientation in the <220> direction. In recent research, the Schottky solar diodes made of 5 μm-thick MIG poly-Si show J<sub>sc</sub> of 12 mA/cm<sup>2</sup> and V<sub>oc</sub> of 0.214 V. In this paper, current transport mechanisms were studied by current-voltage-temperature (I-V-T) testing from 100 K to 400 K for Schottky and P-N junction solar cells. For the samples deposited by the one-step sputtering process, the large deviation of ideality factor from 1 and abnormal increase of barrier height with increased temperature implies that the current transport does not follow the pure thermionic-emission theory, which was proven to be thermionic-field emission due to the highly doped Si film. By using a two-step sputtering process, the ideality factor and gold Schottky barrier height at room temperature were 1.5 and 0.7 eV, respectively, which shows the improvement from one-step sputtering. Hydrogenation by electron cyclotron resonance (ECR) plasma further improved the ideality factor and barrier height of the Schottky diode. However, a thermionic-field emission mechanism was still found by plotting the activation energy (E<sub>0</sub>) versus the temperature, although a low level phosphorous doped Si target was used for poly-Si thin film deposition. Capacitance-voltage (C-V) analysis revealed an unexpected carrier density of  $10^{17} \text{ cm}^{-3}$  level, 1000 times higher than the doping density level in the Si film. An oxygen thermal donor effect was assumed due to high oxygen level ( $10^{20} \text{ cm}^{-3}$ ) detected by SIMS and processing at 600 °C. Increasing of total carrier density in the Si film due to the thermal donor may be responsible for the current transport mechanism changing from pure thermionic emission to thermionic-field emission. To reduce oxygen impurity in the Si film, the sputtering gas was filtered to 50 ppb oxygen level. C-V results then gave  $10^{16} \text{ cm}^{-3}$  level of carrier density after using oxygen filtering. P-N junction solar cells were made by boron ion implantation into the n-type Si film followed by dopant activation at 700 °C. An I-V-T study showed similar curves for the P-N junction device as in the Schottky junction devices. This implies that the current transport was dominated by the Si films instead of the junctions. Recent research shows that the V<sub>oc</sub> of Schottky solar diodes can be further improved to 0.31 V by depositing a thin nanocrystalline Si film on the MIG poly Si active layer.

SESSION L6: III-V Semiconductors

Chair: Daniel Friedman

Wednesday Morning, December 1, 2004

Back Bay A (Sheraton)

#### 8:30 AM \*L6.1

Group III-Nitrides as Photovoltaic Materials: Challenges and Outlook. Wlodek Walukiewicz, Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California.

Group III-nitride alloys have been recently proposed as a new class of materials for high efficiency multijunction solar cells. Special attention has been focused on Ga<sub>x</sub>In<sub>1-x</sub>N alloys whose direct band gaps span the energy range from 0.7 to 3.4 eV, providing a perfect match to the solar spectrum. Implementation of these alloys in solar cell applications will, however, require better control of the material properties. The most crucial issue is achieving p-type doping in InN and In-rich Ga<sub>x</sub>In<sub>1-x</sub>N. I will present results of systematic studies of doping in group III-nitride alloys. We have found recently that in InN and In-rich Ga<sub>x</sub>In<sub>1-x</sub>N alloys the surface Fermi energy is pinned above the conduction band minimum leading to an electron accumulation on surfaces of these materials. For this reason, electron concentrations in mid  $10^{20} \text{ cm}^{-3}$  are found on the InN surface, corresponding to a surface Fermi energy pinned at close to 1 eV above the conduction band edge. It is this low location of the conduction band edge that explains the intrinsic propensity of InN to be strongly n-type. We will describe and discuss our attempts to dope InN with Mg and Be acceptors. We have also studied the effect of high energy proton and electron irradiation on the electrical and optical properties of Ga<sub>x</sub>In<sub>1-x</sub>N alloys. In-rich alloys show a very high resistance to irradiation damage. In a stark contrast to standard photovoltaic materials, high energy particle damage results in an increase of the electron concentration and photoluminescence intensity in InN. Finally, I will briefly discuss the successful synthesis of a new class of multiband semiconductors which could be used for high efficiency single junction solar cells.

#### 9:00 AM \*L6.2

III-V Multi-Junction Materials and Solar Cells on Engineered SiGe/Si Substrates. Steven A. Ringel<sup>1</sup>, Carrie L. Andre<sup>1</sup>, Matthew

Lueck<sup>1</sup>, David Isaacson<sup>2</sup>, Arthur J. Pitera<sup>2</sup> and Eugene A. Fitzgerald<sup>2</sup>; <sup>1</sup>Electrical and Computer Engineering, The Ohio State University, Columbus, Ohio; <sup>2</sup>Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts.

The monolithic integration of high efficiency III-V compound solar cell materials and devices with lower-cost, robust and scaleable Si substrates has been a driving force in photovoltaics (PV) basic research for decades. Recent advances in controlling mismatch-induced defects that result from structural and chemical differences between III-V solar cell materials and Si using a combination of SiGe interlayers and monolayer-scale control of III-V/IV interfaces, have led to a series of fundamental advances at the material and device levels, which establish that the great potential of III-V/Si PV is within reach. These include demonstrations of GaAs epitaxial layers on Si that are anti-phase domain-free with verified dislocation densities at or below  $1 \times 10^6 \text{ cm}^{-2}$  and negligible interface diffusion, minority carrier lifetimes for GaAs on Si in excess of 10 nsec, single junction GaAs-based solar cells on Si with open circuit voltages in excess of 980 mV and efficiencies beyond 18%, and area-independent PV characteristics up to at least  $4 \text{ cm}^2$ . These advances are attributed in large part to the use of a novel "engineered Si substrate" based on compositionally-graded SiGe buffers such that a high-quality, low defect density, relaxed, "virtual" Ge substrate could be developed that can support lattice-matched III-V epitaxy and thus merge III-V technology based on the GaAs lattice constant with Si wafers. This talk will first review the science and technology of III-V/SiGe materials and photovoltaics, and then will focus on recent results that extend this work to the first demonstration of high performance III-V dual junction solar cells on SiGe/Si. Open circuit voltages in excess of 2 V at one-sun have been obtained for lattice-matched InGaP/GaAs dual junction cells on inactive, engineered SiGe/Si, which to our knowledge is the first demonstration of  $> 2 \text{ V}$  solar power generation on a Si wafer. Comparisons with identical cells on GaAs substrates reveal that the Voc on engineered Si retains more than 93% of its homoepitaxial value, and that at present both DJ/GaAs and DJ/SiGe cells are similarly limited by current mismatch in these early cells, and not fundamental defect factors associated with the engineered Si substrates. With current matching, modeling shows that efficiencies of more than 23% (AM1.5) will be achievable at the  $2 \times 10^6 \text{ cm}^{-2}$  threading dislocation density present in these particular DJ cells, with efficiencies above 25-26% being expected for uniform substrate dislocation density reduction to  $8 \times 10^5 \text{ cm}^{-2}$ , which is currently in the development process. Discussion of progress on optimizing the DJ/SiGe cells, bandgap profile optimization, complete DJ materials analysis, and preliminary III-V/SiGe concentrator results will be presented.

