

Monday Afternoon, October 28, 2013

Energy Frontiers Focus Topic

Room: 101 A - Session EN+AS+NS+SS-MoA

Interfacial Challenges in Nanostructured Solar Cells

Moderator: M.A. Filler, Georgia Institute of Technology

2:00pm EN+AS+NS+SS-MoA1 Solar Energy Conversion Beyond the Limit, X.Y. Zhu, Columbia University **INVITED**

This lecture aims to explore key mechanistic issues in an emerging photovoltaic technology based on organic and polymeric molecules, i.e., plastic solar cells. I will present two examples from recent research in my laboratory. The first example is within the realm of conventional theories and we aim to understand a critical step in charge separation at donor/acceptor interfaces in organic photovoltaics, namely the formation and dissociation of interfacial charge transfer excitons [1]. In particular, we show the critical role of hot charge transfer excitons in setting the fundamental time limit for charge separation in organic photovoltaics [2]. The second example shows how an intriguing physical phenomenon, exciton fission in which a singlet exciton breaks up into two triplet excitons in organic semiconductor materials, may be used to build solar cells with power conversion efficiency exceeding the fundamental limit (the so-called Shockley-Queisser limit) of conventional solar cells. We show how singlet exciton fission can occur in organic semiconductors due to a many electron quantum coherent process [3-4], and how we can efficiently extract two electrons from the quantum superposition [5].

[1] M. Muntwiler, Q. Yang, W. A. Tisdale, X.-Y. Zhu, "Coulomb barrier for charge separation at an organic semiconductor interface," *Phys. Rev. Lett.* 101 (2008) 196403.

[2] A. Jailaubekov, et al., "Hot charge transfer excitons set the time limit for charge separation at donor/acceptor interfaces in organic photovoltaics," *Nature Mater.* 12 (2013) 66-73.

[3] W.-L. Chan, M. Ligges, A. Jailaubekov, L. Kaake, L. Miaja-Avila, X.-Y. Zhu, "Observing the Multi-Exciton State in Singlet Fission and Ensuing Ultrafast Multi-Electron Transfer," *Science* 334 (2011) 1541-1545.

[4] W.-L. Chan, M. Ligges, X.-Y. Zhu, "The energy barrier in singlet fission can be overcome through coherent coupling and entropic gain," *Nature Chem.* 4 (2012) 840-845.

[5] W.-L. Chan, J. R. Tritsch, X.-Y. Zhu, "Harvesting singlet fission for solar energy conversion: one versus two electron transfer from the quantum mechanical superposition," *J. Am. Chem. Soc.* 134 (2012) 18295-18302.

2:40pm EN+AS+NS+SS-MoA3 Photocurrent Generation Characteristics of Ge Quantum-Dot Solar Cells, G. Uchida, D. Ichida, H. Seo, K. Kamataki, N. Itagaki, K. Koga, M. Shiratani, Kyushu University, Japan

The pressing need for massively scalable carbon-free energy sources has focused attention on both increasing the efficiency and decreasing the cost of solar cells. Quantum-dot (QD) solar cells employing multiple exciton generation (MEG) have attracted much attention as a candidate for the third generation solar cells, because MEG represents a promising route to increase solar conversion efficiencies up to about 44 % in single junction. Our interest has been concerned with QD solar cells using group IV semiconductor nanoparticles [1-4]. The main purpose of this study is to discuss characteristics of quantum efficiency of Ge QD solar cells in view of the MEG effect.

QD thin films containing Ge nanoparticles were deposited using 13.56 MHz radio-frequency (rf) magnetron sputtering process in Ar and H₂ gas mixture under a high pressure condition of 1.5 Torr. The sputtering target was a poly-crystal Ge disk (1 inch) with a purity of 99.99%. The rf power was 50 W.

