

## Energy Harvesting & Storage Room Lehua - Session EH-TuM

### Surfaces & Interfaces for Solar Cells and Solar Fuels

Moderator: Charles Eddy Jr., US Naval Research Laboratory, USA

8:00am **EH-TuM1 Electrospun Photoelectrodes for Dye-Sensitised Solar Cells**, *J. Macdonald*, University College London, UK; *D. Tune*, KIT, Germany; *R. Dewi*, Zeiss, Australia; *T. Gibson*, *G. Shapter*, Flinders University, Australia; **Thomas Nann**, Victoria University of Wellington, New Zealand  
The performance of dye-sensitised solar cells (DSSCs) depends to a large degree on the material and surface structure of the photoelectrodes (most commonly only the anode is a photoelectrode). Electrospun photoelectrodes offer a very high surface area and inter-connectivity, which should be ideal for this particular application. We will present a study on electrospun titania and nickel oxide photoelectrodes and their application in DSSCs.

Titania (TiO<sub>2</sub>) photoanodes are by far the most studied system for DSSCs. We have shown that the performance of electrospun titania (anatase) fibre-photoelectrodes can be significantly increased by forming a single walled carbon nanotube (SWCNT) composite material [1]. Figure 1 shows scanning electron micrographs (SEMs) of a typical photoanode of this type.

Photocathodes are much less efficient compared with anodes and are replaced by platinum group metal catalysts frequently. We have studied photocathodes that are based on nickel oxide (NiO). The base semiconductors have been 'sensitised' with quantum dots and organic fluorophores. The morphology and nanostructure of the materials have been varied and finally, electrocatalysts have been added. It was found that sensitising can improve the performance of some *p*-type photocathodes significantly, but even the best performing photocathodes did not compare with equivalent TiO<sub>2</sub> photoanodes.

#### References

[1] T. J. Macdonald, D. D. Tune, M. R. Dewi, C. T. Gibson, J. G. Shapter, T. Nann, *ChemSusChem* **2015**, *8*, 3396–3400.

8:20am **EH-TuM2 Combinatorial in-situ Photoelectron Spectroscopy Investigation of Sb<sub>2</sub>Se<sub>3</sub>/ZnS Heterointerfaces**, **Sebastian Siol**, *P. Schulz*, *M. Young*, *K. Borup*, *G. Teeter*, *A. Zakutayev*, NREL, USA

Energy band alignments at heterointerfaces play a crucial role in defining the functionality of semiconductor devices. The search for material systems with suitable electronic band alignments is one of the key challenges in developing novel photovoltaic technologies. Particularly the tuning of band offsets has enabled significant advances in efficiency for several state of the art thin film solar cell technologies. While the theoretical prediction of band alignments at semiconductor heterointerfaces is often very limited, interface experiments utilizing X-ray photoelectron spectroscopy (XPS) measurements can be employed to track the evolution of the electronic structure at the interface. In particular the V-IV binary chalcogenide Sb<sub>2</sub>Se<sub>3</sub> has been identified as a prospective absorber material for the next generation of thin film solar cells [1], yet the understanding of interfacing this compound semiconductor to commonly employed buffer layers such as ZnS is still in its very infancy.

In recent years high throughput, combinatorial materials science methodology has gained tremendous interest [2]. In this work we demonstrate how combinatorial techniques can be utilized to increase the throughput of *in-situ* experiments to investigate the interface formation for respective semiconductor heterojunctions. Thin films are grown with intentional thickness gradients on the substrate, to minimize the required number of depositions and transfers. In addition, other deposition parameters such as the deposition temperature or composition can be systematically co-varied with thickness to cover several individual interface experiments on one substrate.

Using orthogonal thickness and temperature gradients a combinatorial *in-situ* interface experiment was set up, that provided a comprehensive dataset for the extensive investigation of the band alignment at the prototypical Sb<sub>2</sub>Se<sub>3</sub>/ZnS heterojunction. Our findings point to a large conduction band offset of  $\Delta E_{CB} = 1.75 \pm 0.05$  eV along with a potentially detrimental interfacial reaction at the junction. With this result, the study reveals why the choice of a ZnS buffer layer would limit device parameters and gives initial guidelines for alternative buffer layer materials with smaller electron affinities.