#### 9:30 AM L6.3

**Effect of Hydride Partial Pressure on the Growth Rate of GaAs and GaInP.** J. M. Olson, W. E. McMahon and John Geisz; National Renewable Energy Laboratory, Golden, Colorado.

The GaInP/GaAs tandem solar cell is typically grown by MOCVD. It is often assumed that the growth rates of these III-V semiconductors are independent of the partial pressure of the hydride source gas in the MOCVD reactor. Using spectral reflectance from the surface of the growing epilayer, we show that this is not always the case. For example, at a growth temperature and pressure of 640C and 50 torr, the growth rate of GaAs decreases by 16% when the AsH<sub>3</sub> partial pressure is increased from 0.2 torr to 0.8 torr and the growth rate of GaInP<sub>2</sub> decreases by 24% when the PH<sub>3</sub> partial pressure is increased from 1 torr to 4 torr. The composition (Ga mole fraction) of the GaInP changes by less than 1%, suggesting that the observed phenomenon is not dominated by gas phase parasitic reactions. Evidence for a site blocking mechanism will be presented.

#### 10:15 AM \*L6.4

**Metamorphic GaInP-GaInAs layers for the application in photovoltaics.** Andreas Walter Bett and Frank Dimroth; Fraunhofer ISE, Freiburg, Germany.

Monolithic III-V multi-junction solar cells are widely used for the power production in space satellites today. The main reasons are the high efficiency of up to 30 %, recently achieved under the AM0 space solar spectrum, and the excellent electron and proton radiation hardness which is inevitable in the space environment. Another potential high-volume application for III-V multi-junction solar cells are terrestrial concentrators working at high illumination intensities. Recently excellent efficiencies above 37 % under the terrestrial AM1.5 sun spectrum were reported. The best III-V solar cells for terrestrial as well as space applications today are based on the lattice matched material combination of Ga<sub>0.51</sub>In<sub>0.49</sub>P/Ga<sub>0.99</sub>In<sub>0.1</sub>As/Ge. These monolithic triple junction solar cells are grown by metal organic vapor phase epitaxy (MOVPE). A high quality in respect to the electrical performance, i.e. mobility, minority carrier lifetime and diffusion length, are obtained in this lattice matched configuration. However, theoretical calculations show that the chosen bandgap combination of the triple junction cell is not ideal. Higher efficiencies can be achieved with a smaller bandgap of the middle cell. Theoretical calculations of the optimum bandgap combination for space and terrestrial concentrator applications have been performed and will be discussed

in this paper. Lower bandgap energies for the middle cell can be achieved by increasing the In-content in the GaInAs layers. Unfortunately, this also affects the lattice constant of this ternary compound leading to lattice mismatched or metamorphic growth. In the case of such lattice mismatched growth the formation of misfit dislocations has to be carefully controlled. A suitable buffer structure was developed for the growth of Ga<sub>0.83</sub>In<sub>0.17</sub>As layers on GaAs. The dislocation network could be localized within the buffer layer resulting in little threading dislocations. High efficiency metamorphic Ga<sub>0.35</sub>In<sub>0.65</sub>P/Ga<sub>0.83</sub>In<sub>0.17</sub>As concentrator solar cells were grown on GaAs substrates in a production size AIX2600-G3 (24x2") MOVPE reactor. An efficiency of 31.6 % with an external quantum efficiency  $> 95 \%$  was obtained under 300xAM1.5d conditions, showing the high quality of the metamorphic layers. This paper will report on the development of suitable conditions for the metamorphic growth of GaInAs and GaInP on GaAs and Ge substrates. The materials were characterized using transmission electron microscopy (TEM), high resolution x-ray diffraction, Hall measurements and time resolved photoluminescence. Single- and dual-junction solar cells were fabricated and analyzed by dark and light IV-measurements.

#### 10:45 AM L6.5

**Mid- $10^5 \text{ cm}^{-2}$  threading dislocation density in optimized high-Ge content relaxed graded SiGe for III-V solar on Si.** David Isaacson, Saurabh Gupta, Arthur Pitera, Carl Dohrman and Eugene Fitzgerald; Materials Science and Engineering, MIT, Cambridge, Massachusetts.

The relaxed graded SiGe ( $\nabla_x[\text{Si}_{1-x}\text{Ge}_x]$ ) platform has been enormously successful for the engineering of strained channels in metal-oxide-semiconductor devices, as well as the Ge/ $\nabla_x[\text{Si}_{1-x}\text{Ge}_x]$ /Si platform for fabrication of III-V devices such as lasers, waveguides, and solar cells. The key feature of the  $\nabla_x[\text{Si}_{1-x}\text{Ge}_x]$  buffer approach is its effectiveness at minimizing deleterious issues related to lattice mismatch, thereby allowing for fabrication of a scaleable Ge/ $\nabla_x[\text{Si}_{1-x}\text{Ge}_x]$ /Si platform with a threading dislocation density (TDD) on the order of  $10^6 \text{ cm}^{-2}$ . The 0.07% lattice mismatch of GaAs with Ge makes the  $\nabla_x[\text{Si}_{1-x}\text{Ge}_x]$  buffer a nearly ideal platform for III-V integration on Si, and it has been shown that by growing these buffers on offcut Si(001) wafers, subsequent growth of III-V material is free of antiphase boundaries. Despite the success of the Ge/ $\nabla_x[\text{Si}_{1-x}\text{Ge}_x]$ /Si platform, which has enabled record minority carrier lifetimes for GaAs on Si and has defined the state of the art for III-V solar cell integration on Si over the past decade, it remains a continuing goal to further reduce the TDD level. For example, while virtual Ge on Si with a TDD of approximately  $2 \times 10^6 \text{ cm}^{-2}$  has been available from our group for several years, a reduction to approximately the mid- $10^5 \text{ cm}^{-2}$  level is expected to result in nearly identical performance for III-V solar devices fabricated on Ge/ $\nabla_x[\text{Si}_{1-x}\text{Ge}_x]$ /Si platform as on bulk Ge. Virtual Ge on Si with a TDD level in the mid- $10^5 \text{ cm}^{-2}$  range was speculated to be possible, as other relaxed SiGe buffer compositions show TDD levels in this range. Our model for dislocation flow in relaxed buffers shows that it should be possible to achieve the same TDD in Ge on Si. Prior to this work, however, it was unclear as to why the TDD increases dramatically while grading to Ge. We report that through further development of our virtual Ge growth process, we have fabricated relaxed structures lattice-matched to GaAs with TDD levels of  $< 9 \times 10^5 \text{ cm}^{-2}$ , the lowest reliable level reported to date for such structures on Si. This level of threading dislocation density should allow for the fabrication of both n on p and p on n III-V solar cells. In addition, reducing the thickness of the  $\nabla_x[\text{Si}_{1-x}\text{Ge}_x]$  buffer would serve to increase the amount of III-V material that can subsequently be integrated onto the platform. Such a development would be particularly relevant for thick III-V devices such as multi-junction solar cells. To this end, results will be presented on the effects of varying the grading and growth rates in the high-Ge content regime in the hopes of obtaining thinner  $\nabla_x[\text{Si}_{1-x}\text{Ge}_x]$  buffers without penalty from an increased TDD value. Finally, to demonstrate the utility of our process refinements for III-V solar integration on Si, we will evaluate MOCVD-grown GaAs on this optimized Ge/ $\nabla_x[\text{Si}_{1-x}\text{Ge}_x]$ /Si platform.