X-ray diffraction spectra of Ge nanoparticle films show transition from amorphous to crystalline structure by adding H₂ gas, where the diffraction peaks appear at $2\theta = 27^\circ, 45^\circ,$ and 53° corresponding to the (111), (220), and (311) crystal planes of Ge, respectively. Then, optical property of the films was investigated to reveal effects of crystalline Ge nanoparticles on the light absorption properties. For amorphous Ge films, absorption coefficient was $1.5 \times 10^5 \text{ cm}^{-1}$ at 840 nm, while for crystalline Ge films absorption coefficient drastically increased from $0.6 \times 10^5 \text{ cm}^{-1}$ at 840 nm to $4.9 \times 10^5 \text{ cm}^{-1}$ at 450 nm, which is close to $5\text{-}6 \times 10^5 \text{ cm}^{-1}$ at 450 nm in single crystal Ge. Finally, we fabricated Ge QD sensitized solar cells with rectification in the TiO₂/Ge/polysulfide electrolyte system. The incident photo-to-current conversion efficiency increases with decreasing the wavelength, and it is 10 % at 400 nm. The result indicates that excitons generated in Ge

nanoparticles were separated into electrons and holes, and such carriers successfully extracted to the outer circuit.

[1] G. Uchida, et al., *Phys. Stat. Sol. (c)* 8 (2011) 3021.

[2] G. Uchida, et al., *Jpn. J. Appl. Phys.* 51 (2011) 01AD01.

[3] H. Seo, et al., *Electrochim. Acta* 87 (2013) 213.

[4] H. Seo, et al., *Electrochim. Acta* 95 (2013) 43.

3:00pm EN+AS+NS+SS-MoA4 Interfacial Charge Transfer in Extremely Thin Absorber Solar Cells, M.E. Edley, H. Majidi, G.W. Guglietta II, L. Spangler, 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. We report on extremely thin absorber (ETA) solar cells that use ZnO nanowire arrays coated with a thin CdSe layer and filled with a liquid electrolyte. CdSe absorbs visible light, and photoexcited electrons are injected into the ZnO while photoexcited holes oxidize the redox species. Nanowire arrays provide direct pathways for electron transport as well as sufficient surface area for sensitization. The CdSe coatings should be crystalline and conformal with well-controlled thickness. With this ETA architecture, interfacial recombination is the dominant loss process, so controlling the interfacial chemistry, morphology, and microstructure of the materials during processing is critical.

Our approach utilizes a combination of solar cell measurements and ultrafast transient absorption spectroscopy to understand the effects of CdSe thickness, annealing conditions, and interfacial treatments on the dynamics and efficiency of charge carrier separation, and ultimately on the solar-to-electric energy conversion efficiency. These studies provide guidelines for architecture design and materials selection for ETA solar cells. For example, we have found that an optimum thickness exists for planar cells that balances light absorption with photoexcited carrier collection, and that this optimum thickness depends on annealing conditions of the CdSe. Coatings on nanowires should be designed to use the largest thickness that gives the maximum internal quantum efficiency in planar cells, which is ~30 nm when annealing at 400 C. The nanowire geometry is then designed to achieve efficient light harvesting with a coating thickness of 30 nm. Such thin electrodeposited coatings are subject to pinholes and shunt pathways. However, these were overcome through the deposition of an ultrathin (<5 nm) CdS interfacial layer using successive ionic layer adsorption and reaction (SILAR), improving efficiency to above 2%. Ultrafast transient absorption spectroscopy shows that the lifetime of photoexcited carriers depends strongly on defect density, with lifetimes increasing from ~50 ps to ~500 ps upon annealing. Importantly, this lifetime is much longer than the characteristic time for electron transfer into ZnO (~2 ps) and hole transfer into the electrolyte (~100 ps), indicating that charge separation is very efficient.