The method presented in this contribution can easily be applied for other material systems and will enable other researchers to quickly acquire comprehensive data for a more accurate picture of electronic processes across potential device interfaces.

[1] Y. Zhou et al. *Nat. Photonics* **2015**, *9*, 409.

[2] M. L. Green et al. *J. Appl. Phys.* **2013**, *113*, 231101.

8:40am **EH-TuM3 High Performance Transparent Electrode Based on Silver Nanowires with Plasma Treatment for Flexible Solar Cell Applications**, **Sunghoon Jung**, *W. Ahn*, *D.G. Kim*, Korea Institute of Materials Science, Republic of Korea

The random networks of silver nanowires (AgNWs) have been noticed as next generation transparent electrode which satisfies the high conductivity, transmittance and flexibility at the same time. Thus, AgNWs have a great potential for replacement of indium-tin-oxide (ITO) transparent electrode which have been used most widely. Although the nature of the superb self-electrical, optical and mechanical properties, some disadvantages of the transparent electrode such as chemical, environmental stability and contact resistance are bottle-necks for practical applications.

A simple approach to improve the stability of AgNW electrode is to form low-reactive materials such as graphene, graphene oxide and alumina on the top of AgNWs as passivation layers. Chemical and environmental stability is increased and electrical resistance is decreased. However, there are some negative aspects which are losses of transmittance, increasing vertical electrical resistance and upper layer and unisotropic chemical etching.

In this study, plasma techniques are applied to augment the electrical and environmental properties of AgNWs transparent electrode. The electrical resistance is decreased and environmental stability is improved. Moreover, AgNWs with plasma treatment showed much improved thermal stability compared to untreated AgNWs. We applied the plasma treated AgNWs to flexible organic photovoltaic devices as transparent electrode, and its power conversion efficiency is similar to organic photovoltaics based on ITO/Glass.

9:00am **EH-TuM4 Visible Light Responsive Photocatalysts toward Solar Hydrogen Production**, **Ryu Abe**, Kyoto University, Japan **INVITED**

Water splitting into H<sub>2</sub> and O<sub>2</sub> using semiconductor photocatalysts has received much attention recently due to the potential for the clean production of H<sub>2</sub> from water utilizing solar energy [1]. Because almost half of all incident solar energy at the Earth's surface falls in the visible region, the efficient utilization of visible light remains indispensable for realizing practical H<sub>2</sub> production. We have developed a new type of photocatalytic water splitting system, mimicking the mechanism of photosynthesis in green plants [2-6]. In this system, the water splitting reaction is broken up into two stages: one for H<sub>2</sub> evolution and the other for O<sub>2</sub> evolution; these are combined by using a shuttle redox couple (Red/Ox) in the solution. Over a H<sub>2</sub> evolution photocatalyst, the photoexcited electrons reduce water to H<sub>2</sub> and holes oxidize a reductant (Red) to an oxidant (Ox). The Ox is reduced back to the Red by photoexcited electrons generated over an O<sub>2</sub> evolution photocatalyst, where the holes oxidize water to O<sub>2</sub>. This system reduces the energy required to drive each photocatalysis process, allowing visible light to be utilized more efficiently than in conventional system. We have achieved water splitting using various visible light responsive photocatalysts, such as SrTiO<sub>3</sub> doped with Cr [3], tantalum oxynitrides (TaON or BaTaO<sub>2</sub>N) [4], and organic dyes [5], which work as a H<sub>2</sub> evolution photocatalyst, combined with tungsten oxide (WO<sub>3</sub>) for O<sub>2</sub> evolution in the presence of a shuttle redox mediator such as iodate/iodide. Some oxyhalides such as Bi<sub>4</sub>NbO<sub>8</sub>Cl have also been proven as stable and efficient O<sub>2</sub>-evolving photocatalysts under visible light, enabling a Z-scheme overall water splitting with iron redox [6]. We have also demonstrated that the porous photoanodes of tantalum oxynitrides can stably oxidize water with significantly high quantum efficiency, after loading of IrO<sub>2</sub> or CoO<sub>x</sub> nanoparticles as a cocatalyst; enabling water splitting under visible light with a relatively small applied bias [7].

#### References

[1] J. Photochem. Photobiol. C: Photochem. Rev. **11** (2011) 179.