#### 11:00 AM L6.6

**The Growth and Characterization of MOVPE InGaAs/GaAs QD Superlattices for Intermediate Band Solar Cells.**

Andrew Gordon Norman, Mark C. Hanna, Pat Dippo, Dean Levi, Bob Reedy, Scott Ward and Mowafak M. Al-Jassim; National Renewable Energy Laboratory, Golden, Colorado.

We report here the MOVPE growth and characterization of InGaAs/GaAs Stranski-Krastanov quantum dot (QD) superlattices for application in intermediate band solar cell devices as proposed by Luque and Martí. Stacks of up to 50 InGaAs QD layers, separated by thin GaAs barrier layers, have been grown on both (001) and (113)B orientation GaAs substrates. These QD superlattices have been structurally characterized by atomic force microscopy, transmission

electron microscopy, and x-ray diffraction. Optical properties of the samples have been assessed by photoluminescence and optical absorption studies. Test solar cells incorporating QD superlattice absorbing regions have been fabricated and their performance compared with reference GaAs cells having an identical structure but without the quantum dot layers, and GaAs cells containing an absorption region consisting of a superlattice of thin two-dimensional strained InGaAs layers. Results indicate a photo-response extended to longer wavelengths for the QD superlattice solar cells in comparison to the reference cells.

#### 11:15 AM L6.7

##### 1MeV Electron Irradiation Effects of GaAs/Si Solar Cells.

Nallathambi Chandrasekaran<sup>1</sup>, Tetsuo Soga<sup>1</sup>, Yousuke Inuzuka<sup>1</sup>, Hironori Taguchi<sup>1</sup>, Takashi Jimbo<sup>1</sup> and Mitsuru Imaizumi<sup>2</sup>;  
<sup>1</sup>Department of Environmental Technology and Urban Planning, Nagoya Institute of Technology, Nagoya, Japan; <sup>2</sup>Japan Aerospace Exploration Agency, Tsukuba, Japan.

Si is an alternative substrate material for the growth of GaAs solar cell for space application, because it is low cost, lightweight and large area when compared with GaAs substrate. The previous results showed that the beginning-of-life (BOL) efficiency of GaAs solar cell on Si substrate is inferior to GaAs cell on GaAs substrates. When the solar cell is used in space environment, the end-of-life (EOL) efficiency is more important than BOL efficiency. Till now the papers on radiation effects on GaAs/Si are very few. In this article we describe the comparison of GaAs solar cells grown on Si substrate with those on GaAs substrate after 1MeV electron irradiation. The GaAs solar cell structures on Si substrate were grown by metal organic chemical vapor deposition (MOCVD) technique with two-step growth method. The same structure GaAs solar cells on GaAs substrate were also grown by the same technique for comparison. The fabricated solar cells were subjected to high-energy (1MeV, fluences from  $1 \times 10^{13}$   $\text{cm}^{-2}$  to  $1 \times 10^{16}$   $\text{cm}^{-2}$ ) electron irradiation from tandem accelerator. Before and after irradiation, the solar cell parameters such as short-circuit current ( $I_{sc}$ ), open circuit-voltage ( $V_{oc}$ ) and conversion efficiency were measured by current-voltage (I-V) measurements under dark and AM 0 condition at 1 sun. The remaining factor of  $I_{sc}$  for GaAs/Si solar cell decreases according to higher electron fluences. The electron irradiation generates the recombination and compensating centers to the base layer. It has reduced the minority carrier lifetime, so the photocurrent of the cell decreases at higher fluences. The rate of degradation for GaAs/GaAs and GaAs/Si are almost equal. This is due to the same degradation rate of minority carrier lifetime for GaAs/Si cell and GaAs/GaAs cell. But in the case of  $V_{oc}$ , the remaining factor for GaAs/GaAs solar cell decreases rapidly than that of GaAs/Si solar cell with respect to higher fluences. The high remaining factor at  $10^{16}$   $\text{cm}^{-2}$  for GaAs/Si solar cell is due to high radiation resistance of saturation current. It has been due to slow generation of arsenic vacancy related defect ( $V_{As}$ ) in the GaAs/Si solar cell. The saturation current of GaAs/Si cell is larger than that of GaAs/GaAs cell before irradiation because of high dislocation density. However, degradation rate of saturation current for GaAs/Si cell is smaller than that of GaAs/GaAs cell after  $10^{16}$   $\text{cm}^{-2}$  irradiation. Therefore, the remaining factor of  $I_{sc}$  for GaAs/Si cell is higher than GaAs/GaAs cell. In summary, the 1MeV electron irradiation effects were investigated for the GaAs solar cells on GaAs substrate and Si substrate. It was shown that the radiation resistance of GaAs solar cell grown on Si substrate is higher than that on GaAs substrate after 1MeV electron irradiation. We hope that in future GaAs solar cell on Si substrate will be suitable for space applications.

#### SESSION L7: II-VI Semiconductors and Transparent

Conducting Oxides

Chair: D. S. Ginley

Wednesday Afternoon, December 1, 2004

Back Bay A (Sheraton)

#### 1:30 PM \*L7.1

**Interface Analysis of Real-World Cu(In,Ga)(S,Se)<sub>2</sub> Thin Film Solar Cells.** Clemens Heske, Department of Chemistry, University of Nevada, Las Vegas, Las Vegas, Nevada.

The investigation and understanding of interfaces is of great importance in many semiconductor devices. This is particularly true for Cu(In,Ga)(S,Se)<sub>2</sub> (CIGS) thin film solar cells, in which "real-world" interfaces, i.e., interfaces in samples taken directly from industrial process lines, frequently exhibit quite different properties than expected from an academic point of view. This talk will review some of the recent progress achieved by combining photoelectron spectroscopy (PES), inverse photoemission (IPES), and soft X-ray emission spectroscopy (XES) to shed light on the electronic and chemical properties of (buried) interfaces in CIGS cells. Particular emphasis will be placed on the electronic band alignment in valence

and conduction band as well as on the electronic surface band gaps. Furthermore, we will discuss the impact of surface modification treatments frequently used for high-efficiency cells with alternative buffer layers, and will present results that elucidate the impact of humidity on CIGS absorbers and ZnO-containing interfaces.