3:40pm EN+AS+NS+SS-MoA6 Solar Photochemical Fuel Generation using Semiconductor Nanocrystals, G. Dukovic, University of Colorado, Boulder **INVITED**

Semiconductor nanocrystals are remarkable light harvesters with readily tunable absorption spectra and surface chemistry. They have recently been coupled with redox catalysts to drive photochemical multi-electron transfer reactions such as generation of H₂. We use ultrafast laser spectroscopy to characterize the excited state dynamics of nanocrystal-catalyst hybrids and measure the rates and efficiencies of charge transfer processes necessary for photochemical fuel generation. This presentation will focus on the relationships between charge transfer dynamics and overall photochemical reactivity. The design principles derived from the insights provided by these experiments will be described.

4:40pm EN+AS+NS+SS-MoA9 Graphene as a Transparent Front Contact for Heterojunction Silicon Solar Cells, K. Sharma, D. Deligiannis, Delft University of Technology, Netherlands, J. Willem Weber, S. Smit, A.A. Bol, Eindhoven University of Technology, Netherlands, M.C.M. van de Sanden, Dutch Institute for Fundamental Energy Research (DIFFER), Netherlands, M. Creatore, Eindhoven University of Technology, Netherlands, R.A.C.M.M. van Swaaij, Delft University of Technology, Netherlands, W.M.M. Kessels, Eindhoven University of Technology, Netherlands

Silicon heterojunction solar cells (SHJ) have achieved excellent conversion efficiencies both at lab (~25%) and industrial scale (>20%).¹ Further enhancement towards theoretical efficiencies (~28%) is expected to occur when novel concepts and/or new functional materials are implemented to

address the present optical and resistive losses in ITO and doped layers utilized in SHJ solar cells. Recently, graphene on silicon has been successfully tested as a Schottky barrier junction.² Innovative solar cell structures are required to realize the true potential of graphene. To this end, we are reporting a novel device structure where undoped graphene was tested as a transparent conductive layer. Conversion efficiencies of about 10% have been achieved, which is an order of magnitude higher than reported so far in the literature for undoped graphene. CVD grown graphene was transferred onto SHJ device structures in an advanced multi-step procedure and the following solar cell layouts were used: stack A-graphene/(i)a-Si:H/(n)c-Si/(i)a-Si:H/(n)a-Si:H; and stack B-graphene/(p)a-Si:H/(i)a-Si:H/(n)c-Si/(i)a-Si:H/(n)a-Si:H. The amorphous silicon layers were deposited by means of RF-PECVD in a cluster tool. Current-voltage (J-V) and external quantum efficiency (EQE) measurements were carried out to characterize the devices. A minority carrier lifetime as high as 2 ms was achieved for the investigated stacks, largely due to the excellent surface passivation induced by (i)a-Si:H layers. Open-circuit voltage, short-circuit current density, fill-factor, and conversion efficiency values of 384 mV, 25 mA/cm², 60%, and 5.8%, respectively, were achieved for stack A. Simulations of the band structure have shown that graphene, due to its self-adaptive nature² acts as an energy barrier for charge transport, which could be further enhanced if the graphene is doped. For stack B, with the graphene applied onto a p-type a-Si:H layer, the open-circuit voltage was significantly enhanced up to 569 mV, while the fill-factor increased to 74%. However, in this case the short-circuit current density dropped to 24 mA/cm² due to enhanced absorption losses in the (p)a-Si:H. The conversion efficiency of 10.1% was achieved. These initial results suggest that graphene can potentially be used to decouple electrical and optical properties of the front contact in SHJ solar cells to achieve higher conversion efficiencies.

¹ A. Descoedres, Z.C. Holman, L. Barraud, S. Morel, S. De Wolf, and C. Ballif, *IEEE Journal of Photovoltaics* **3**, 83 (2013).