[2] Bull. Chem. Soc. Jpn. **84** (2011) 1000.

[3] J. Phys. Chem. B **109** (2005) 16052.

[4] a) Chem. Commun. (2005) 3829; b) Chem. Mater. **21** (2009) 1543; b) J. Am. Chem. Soc. **132** (2010) 5858; c) ChemSusChem **4** (2011) 228.

[5] J. Am. Chem. Soc. **135** (2013) 16872.

[6] J. Am. Chem. Soc. 38 (2016) 2082.

[7] a) J. Am. Chem. Soc., 132 (2010) 11828; b) Energy Environ. Sci. 4 (2011) 4138; c) J. Am. Chem. Soc. 134 (2012) 6968; d) J. Am. Chem. Soc. 135 (2013) 10238.

## 9:40am EH-TuM6 *In Situ* Growth and Degradation Mechanisms in Methylammonium Lead Halide Perovskites for Graphene-Based Solar Cells, *Muge Acik, S.B. Darling*, Argonne National Laboratory, USA

High power conversion efficiency of perovskite-based solar cells offers promise for low-cost and scalable production of renewable energy. The need to harness solar energy has recently motivated the search to alternate ETL/HTL hybrid materials, specifically graphene/perovskite films. Hybrid organic-inorganic methylammonium lead halides, MAPbX<sub>3</sub> (X=I, Br, Cl)/mixed-halides (I<sub>3-x</sub>Cl<sub>x</sub>, I<sub>3-x</sub>Br<sub>x</sub>) have been reported as light harvesting layers with their superior optoelectronic properties: tunable bandgap, long electron-hole diffusion lengths and high electron/hole mobility. Nevertheless, halide-based perovskites require *in situ* investigation for film growth, degradation and perovskite formation mechanisms to overcome detrimental effects of incomplete lead precursor conversion, inconsistent crystallite formation/film uniformity, and weak cation-anion-solvent coordination. Graphene-derived hybrids have recently emerged as an ETL/HTL replacement in these devices, however understanding the origin of interfacial chemical reactions between deposited perovskite films over graphene-derived materials is still lacking, especially at the ETL/perovskite/HTL interfaces. Moreover, effect of film thickness, stoichiometry control, overlayer/ underlayer morphology/composition, stability issues and cation-anion electrostatic interactions ought to be examined for better charge transport. To address scalability and stability issues, we examined degradation, nucleation and growth mechanisms in reduced graphene/graphite oxide (RGO) upon halide-based (I, Cl, Br) perovskite deposition. Chemical interactions were interpreted at perovskite/RGO interfaces for the grain size, orientation, boundaries, and surface/bulk effects using variable-temperature ( $\leq 600^\circ\text{C}$ , Ar(g)) *in situ* spectroscopy (infrared absorption, micro-Raman, UV-vis-NIR, luminescence) and SEM, XRD, XPS, TEM, and AFM for morphology characterization. Controlled perovskite formation was achieved at room temperature for bromide/chloride-based perovskites resulting in improved chemical stability with heat (vs. iodide derivative). Overall, perovskite decomposition and oxygen-induced chemical reactions occurred at  $\leq 150^\circ\text{C}$ , eliminated hydroxyls/carboxyls in RGO, and maintained ethers/epoxides upon perovskite decomposition. Poor perovskite formation was observed on RGO due to varying electron affinity and reactivity of precursor halides, resulting in film degradation in air (O<sub>2</sub>, H<sub>2</sub>O). References: (1) M Acik, SB Darling. J. Mater. Chem. A (2016) 4, 6185-6235. (2) J Gong, SB Darling, F You, Energy Environ. Sci. (2015) 8, 1953-1968 (3) M Acik, G Lee, C Mattevi, M Chhowalla, K Cho, YJ Chabal. Nature Materials (2010) 9 (10), 840-845.

Use of the Center for Nanoscale Materials was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357. The abstract has been created by UChicago Argonne, LLC, Operator of Argonne National Laboratory ("Argonne"). Argonne, a U.S. Department of Energy Office of Science laboratory, is operated under Contract No. DE-AC02-06CH11357. The U.S. Government retains for itself, and others acting on its behalf, a paid-up nonexclusive, irrevocable worldwide license in said article to reproduce, prepare derivative works, distribute copies to the public, and perform publicly and display publicly, by or on behalf of the Government. Office of Science User Facility under Contract No. DE-AC02-06CH11357. M.A. also acknowledges support from the Joseph Katz Named Fellowship at Argonne National Laboratory.