#### 2:00 PM L7.2

Abstract Withdrawn

#### 2:00 PM \*L7.3

**Photoemission and Photoinduced Current of Cu(In,Ga)Se<sub>2</sub> in Scanning Tunneling Microscopy.** Manuel J. Romero, Chun-Sheng Jiang, Rommel Noufi and Mowafak M. Al-Jassim; National Renewable Energy Laboratory, Golden, Colorado.

Solar cells based on Cu(In,Ga)Se<sub>2</sub> (CIGS) chalcopyrite compounds have demonstrated record photoconversion efficiencies. The intense research effort conducted in the last decade has revealed that (i) the anomalous behavior observed for grain boundaries and (ii) the surface electronic properties are critical to this success. Indeed, the absence of both built-in potential at grain boundaries and type inversion at the surface in CuGaSe<sub>2</sub> are believed to be major obstacles in achieving high efficiency. In this contribution, we report on scanning tunneling microscopy (STM) observations of CIGS, which provide excellent spatial resolution to investigate the electronic properties of the surface and resolve individual grain boundaries. Photoemission and photoinduced currents are measured simultaneously to the scanning of the STM tip on the surface of CIGS, in constant current mode. When semiconductors are observed under the STM, photons are emitted by recombination of the tunneling current. The opportunity to use tunneling effects for a photoemission spectroscopy offering high resolution is obviously of great interest. In CIGS, when the emission of photons is primarily due to recombination of minority carriers, dislocations and grain boundaries are imaged by their reduced emission. However, enhanced emission is observed at grain boundaries in the field emission regime of the STM, although the very interior of the grain boundary shows reduced emission. These results suggest that the very interior of the grain boundary is depleted of holes. In order to explain carriers building up around the grain boundary, we have to consider the effect of the tip on the built-in potential at boundaries. For imaging of photoinduced currents, STM observations are performed under modulated, external illumination. Higher photocurrent has been measured at grain boundaries under certain conditions. Combining these results with cathodoluminescence and scanning Kelvin probe microscopy, we discuss a model for grain boundaries in CIGS.

#### 3:15 PM L7.4

**Expanded Experimental Space for Luminescence Studies of CdS/CdTe Thin Film Solar Cells.** Scott Feldman, T. R. Ohno, R. T. Collins and V. Kayndanov; Physics, Colorado School of Mines, Golden, Colorado.

We have explored a large range of experimental space for photoluminescence (PL) and electroluminescence (EL) measurements of CdS/CdTe solar cells. This space includes changes in temperature, injection intensity (laser power for PL, current for EL), and bias (electrical bias for PL, light bias for EL). Measurements were resolved both spectrally and spatially (2D for EL, 1D for PL). Greatest spectral resolution was obtained with low temperature EL at low injection rates. High injection EL as well as high forward biased PL suppressed band-edge emission at low temperatures. Combination of EL and PL measurements revealed that most spatial inhomogeneity was the result of non-uniform current transport rather than local variations in recombination rate. Light bias at room temperature decreased this spatial non-uniformity in EL.

#### 3:30 PM L7.5

**Preparation and characterization of monolithic HgCdTe/CdTe tandem cells.** Shanli Wang, Jennifer Drayton, Viral Parikh, Anthony Vasko, Akhlesh Gupta and Alvin D. Compaan; Department of Physics & Astronomy, University of Toledo, Toledo, Ohio.

A tandem structure solar cell composed of two different spectral response p-n junctions should achieve a conversion efficiency as high as 28%. The optimum band gaps of a two-junction tandem cell would have a wide band gap of 1.72eV and a narrow band gap of 1.14eV.[1] For the bottom cell in such tandem structure, the candidates can be a HgCdTe cell or a CuInSe<sub>2</sub> cell. Hg<sub>1-x</sub>Cd<sub>x</sub>Te has a large absorption coefficient above the band gap which can easily be tailored from -0.15eV to 1.49eV. For a band gap of 1.0-1.1eV, a Cd content of 0.77-0.82 is required. For a monolithic tandem cell fabrication process, however, multi-layer deposition and treatments must be carried out on single substrate, and subsequent processes can affect existing layers, so that, although CuInSe<sub>2</sub> also has a band gap near 1.1eV and excellent photovoltaic properties, the required high temperature (about 600°C) processing will result in unwanted diffusion in already

deposited top cell, and hence can seriously affect cell performance. By contrast, the low processing temperature of Hg<sub>1-x</sub>Cd<sub>x</sub>Te devices can effectively avoid such process-induced deterioration. In this paper, we present details of the preparation and characterization of HgCdTe/CdTe tandem cells. The characteristics of Hg<sub>1-x</sub>Cd<sub>x</sub>Te films on glass were analyzed by energy dispersive x-ray spectra, infrared transmission spectra, x-ray diffraction, and Raman spectroscopy. P-type Hg<sub>1-x</sub>Cd<sub>x</sub>Te films with a band gap of 1.1eV were obtained after a brief annealing process. A single junction of Hg<sub>1-x</sub>Cd<sub>x</sub>Te/CdS yielded Voc=0.39V and Jsc=13.2 mA/cm<sup>2</sup>. I-V measurements of ZnO:Al/ZnTe:N recombination junctions indicate low resistance (2 Ω-cm<sup>2</sup>) interconnects are possible. A superstrate configuration two-terminal tandem cell with Hg<sub>1-x</sub>Cd<sub>x</sub>Te and CdTe absorbers was fabricated by sputtering which included a CdTe/CdS top cell, a ZnO/ZnTe recombination junction and a Hg<sub>1-x</sub>Cd<sub>x</sub>Te/CdS bottom cell on glass. Voc=0.99V and Jsc= 2.1 mA /cm<sup>2</sup> were obtained at one sun (AM1.5). According to individual single junction cell I-V measurement results, this value of Voc includes 60% top cell and 40% bottom cell contributions. Quantum efficiency measurements show that the Jsc is limited by low short circuit current density of the bottom Hg<sub>1-x</sub>Cd<sub>x</sub>Te cell. This results from relatively poor transmission of the top CdTe cell (transmission of 50% for energy < 1.5 eV) but the current appears not to be seriously limited by the interconnect junction. This work supported by NREL High Performance PV project. Reference: [1] T.J. Coutts, J.S.Ward, D.L.Young, K.A.Emery, T.A.Gessert, and R.Noufi, Prog.Photovolt: Res. Appl. 11 (2003) 359

### 3:45 PM L7.6

**Optimization of phase-pure CuInO<sub>2</sub> p-type transparent conducting oxide thin films deposited from Cu<sub>2</sub>In<sub>2</sub>O<sub>5</sub> targets by PLD.** Charles Teplin<sup>1</sup>, Tatiana Kaydanova<sup>1</sup>, Matthew Dabney<sup>1</sup>, David L. Young<sup>1</sup>, John D. Perkins<sup>1</sup>, David S. Ginley<sup>1</sup>, Aiko Ode<sup>2</sup> and Dennis J. Readey<sup>2</sup>; <sup>1</sup>NREL, Golden, Colorado; <sup>2</sup>Colorado School of Mines, Golden, Colorado.

