

Wednesday Morning, November 2, 2011

Energy Frontiers Focus Topic

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

Quantum Dot and Nanowire Solar Cells

Moderator: K. Leschkes, Applied Materials Inc.

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

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

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

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

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

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

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

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

heterostructures, and superstructures for advanced photovoltaic device applications.

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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