## 10:20am EH-TuM8 Back Contact Passivation via Atomic Layer Deposition for Increased Device Performance of Earth-Abundant Cu<sub>2</sub>ZnSn(S,Se)<sub>4</sub> Solar Cells, *Priscilla Antunez, D.B. Farmer, D.M. Bishop, R.A. Haight*, IBM T.J. Watson Research Center, USA

Thin film solar cell absorbers composed of earth-abundant elements such as Cu<sub>2</sub>ZnSn(S,Se)<sub>4</sub> (CZTSSe) are particularly attractive due to their relative low toxicity and their record maximum power conversion efficiency of 12.6% using an antireflective coating. Despite rapid progress, further improvements in efficiency are needed to enable the commercial-scale implementation of CZTSSe as a solar cell absorber. Our recent efforts have identified the deleterious impact of recombination at the interface between the CZTSSe absorber and the molybdenum back contact, which results in decreased lifetime, compared to the bulk, and a reduced open circuit voltage (V<sub>oc</sub>), compared to theoretical expectations. To address this limitation, we have employed two approaches designed to increase device

performance. The first approach involves the deposition of Al<sub>2</sub>O<sub>3</sub>, via ALD, onto the Mo/glass substrate prior to the CZTSSe growth. In the second approach, the CZTSSe device is exfoliated to expose the back surface of the absorber, and a thin Al<sub>2</sub>O<sub>3</sub> layer is then deposited to passivate the back of the solar cell. The passivating ALD step is then followed by the deposition of a high work function back contact. The high work function material further reduces recombination by imposing an electrostatic field, which drives the separation of electrons and holes to increase device performance. These effects are supported by device simulations and confirmed with experimental results that show an increase in several performance parameters, like V<sub>oc</sub> and J<sub>sc</sub>, when high work function back contacts are employed in conjunction with careful control of absorber thickness. With this approach, along with the inclusion of the Al<sub>2</sub>O<sub>3</sub> passivating layer designed to inhibit recombination, efficiencies as high as 11.6% have been achieved without the use of an antireflective coating.

## 10:40am EH-TuM9 Nanoscale Imaging of Charge Carrier Transport in Monoclinic Bismuth Vanadate Photoanodes Via Atomic Force Microscopy, *Johanna Eichhorn, J.K. Cooper, L.H. Hess*, Lawrence Berkeley Lab, USA; *D. Ziegler*, Scuba Probe Technologies LLC, USA; *D.M. Larson, M.K. Gilles, I.D. Sharp, F.M. Toma*, Lawrence Berkeley Lab, USA

Photoelectrochemical water splitting is a promising route for efficient conversion of solar energy to chemical fuel. Among different photoelectrode materials, bismuth vanadate (BiVO<sub>4</sub>) is one of the most actively investigated oxide semiconductors due to its moderate bandgap, favorable conduction band position, and relatively long photocarrier lifetimes.[1] However, under relevant operating conditions, pristine BiVO<sub>4</sub> thin films are subjected to degradation at the exposed surface facets. The degradation process in solution is accelerated by photoexcitation, which causes trapping of photogenerated holes at localized surface sites.[2] Therefore, developing approaches to stabilize these efficient semiconductor nanostructures requires a detailed understanding and control of charge separation, transport, and recombination mechanisms at their relevant length scales.

Here, we use photoconductive atomic force microscopy in combination with Kelvin probe force microscopy to correlate local surface morphology with generated photocurrent and contact potential difference maps at individual grain facets in polycrystalline BiVO<sub>4</sub> films. Furthermore, we employ scanning transmission X-ray microscopy to trace the changes in local chemical structure and composition in pristine and photodegraded BiVO<sub>4</sub>.