P-type transparent conductors could be used as contacts in organic photovoltaic (PV) cells, in tunnel junctions in tandem thin film solar cells, or as UV-junction layers in 3rd generation PV technologies. However, there are few direct reproducible synthesis routes to p-type materials. Here, we report that thin films of Ca-doped CuInO<sub>2</sub>, a p-type transparent conducting oxide (TCO), have been deposited from easily prepared Ca-doped Cu<sub>2</sub>In<sub>2</sub>O<sub>5</sub> targets using pulsed laser deposition. Among the new p-type transparent conductors, CuInO<sub>2</sub> is unusual because it can be doped with both p-type (Ca-doping) and n-type (Sn-doping) carriers, perhaps simplifying device fabrication. Our discovery of a simple technique for preparing CuInO<sub>2</sub> films is important because previous reports on this material required the use of difficult-to-fabricate CuInO<sub>2</sub> targets. X-ray diffraction measurements show that phase-pure CuInO<sub>2</sub> thin films can be reliably deposited from Cu<sub>2</sub>In<sub>2</sub>O<sub>5</sub> targets over a range of deposition conditions. For a 5% Ca-doped Cu<sub>2</sub>In<sub>2</sub>O<sub>5</sub> target, films deposited at 550°C with 5 mT of oxygen partial pressure show a p-type conductivity of 3·10<sup>-3</sup> S/cm and a Seebeck coefficient of + 472 ± 10 μV per °C. The optical properties of these films have been measured from 250nm to 1400nm using spectroscopic ellipsometry in order to provide accurate values of the optical constants, n and k, relevant to possible applications requiring transparency in the visible and near-IR spectrum. We will also report on how the conductivity of these films depends on the amount of Ca-doping.

### 4:00 PM L7.7

**Transparent Conductive Oxides: Deposition of Doped Indium Oxide and Combinatorial Optimization.** M. F.A.M. van Hest<sup>1</sup>, C. W. Teplin<sup>1</sup>, J. D. Perkins<sup>1</sup>, D. S. Ginley<sup>1</sup>, A. E. Delahoy<sup>2</sup> and S. Guo<sup>2</sup>; <sup>1</sup>National Renewable Energy Laboratory, Golden, Colorado; <sup>2</sup>Energy Photovoltaics, Inc., Princeton, New Jersey.

Transition metal doped In<sub>2</sub>O<sub>3</sub> has shown excellent properties as a TCO in terms of both transparency and mobility. Reactive-environment, hollow cathode sputtering has produced outstanding initial results for Ti-doped indium oxide, reaching a resistivity of 1.8 x 10<sup>-4</sup> Ω cm and a mobility of 80.6 cm<sup>2</sup>/Vs.<sup>1</sup> In this study we use combinatorial/high through-put research tools to study Mo and Ti doped indium oxide materials. Combinatorial co-sputtering from two different targets has been used to produce transparent conducting oxides films on 200 x 200 glass substrates. The sputtering targets are located in such a way that the composition of the deposited material varies smoothly and in a controllable way across the substrate. This allows for a large or small composition gradients across a deposited film. Material ratios in a range from 0 to 100 % can be mapped in as little as five depositions. The doped indium oxide materials are grown using one indium oxide target. The other target is either a doped indium oxide target or a pure metal oxide target. The targets have been sputtered using RF power in an argon gas atmosphere. Deposition temperatures range from room temperature to 550 °C. The metal dopants studied result in films with very good

conductivity (<2.0 x 10<sup>-4</sup> Ω cm) and high mobility (>60 cm<sup>2</sup>/Vs). Typically the best conductivity is obtained when the doping is in the range from 1 to 4% for the films deposited at high temperature (550 °C). The metal doping content has been determined by means of electron probe micro analysis. Also the sputtered films have been analyzed by XRD and optical transmission and reflection spectroscopy. The best films are highly crystalline and high optical transmission across the visible portion of the spectrum (>85%).<sup>1</sup> A.E. Delahoy et al., 19th European PVSEC, Paris, June 7-11, 2004

### 4:15 PM L7.8

**Understanding a New Class of Transparent Conductors.**

Peter V. Sushko<sup>1</sup>, Alexander L. Shluger<sup>1</sup>, Katsuro Hayashi<sup>2</sup>, Masahiro Hirano<sup>2</sup> and Hideo Hosono<sup>2</sup>; <sup>1</sup>Physics and Astronomy, University College London, London, United Kingdom; <sup>2</sup>Transparent and Electro-Active Materials Project, Exploratory Research for Advanced Technology (ERATO), Japan Science and Technology Corporation, Sakado, Takatsu-ku, Kawasaki, Japan.

We present the results of the ab initio calculations of the electronic properties of a nano-porous main group oxide 12CaO · 7Al<sub>2</sub>O<sub>3</sub> (C12A7). The C12A7 doped with hydrogen is a wide-band gap insulator but it is converted to a persistent transparent conductor by the UV irradiation [1]. The mechanism of conductivity in C12A7 is very different from that of other transparent conducting oxides (TCOs) and is primarily governed by its unusual structure: the framework built of 12 cages with is an effective positive charge of each cage (1/3 e) compensated by two extra-framework O(2-) ions. Pure C12A7 samples are optically transparent up to 5.0 eV. When loaded with hydrogen and then irradiated with UV light the C12A7 acquires simultaneously a high electrical conductivity and a strong EPR feature due to formation of a significant number of unpaired electrons. This is accompanied by formation of two broad optical absorption bands with maxima at about 0.4 eV and 2.8 eV. Our embedded cluster calculations [2] suggest that the unpaired electrons are localised in framework cages and stabilised by the lattice relaxation. We explain the good conductivity of this material by very small barriers for hopping of localised electrons between neighbouring positive cages. The optical absorption of C12A7 in infrared region and at energies higher than 2.7 eV is due to inter-cage and intra-cage electron transitions, respectively. 1. K. Hayashi, S. Matsui, T. Kamiya, M. Hirano, H. Hosono, Nature, v.419, p.462, (2002) 2. P. V. Sushko, A. L. Shluger, K. Hayashi, M. Hirano, H. Hosono, Phys Rev. Lett., v.91, p.126401, (2003)

SESSION L8: Silicon Thin Films

Chair: J. Olson

Thursday Morning, December 2, 2004

Back Bay A (Sheraton)

### 8:30 AM L8.1

**Effects of Grain Boundaries in Amorphous/Multicrystalline Silicon Heterojunction Photovoltaic Cells.** Mahdi Farrokhi Baroughi and Siva Sivothythaman; Electrical and Computer Engineering, University of Waterloo, Waterloo, Ontario, Canada.