² H. Zhong, Z. Liu, G. Xu, Y. Fan, J. Wang, X. Zhang, L. Liu, K. Xu, and H. Yang, *Applied Physics Letters* **100**, 122108 (2012). (ref. 7-9 therein)

5:00pm **EN+AS+NS+SS-MoA10 Tuning Energy Level Alignment at Organic/Semiconductor Interfaces using a Built-in Dipole in Chromophore-Bridge-Anchor Compounds**, *S. Rangan, A. Batarseh, K.P. Chitre, A. Kopecky, E. Galoppini, R.A. Bartynski*, Rutgers University

The problem of energy level alignment at heterointerfaces is central to the issues of charge transport and charge separation in solid state or hybrid photovoltaic devices, as well as in organic electronic and water splitting applications. In most cases, the energy alignment at interfaces is an ad-hoc property of two materials brought into contact, with the relative ionization or affinity energies possibly altered by charge reorganization at the interface, often called the interface dipole. Attempts to alter this ad-hoc energy alignment have employed strategies ranging from modifying bulk properties to intentionally altering charge redistribution at the interface by local doping. Such approaches, however, offer a very limited level of control.

In this work, we demonstrate that it is possible to separate the contributions of ad-hoc interfacial dipoles from a designed oriented dipole in order to finely tune energy alignment at the interface between a chromophore and a wide band gap oxide. The approach employs a chromophore-bridge-anchor molecular architecture where the three components are electronically decoupled. By introducing electron donor (D) and acceptor (A) groups to the bridge, an intramolecular dipole is introduced between the chromophore and the anchor. When a monolayer of such molecules is bonded to a metal oxide surface, the resulting dipole layer establishes a potential difference that shifts the chromophore levels with respect to those of the substrate.

This concept is demonstrated using a chromophore (ZnTPP)-bridge (substituted with an electron donating (NMe₂) and electron withdrawing (NO₂) groups to create a built-in dipole)-anchor (Isophthalic acid) architecture. Shifts of the chromophore's HOMOs on the order of plus or minus 0.1 eV with respect to the ZnO valence band edge have been observed, without altering the photoabsorption properties of the chromophore or the HOMO-LUMO gap. An important strength of this concept is that it provides a general design applicable to a large number of anchoring functional groups, built-in dipole bridges, and redox-active centers.

5:20pm **EN+AS+NS+SS-MoA11 Plasmonic Sensing of Impregnation Kinetics of Dye Sensitized Solar Cells (DSSC)**, *V. Gusak*, Chalmers University of Technology, Sweden, *LP. Heiniger*, Ecole Polytechnique Fédérale de Lausanne, Switzerland, *V. Zhdanov*, Boreskov Institute of Catalysis, Russian Federation, *M. Graetzel*, Ecole Polytechnique Fédérale de Lausanne, Switzerland, *B.H. Kasemo*, *C. Langhammer*, Chalmers University of Technology, Sweden

Dye sensitized solar cells (DSSCs) represent a low cost and environmentally friendly alternative to conventional Si solar cells. Recent

advances (electrolyte and sensitizer) have resulted in a boost of their efficiency up to 13%. In DSSCs, interaction between dye molecules and the TiO₂ electrode influences the device performance. The kinetics of impregnation of mesoporous TiO₂ films with dye molecules is an important step in fabrication and key for potential mass production. Employing localized surface plasmon resonance (LSPR) sensing we explored the dye adsorption and impregnation process for flat TiO₂ films and mesoporous TiO₂ electrodes (1 - 10 μm thick) of the kind used as photoelectrodes in DSSCs. The flat films provide detailed monolayer adsorption - desorption kinetics that assist interpretation of the data from the complex mesoporous samples. For the latter the dye impregnation kinetics were followed, in real time, by a special version of LSPR sensing, Hidden Interface-Indirect Nanoplasmonic Sensing (HI-INPS) combined with optical absorption spectroscopy. The LSPR/HI-INPS technique employs plasmonic sensor nanoparticles embedded under the flat films or under the mesoporous TiO₂ sample. In the former case this yields submonolayer sensitivity to dye molecule adsorption/desorption. For the mesoporous samples HI-INPS detects when dye molecules reach the "bottom" of the sample. The typical sensing range in this work was < 70 nm, a few percent or less of the mesoporous sample thicknesses. The measurements revealed an initial fast (minutes) and a later slow (>> 1hour) impregnation process (responsible for ca. 70 and 30 %, respectively, of the total uptake). The dye percolation time to the bottom of the 2 - 10 μm thick TiO₂ photoelectrode films, was measured by HI-INPS for the dye Z907 in a mixture of acetonitrile and *tert*-butanol for *different dye concentrations* and for *different thicknesses* of the TiO₂ sample. The total amount of adsorbed dye was simultaneously measured by optical absorption spectroscopy. The experimental data for the fast impregnation process were analyzed, with excellent agreement, by employing a diffusion-front model, combining diffusion and first order Langmuir type adsorption, which allows extracting the effective diffusion coefficient for the system. The latter value is about 15 μm²/s, an order of magnitude or more smaller than that for "free" diffusion of dye molecules in bulk solvents. The data from flat films, in addition to providing adsorption kinetics, also reveals that dye desorption and time dependent reorganization of dye molecules in the dye adlayer are significant processes.