The photocurrent and contact potential difference maps reveal the impact of different working conditions, such as bias voltage, excitation energy or excitation power, on the local charge carrier dynamics. Both for excitation above the bandgap (405 nm) and sub-bandgap illumination (532 nm), the photocurrent maps resolve the contributions from individual grains with nanometer spatial resolution. The photoelectrochemical performance of BiVO<sub>4</sub> can be significantly enhanced by varying the oxygen vacancy defects and hydrogen impurities, through hydrogen annealing. Therefore, we compare the photocurrent generation of pristine and hydrogen annealed BiVO<sub>4</sub>. This careful analysis allows us to identify locally the charge transfer and loss mechanisms in these materials which ultimately contribute to desired photocurrent generation or undesired photocorrosion.[3]

[1] J. K. Cooper et al., The role of hydrogen in defining the n-type character of BiVO<sub>4</sub> photoanodes, *Chem. Mater.* **2016**.

[2] F. M. Toma et al., Mechanistic insights into chemical and photochemical transformations of bismuth vanadate photoanodes, *Nat. Commun.* **2016**.

[3] J. Eichhorn et al., Nanoscale photocurrent imaging of monoclinic BiVO<sub>4</sub> films via atomic force microscopy, **2016** (in preparation).

## 11:00am EH-TuM10 Energy Level Alignment at Interfaces in Hybrid Lead Halide Perovskite Photovoltaics, *Philip Schulz, A.A. Dameron, P.F. Ndione, M. Yang, K. Zhu, J.J. Berry*, NREL, USA

Hybrid organic/inorganic perovskites define an emerging class of solar cell absorber materials which advances to the lead in maximum power conversion efficiencies in the area of thin-film solar cells.<sup>1</sup> In the photovoltaic device the electronic interaction between the perovskite absorber and adjacent charge extraction and transport layers is key to maximize cell functionality. We identified that device characteristics such as the open circuit voltage can be affected by the alignment of the electronic energy levels of an organic charge extraction layer with the electronic transport levels in the perovskite film.<sup>2</sup> Furthermore, we found that the doping characteristic of the underlying oxide substrate can be used to rigidly tailor the Fermi level position in a subsequently deposited

# Tuesday Morning, December 13, 2016

perovskite film. For future applications such as the integration of a perovskite subcell into a tandem device, precise control over the electronic alignment processes is required.<sup>3</sup>

Here we present our recent findings in which we examine a selection of incrementally deposited oxide charge carrier transport layers on top of methylammonium and formamidinium lead iodide perovskite films. Functional *n*-type (e.g. TiO<sub>2</sub>, MoO<sub>x</sub>), *p*-type (e.g. NiO) and intrinsic oxides (e.g. Al<sub>2</sub>O<sub>3</sub>) are grown by pulsed laser and atomic layer deposition techniques on top of the perovskite absorber layer. We then use ultraviolet and X-ray photoemission spectroscopy (UPS/XPS) to determine the electronic energy level alignment at the oxide/perovskite interface while at the same time tracking changes in the interface chemistry. Using this approach we are able to explain band offset changes induced in the perovskite layer by chemical interactions with the oxide on top, changes in the electrostatic potential and the formation of defective surface layers. The results are not only used to give guidelines about how to embed oxide layers into perovskite photovoltaic devices but also inform to what extent the electronic structure of the perovskite is subject to extrinsic perturbations on a more universal scale.

[1] K. Emery, Best research-cell efficiencies. [http://www.nrel.gov/ncpv/images/efficiency\\_chart.jpg](http://www.nrel.gov/ncpv/images/efficiency_chart.jpg), Ed. NREL: 2016

[2] P. Schulz, E. Edri, S. Kirmayer, G. Hodes, D. Cahen, A. Kahn, *Energy Environ. Sci.* **2014**, *7*, 1377

[3] P. Schulz, L. L. Whittaker-Brooks, B. A. MacLeod, D. C. Olson, Y.-L. Loo, A. Kahn, *Adv. Mater. Interfaces* **2015**, *2*, 1400532

11:20am **EH-TuM11 Facet-dependent Photovoltaic Efficiency Variations in Single Grains of Hybrid Halide Perovskite**, *Alexander Weber-Bargioni*, Lawrence Berkeley National Laboratory, USA