Cost reduction is an important issue in the fabrication of silicon (Si) photovoltaic (PV) cells, where the material cost accounts for nearly half of the overall cost. Materials like multicrystalline Si (mc-Si), Si ribbons etc., offer a cost effective option for Si PV cells compared to single crystalline Si. In most of those materials however, the presence of large number of grains (mm to cm scale), grain boundaries, and crystallographic defects necessitates defect passivation. Defect passivation by atomic hydrogen is a very efficient method. However, this imposes a temperature (T) limit for any post-passivation process such as pn junction diffusion at high-T. Implementation of amorphous Si (a-Si)/crystalline Si heterojunctions (by means of a low-T PECVD) in place of diffused homojunctions in defective Si can keep the process temperature low thereby preserving the defect passivation. In this work we have investigated the effects of grain boundaries and other crystalline defects on the heterojunction properties. Devices with (n)-a-Si/(p)mc-Si heterojunction have been fabricated for the studies. Amorphous Si films and transparent conductive films (ITO) were deposited by PECVD and sputtering respectively. Quantum efficiency of the heterojunction PV cells is measured inside grains, on the grain boundaries, and on the twin boundaries of mc-Si substrates. Characterization setup includes a conventional lock-in based spectral response setup equipped with optical monochromator and lenses to achieve small monochrome light spot. This small and narrow monochrome beam with about 100um width and 3mm length is focused right on the grain boundary using a fine micromanipulator keeping the boundary at the center of the beam. Quantum efficiency analysis shows that charge collection efficiency on the grain boundary for the characterization setup is 6 to 10% less than the quantum efficiency inside the grain for the same characterization setup. The same analysis is performed on twin boundaries and the results are

compared. I-V characteristics of heterojunction diodes with different sizes fabricated inside grains, on the grain boundaries, and on the twin boundaries are measured and compared as well. This study shows that for devices on mc-Si substrates with large grains (several mm to cm), the effect of recombination of photo-generated minority carriers in the grain boundaries is small compared to the recombination in the intra-grain bulk defects. For fine-grained mc-Si material, hydrogen passivation of both bulk defects and of grain boundaries becomes important.

#### 8:45 AM [L8.2](#)

**Improved Efficiency in Hydrogenated Amorphous Silicon Solar Cells Irradiated by Excimer Laser.** [A. A. D. T. Adikaari](#), S. R. P. Silva, M. J. Kearney and J. M. Shannon; Advanced Technology Institute, University of Surrey, Guildford, Surrey, United Kingdom.

Excimer laser crystallisation has been the preferred technique for the production of microcrystalline silicon for thin film transistor applications on cheap substrates. Due to the high absorption of radiation by amorphous silicon, substrates such as glass can be used, which in general cannot withstand conventional annealing temperatures. The same technique can be utilised for photovoltaic applications of thin film amorphous silicon on glass. Instead of converting the amorphous silicon completely to microcrystalline silicon, properties of thin films can be modified in a stratified manner, for efficiency improvements. We report initial findings on possible quantum efficiency improvements on thin amorphous silicon schottky barrier solar cells upon excimer laser treatment with values up to 50%. Optical and transport properties of the resulting structures are presented and discussed.

#### 9:00 AM [L8.3](#)

**Efficient Energy Conversion in Three-Dimensional Porous Silicon p-n Diodes.** [Wei Sun](#)<sup>1</sup>, [Nazir Kherani](#)<sup>2</sup>, [Karl Hirschman](#)<sup>3</sup>, [Larry Gadeken](#)<sup>4</sup> and [Philippe Fauchet](#)<sup>5,1</sup>; <sup>1</sup>Biomedical Engineering, University of Rochester, Rochester, New York; <sup>2</sup>Electrical and Computer Engineering, University of Toronto, Toronto, Ontario, Canada; <sup>3</sup>Microelectronic Engineering, Rochester Institute of Technology, Rochester, New York; <sup>4</sup>BetaBatt, Inc, Houston, Texas; <sup>5</sup>Electrical and Computer Engineering, University of Rochester, Rochester, New York.

We demonstrate a novel approach for directly and efficiently producing electricity from nuclear and solar energy. The basis of this new technology is macroporous silicon, prepared using electrochemical etch techniques. Specifically, p-type silicon ( $\approx 25 \Omega\text{-cm}$ ) was anodized to produce deep, straight pores ( $50 \mu\text{m}$  deep by  $1 \mu\text{m}$  diameter) perpendicular to the planar wafer surface. A continuous and uniform p-n junction was fabricated on the surface of each pore wall by solid source diffusion of phosphorous at  $1000^\circ\text{C}$ . Current-voltage (I-V) measurements show that the resulting 3D p-n diodes had excellent diode responses in the dark. Details of the fabrication procedure will be presented. The betavoltaic effect is the conversion of kinetic energy of beta particles (electrons) into electrical energy via the production and separation of electron-hole pairs in a semiconductor junction device. Experiments were carried out using tritium gas as an energy source for both 3D porous silicon diodes and otherwise identical planar silicon diodes. A comparison of the I-V response data showed a much higher utilization of tritium decay beta energy for the 3D betavoltaic diodes. The porous structure demonstrated a 10X geometrical efficiency enhancement. Improvements of the 3D betavoltaic device performance are under way by increasing the beta energy density and optimizing the diode characteristics. Pronounced photovoltaic response under visible illumination was observed for these 3D diodes. Initial I-V measurements showed fill factor values as high as 0.65 even though no device refinement was attempted. 3D porous silicon diodes are thus promising as high-efficiency, low-material, low-cost photovoltaic devices.

#### 9:15 AM [L8.4](#)

**Fundamental Mechanisms of Surface Smoothing in Plasma-Deposited Amorphous Silicon Thin Films: A Molecular-Dynamics Analysis.** [Mayur S. Valipa](#)<sup>1,2</sup>, [Eray S. Aydi](#)<sup>2</sup> and [Dimitrios Maroudas](#)<sup>1</sup>; <sup>1</sup>Chemical Engineering, University of Massachusetts, Amherst, Massachusetts; <sup>2</sup>Chemical Engineering, University of California, Santa Barbara, California.