Authors Index

Bold page numbers indicate the presenter

— B —

Bartynski, R.A.: EN+AS+NS+SS-MoA10, 2
Batarseh, A.: EN+AS+NS+SS-MoA10, 2
Baxter, J.B.: EN+AS+NS+SS-MoA4, 1
Bol, A.A.: EN+AS+NS+SS-MoA9, 1

— C —

Chitre, K.P.: EN+AS+NS+SS-MoA10, 2
Creatore, M.: EN+AS+NS+SS-MoA9, 1

— D —

Deligiannis, D.: EN+AS+NS+SS-MoA9, 1
Dukovic, G.: EN+AS+NS+SS-MoA6, 1

— E —

Edley, M.E.: EN+AS+NS+SS-MoA4, 1

— G —

Galoppini, E.: EN+AS+NS+SS-MoA10, 2
Graetzel, M.: EN+AS+NS+SS-MoA11, 2
Guglietta II, G.W.: EN+AS+NS+SS-MoA4, 1
Gusak, V.: EN+AS+NS+SS-MoA11, 2

— H —

Heiniger, LP.: EN+AS+NS+SS-MoA11, 2

— I —

Ichida, D.: EN+AS+NS+SS-MoA3, 1
Itagaki, N.: EN+AS+NS+SS-MoA3, 1

— K —

Kamataki, K.: EN+AS+NS+SS-MoA3, 1
Kasemo, B.H.: EN+AS+NS+SS-MoA11, 2
Kessels, W.M.M.: EN+AS+NS+SS-MoA9, 1
Koga, K.: EN+AS+NS+SS-MoA3, 1
Kopecky, A.: EN+AS+NS+SS-MoA10, 2

— L —

Langhammer, C.: EN+AS+NS+SS-MoA11, 2

— M —

Majidi, H.: EN+AS+NS+SS-MoA4, 1

— R —

Rangan, S.: EN+AS+NS+SS-MoA10, 2

— S —

Seo, H.: EN+AS+NS+SS-MoA3, 1
Sharma, K.: EN+AS+NS+SS-MoA9, 1
Shiratani, M.: EN+AS+NS+SS-MoA3, 1
Smit, S.: EN+AS+NS+SS-MoA9, 1
Spangler, L.: EN+AS+NS+SS-MoA4, 1

— U —

Uchida, G.: EN+AS+NS+SS-MoA3, 1

— V —

van de Sanden, M.C.M.: EN+AS+NS+SS-MoA9, 1
van Swaaij, R.A.C.M.M.: EN+AS+NS+SS-MoA9,
1

— W —

Willem Weber, J.: EN+AS+NS+SS-MoA9, 1

— Z —

Zhdanov, V.: EN+AS+NS+SS-MoA11, 2
Zhu, X.Y.: EN+AS+NS+SS-MoA1, 1