Photovoltaic devices based on hybrid perovskite materials have exceeded 22% efficiency due to high charge carrier mobilities and lifetimes. Properties such as photocurrent generation and open circuit voltage are influenced by the microscopic structure and orientation of the perovskite crystals, but are difficult to quantify on the intra-grain length scale and are often treated as homogenous within the active layer. Here, we map the topography, local short circuit photocurrent, open circuit photovoltage, and local powerconversion efficiency in state-of-the-art methylammonium lead iodide perovskite solar cells using photoconductive atomic force microscopy. We find, within individual grains, spatially-correlated heterogeneity in short circuit current and open circuit voltage up to 0.6 V. These variations are related to different crystal facet surfaces and have a direct impact on the macroscopic power conversion efficiency. We attribute this heterogeneity to a facet-dependent density of trap states at the surface [1]. These results imply that controlling crystal grain and facet orientation will enable a systematic optimization of polycrystalline and single crystal devices for photovoltaic and lighting applications.

[1] *Nature Energy* **1**, Article number: 16093 (2016)

11:40am **EH-TuM12 Atomic Scale Understanding of the CdS/Cu(In,Ga)Se<sub>2</sub> Interface in Alkali-incorporated Solar Cells**, *Mowafak Al-Jassim*, NREL, USA

Polycrystalline thin film technologies are rapidly evolving to be an important part of the solar energy portfolio and currently have about 10% of the photovoltaics market share. Cell efficiencies exceeding 22% have been reported for CIGS, which makes thin film solar cells competitive with wafer Si cells. However, this is still considerably lower than the theoretical efficiency limit. In this work we investigate carrier loss mechanisms in CIGS thin films associated with grain boundaries and interfaces. We combined scanning electron microscopy (SEM)-based cryogenic cathodoluminescence (CL) spectrum imaging and electron backscatter diffraction (EBSD) in order to map the spatial distribution of various atomic-level defects as a function of deposition and film processing. These investigations were complemented with atom probe tomography and high resolution STEM-EELS to study the chemical nature of the defects. In addition to investigating the structural and chemical properties of grain boundaries and interfaces in CIGS cells, considerable emphasis was placed on understanding the role of alkali post-deposition treatment in improving cell efficiency. These results will be presented and discussed.

## Author Index

**Bold page numbers indicate presenter**

— A —

Abe, R.: EH-TuM4, **1**  
Acik, M.A.: EH-TuM6, **2**  
Ahn, W.: EH-TuM3, **1**  
Al-Jassim, M.: EH-TuM12, **3**  
Antunez, P.D.: EH-TuM8, **2**  
— B —  
Berry, J.J.: EH-TuM10, **2**  
Bishop, D.M.: EH-TuM8, **2**  
Borup, K.: EH-TuM2, **1**  
— C —  
Cooper, J.K.: EH-TuM9, **2**  
— D —  
Dameron, A.A.: EH-TuM10, **2**  
Darling, S.B.: EH-TuM6, **2**  
Dewi, R.: EH-TuM1, **1**  
— E —  
Eichhorn, J.: EH-TuM9, **2**

— F —

Farmer, D.B.: EH-TuM8, **2**  
— G —  
Gibson, T.: EH-TuM1, **1**  
Gilles, M.K.: EH-TuM9, **2**  
— H —  
Haight, R.A.: EH-TuM8, **2**  
Hess, L.H.: EH-TuM9, **2**  
— J —  
Jung, S.H.: EH-TuM3, **1**  
— K —  
Kim, D.G.: EH-TuM3, **1**  
— L —  
Larson, D.M.: EH-TuM9, **2**  
— M —  
Macdonald, J.: EH-TuM1, **1**  
— N —  
Nann, T.: EH-TuM1, **1**  
Ndione, P.F.: EH-TuM10, **2**

— S —

Schulz, P.: EH-TuM10, **2**; EH-TuM2, **1**  
Shapter, G.: EH-TuM1, **1**  
Sharp, I.D.: EH-TuM9, **2**  
Siol, S.: EH-TuM2, **1**  
— T —  
Teeter, G.: EH-TuM2, **1**  
Toma, F.M.: EH-TuM9, **2**  
Tune, D.: EH-TuM1, **1**  
— W —  
Weber-Bargioni, A.: EH-TuM11, **3**  
— Y —  
Yang, M.: EH-TuM10, **2**  
Young, M.: EH-TuM2, **1**  
— Z —  
Zakutayev, A.: EH-TuM2, **1**  
Zhu, K.: EH-TuM10, **2**  
Ziegler, D.: EH-TuM9, **2**