Under conditions of low  $\text{SiH}_4$  dissociation during the plasma-assisted deposition of hydrogenated amorphous silicon (a-Si:H) thin films, the dominant deposition precursor is the  $\text{SiH}_3$  radical. The remarkable smoothness of device-quality a-Si:H films grown under these conditions has been used to conclude that the deposition precursor is very mobile and can fill surface valleys after adsorbing onto the film. However, the fundamental atomic-scale processes that determine the surface morphology of a-Si:H films during deposition are not well understood. In this presentation, we discuss such atomic-scale mechanisms as derived through a detailed fundamental analysis based

on atomistic simulation. Using molecular-dynamics (MD) simulations of repeated impingement of  $\text{SiH}_3$  radicals on the growth surface, we modeled the deposition of a-Si:H films on initially H-terminated  $\text{Si}(001)\text{-(}2\times 1\text{)}$  surfaces. The simulated evolution of the film's structure, surface morphology and roughness, and surface reactivity was investigated systematically. The surfaces of these MD-grown films were found to be remarkably smooth due to a valley-filling mechanism where mobile precursors, such as  $\text{SiH}_3$  and  $\text{Si}_2\text{H}_6$ , diffuse and passivate dangling bonds present in surface valleys or at the edges of such valleys. The mechanisms of  $\text{SiH}_3$  precursor diffusion on the a-Si:H surface were studied with special emphasis placed on elucidating the role of the surface bond strain in mediating the valley-filling phenomena. Migration of the  $\text{SiH}_3$  precursor on the growth surface was found to be driven by the Si-Si bond strain distribution on the surface, which is strongly coupled with the surface morphology and reactivity. Analysis of the MD trajectories for numerous  $\text{SiH}_3$  radical migration paths revealed the development of tensile strain regions along these paths, which typically lead to surface Si dangling bonds. Adsorbed  $\text{SiH}_3$  radicals follow these tensile strain paths and passivate dangling bonds present in valleys or at valley edges, thus leading to valley filling and surface smoothening.

#### 10:15 AM [L8.5](#)

**Theoretical Analysis of Precursor-Surface Interactions in the Plasma Deposition of Silicon Thin Films.** [Tamas Bakos](#) and [Dimitrios Maroudas](#); Chemical Engineering, University of Massachusetts, Amherst, Massachusetts.

Plasma-enhanced chemical vapor deposition is used widely for growing hydrogenated amorphous silicon (a-Si:H) thin films for photovoltaic applications. Properties of the deposited films, such as H content, crystallinity, and surface roughness are determined by the identities and fluxes of reactive radicals and the ensuing radical-surface interaction mechanisms; these radical precursors originate in the plasma and impinge on the growth surface leading to film deposition. In this presentation, we report results of first-principles density functional theory (DFT) calculations on the reactions and diffusion of the  $\text{SiH}_3$  radical, the dominant precursor for deposition of device-quality a-Si:H films, on the H-terminated  $\text{Si}(100)\text{-(}2\times 1\text{)}$  surface. In particular, we show that the  $\text{SiH}_3$  radical can insert into surface Si-Si dimer bonds and abstract H from surface Si atoms following barrierless reaction pathways. In addition, we analyze thermally activated H abstraction processes governed by Langmuir-Hinshelwood and 'precursor-mediated' mechanisms. In the precursor-mediated mechanism, prior to abstraction, the radical may hop between overcoordinated surface Si atoms; this is accompanied by subsurface bond breaking and bond reforming resulting in the lowering of the activation energy barrier for the reaction. The activation barrier for  $\text{SiH}_3$  diffusion on the H-terminated  $\text{Si}(100)\text{-(}2\times 1\text{)}$  surface is found to be commensurate with the barrier for precursor-mediated abstraction; this implies that several radical migration events may occur prior to an abstraction event. The particular reaction and diffusion mechanisms that we have studied by DFT on the  $\text{Si}(100)\text{-(}2\times 1\text{)}$ :H surface were observed to be the dominant atomistic processes in molecular-dynamics simulations of a-Si:H thin film growth. Therefore, our electronic-structure analysis can be considered as representative of surface reactions also occurring on amorphous Si growth surfaces. Furthermore, the existence of barrierless H abstraction and insertion reaction pathways is consistent with the experimentally observed temperature independence of the  $\text{SiH}_3$  surface reactivity during plasma deposition of a-Si:H films. Finally, the role of the precursor-mediated H abstraction process in determining the hydrogen content of a-Si:H films deposited at higher temperatures is also discussed.

#### 10:30 AM [L8.6](#)

**Structural and electrical characterization of biaxially-oriented Si thin films on polycrystalline substrates.** [Woong Choi](#), [Paul Arendt](#), [Quanxi Jia](#), [Vlad Matias](#) and [Alp T. Findikoglu](#); Materials Science and Technology Division, Los Alamos National Laboratory, Los Alamos, New Mexico.

The growth of highly crystalline Si thin-films on polycrystalline or amorphous substrates is attractive for solar cell applications because it could combine high conversion efficiency with low materials cost. Recently, laser crystallization of small-grained Si films and transfer of single crystalline Si layers on polycrystalline substrates have been reported as possible methods to achieve high efficiency and low cost. In this study, we used a new buffer layer architecture to prepare highly crystalline (biaxially oriented) Si films directly on polycrystalline substrates. The x-ray diffraction analysis on these Si films showed bi-axial texture with in- and out-of-plane orientation distributions of about  $1.4^\circ$  and  $2^\circ$ , respectively. The conduction type of the Si thin films could be controlled by either in situ or ex situ doping. The highest Hall mobility we measured so far is  $75 \text{ cm}^2/\text{V}\cdot\text{s}$  at the doping concentration of  $1 \times 10^{17} \text{ holes}/\text{cm}^3$ . We have also performed pseudo-metal-oxide-semiconductor field effect transistor

measurements, which provided additional information about the carrier concentration and mobility. We are currently performing further structural and electrical characterization of these Si films.

#### 10:45 AM L8.7

**Properties of Laser-Crystallized Polycrystalline SiGe.** M. Weizman<sup>1</sup>, Norbert H. Nickel<sup>1</sup>, I. Sieber<sup>1</sup> and B. Yan<sup>2</sup>; <sup>1</sup>SE1, Hahn-Meitner-Institut, Berlin, Germany; <sup>2</sup>United Solar Systems Corp., Troy, Michigan.

Crystalline silicon-germanium alloys, among other applications, could be a good substitute for the Si absorber layer in solar cells. The enhanced absorption of SiGe compared to Si makes it a very promising material. The SiGe specimens investigated in this work were fabricated by the following steps. Initially, amorphous silicon-germanium films (a-Si<sub>1-x</sub>Ge<sub>x</sub>:H) were deposited by glow-discharge decomposition of a mixture of silane and germane to a thickness of 100 to 255 nm. The Ge content of the resulting samples was determined from elastic recoil detection analysis (ERDA) measurements and varied between 19 and 84 %. The amorphous samples were crystallized employing a XeCl excimer laser. Because of the large hydrogen content a step-by-step crystallization process was used to avoid ablation of the layers. The poly-SiGe films were characterized with Raman backscattering measurements and energy dispersive X-ray (EDX) measurements. Information on the grain-size was obtained from scanning electron microscopy (SEM) and atomic force microscopy (AFM) micrographs. The Raman phonon spectra exhibit three main vibrational modes located at about 300, 400, and 500 cm<sup>-1</sup> that are due to Ge-Ge, Si-Ge, and Si-Si lattice vibrations, respectively. Deviations of the position of these phonon modes compared to single crystal SiGe samples and/or peak splitting can reveal information about stress and segregation effects. For poly-Si<sub>1-x</sub>Ge<sub>x</sub> with x > 0.33 peak splitting is observed indicating that laser crystallization results in the segregation of Si and Ge into silicon rich and germanium rich phases. The segregation effect becomes more pronounced with increasing laser fluence. This observation is supported by EDX measurements that show an enrichment of the Ge phase of up to 35% for poly-Si<sub>55</sub>Ge<sub>45</sub>. A further surprising result is the fact that these samples do not reveal super lateral growth; the average grain size is independent of the laser fluence. The results will be discussed in terms of models developed for the laser crystallization process.

#### 11:00 AM L8.8

**Experimental and Theoretical Analysis of the Performance of Quasi Monocrystalline Porous Silicon (QMPS) Based Thin Silicon Solar Cell.** Utpal Gangopadhyay<sup>1,2</sup>, M. Banerjee<sup>1</sup>, S. K. Dutta<sup>1</sup>, D. Majumdar<sup>1</sup>, H. Saha<sup>1</sup> and J. Yi<sup>2</sup>; <sup>1</sup>Electronics & Telecommunication Engg. Dept., IC Design & Fabrication Centre, E. T. C. E. Dept., Jadavpur University, Kolkata, India, Kolkata, West Bengal, India; <sup>2</sup>School of Electrical and Computer Engg., Sungkyunkwan University, 300, Chunchun dong, Suwon, South Korea.

The idea of layer transfer process employing the transfer of a very thin Si layer on a foreign low-cost substrate /superstrate, have attracted many research workers since last few years for fabrication of cost-effective as well as efficient thin Si solar cell. Quasi Monocrystalline Porous Silicon (QMPS) layer [1] (of thickness 4-5 μm), formed by high temperature sintering of double layer porous silicon in hydrogen ambient, is one of the promising material in this area. The aim of our present work is to analyze the solar cell performance experimentally as well as theoretically by investigating the structural and electrical transport properties of the mentioned layer with a view to apply it as active material for thin Si solar cell. The interesting experimental result of high optical absorption coefficient of QMPS layer obtained over a wide spectral region [2,3] can be well justified by suitable modeling of light trapping inside the layer [4]. Fabrication of QMPS solar cell without lifting it off from the substrate yields promising results. Simulation of cell parameters has been performed by modeling of transport parameters of QMPS layer [5]. The low value of open circuit voltage (400 mV) can be attributed to the high value of minority carrier density at the silicon-void interface. The improvement of the cell performance depends on the passivation of these interface states. The next challenge will be to fabricate cell on the transferred layer itself, using a low-cost substrate /superstrate. Results are summarized as follows: (1) The open circuit voltage Voc 400 mV and the short circuit current density Jsc 20 mA/cm<sup>2</sup> on the QMPS based solar cell (without lift-off) is observed neither doing photolithography nor epitaxy and ARC. (2) Further improvement in cell performance can be expected by passivating the silicon-void interface states. (3) The simulated mobility and diffusion length values [5] of the QMPS layer matched quite well with the experimental results [2]. References: [1] M. Banerjee, D. Majumdar, S.K. Dutta, S.M. Hossain and H. Saha; Quasi-Monocrystalline Porous Silicon: a promising active material for solar cell, 12th IWPSD, IIT Chennai, India, Proc. Vol. 2, 947 (16-20 Dec. 2003). [2] T.J. Rinke, R. B. Bergmann, R. Bruggemann and

J.H. Werner; Ultrathin Quasi-Monocrystalline silicon films for electronic devices, Solid State Phenomena, 1999; 67-68: 229-34. [3] N. Ott, M. Nerding, G. Muller, R. Brendel and H. P. Strunk; Evolution of the microstructure during annealing of porous silicon multilayers. Journal of Applied Physics, 2004; 95(2): 497-503. [4] D. Majumdar, S. Chatterjee, M. Dhar, S. K. Dutta and H. Saha; Light trapping in layer transferred quasi-monocrystalline porous silicon solar cell; Sol. Energy Mat. and Sol. Cells, 2003; 77(1): 51-64. [5] M. Banerjee, S.K. Dutta, U. Gangopadhyay, D. Majumdar and H. Saha; communicated to Solid State Electronics.

#### 11:15 AM L8.9

**Density of States in Tritiated Amorphous Silicon Measured Using CPM.** Simone Pisana<sup>1</sup>, Stefan Costea<sup>1</sup>, Tome Kostasik<sup>1</sup>, Nazir P. Kherani<sup>1</sup>, Stefan Zukotynski<sup>1</sup> and Walter T. Shmays<sup>2</sup>; <sup>1</sup>Electrical & Computer Engineering, University of Toronto, Toronto, Ontario, Canada; <sup>2</sup>Laboratory for Laser Energetics, University of Rochester, Rochester, New York.

Hydrogenated amorphous silicon (a-Si:H) has been extensively investigated for thin film photovoltaic applications and others. Under illumination, a-Si:H experiences an increase in its defect density and accordingly a deterioration in the device efficiency. The dynamics of defect states have been studied widely and various models describing the same have been proposed. Tritium is a radioactive isotope of hydrogen that can be easily incorporated in the a-Si:H network during film deposition. The predictable decay of tritium ( $T \rightarrow {}^3\text{He}^+ + \beta^-$ ,  $t_{1/2} = 12.3$  yrs) can be used to generate defect states at a constant rate in tritiated amorphous silicon and thus provide an alternative approach to the study of defect reactions. Moreover, this technique can be used to investigate the susceptibility of material properties to the creation of defects. Tritiated hydrogenated amorphous silicon (a-Si:H:T) was deposited using the dc saddle-field plasma deposition technique. Tritiated samples were deposited at a pressure of 150 mTorr on a heated substrate holder at temperatures of 200°C and 250°C. The gas mixture composition was 5:4:1 of silane, hydrogen and tritium, with a total flow rate of 10 sccm. The anode current was 14 mA or 20 mA. Tritium content of the samples examined in this study was of the order of 1.5 at.%; the concentration was measured by tritium effusion. Using the constant photocurrent method (CPM), the electronic density of states from the valence band edge to the mid-gap of tritiated a-Si:H:T samples were studied. CPM measurements were carried out 2.5 years after the samples were prepared. CPM measurements show a high mid-gap defect state density, consistent with the large aging period. Thermal annealing decreases the CPM defect state density. Time evolution of the CPM defect density follows a stretched exponential. The position of the peak of the defect states in the band gap suggests that the majority of the defect states are doubly occupied dangling bonds ( $D^-$ ). The CPM defect density is higher than that expected from tritium decay calculations. The high density of  $D^-$  states may be attributed to the trapping of excess electrons. On the average energetic tritium decay betas produce 1500 electron-hole pairs per beta particle.