

Energy Harvesting & Storage

Room: Lehua - Session EH-MoM

Nano-based Approaches for Photovoltaics

Moderator: Jason Baxter, Drexel University, USA

8:40am **EH-MoM1 Thin Film Solar Cells from Colloidal Nanoparticle Dispersions**, *Eray Aydil, B. Chernomordik, N. Trejo*, University of Minnesota **INVITED**

The global installed capacity to generate electricity using solar cells has doubled every 2.5 years since 1975, an exponential growth similar to the Moore's law which states that the number of transistors on a computer chip doubles every 2 years.¹ Maintaining this aggressive Moore-like growth requires sustainable, high-throughput low-cost production of thin film solar cells. Copper zinc tin sulfide (Cu₂ZnSnS₄ or CZTS), copper zinc tin selenide (Cu₂ZnSnSe₄ or CZTSe) and their alloys (Cu₂ZnSn(S_xSe_{1-x})₄ or CZTSSe) are emerging as promising solar absorber materials for thin-film solar cells because they are comprised of earth abundant elements and can potentially help increase the solar electricity production to terawatt levels without the concerns associated with the toxicity and low abundance of the elements in the current commercial thin-film solar cells. A potentially high-throughput and low-cost approach to making thin polycrystalline CZTSSe films is through annealing of coatings cast from colloidal dispersions (inks) of CZTS nanocrystals in sulfur and/or selenium vapor. In this way, the nanocrystal coatings are transformed into polycrystalline films with micrometer size grains, a suitable morphology for making solar cells. The transformation of the nanocrystal coating to a polycrystalline coating is driven by the high surface area of the nanocrystals and, consequently, the high total surface energy of the nanocrystal coating. This approach is well suited for high throughput low-cost roll-to-roll manufacturing. However, many scientific and technical challenges remain. In this talk we will review the advances made towards this end and the remaining challenges. Specifically, we will describe our most recent findings on the effects of sulfidation/selenization time, temperature, sulfur and selenium vapor pressures, presence of alkali and carbon impurities on the microstructure of CZTSSe films.

¹ D. J. Norris and E. S. Aydil, "Getting Moore from Solar Cells," *Science* **338**, 625-626 (2012).

9:20am **EH-MoM3 XPS Analysis of Solution-Based Thin Films of Nano Structured Chalcogenides for Solar Cells Applications**, *F. Servando Aguirre-Tostado, R. Garza-Hernández*, CIMAV, Mexico **INVITED**

The employment of solution based methods for the deposition of semiconductor materials for solar cells applications comes with promise of enabling large area applications at the same time of driving down costs. The optimization of thin film semiconductors such as CuZnSnS requires the understanding of the structure and chemical reactions taking place during deposition of thin films and post-deposition thermal treatments. In this respect, X-ray photoelectron spectroscopy (XPS) is uniquely suited for tracking down chemical reactions occurring at the surface and interface of nanometric layers. The chemical analysis and thermal stability for surface and interface reactions of binary chalcogenide semiconductors is presented. CuS, ZnS, and SnS₂ thin films were deposited on top of CdS by the successive ionic layer absorption and reaction method (SILAR) in a glove-box attached to the XPS load-lock chamber for in-situ analyses. Step by step XPS analysis of the SILAR process reveals an incubation period that depends on temperature and ion concentrations. Multilayer structure stability is discussed in terms of chemical reactivity and diffusion of cations. Finally, a demonstration of how the obtained results can help to engineer a more stable structures is presented.

10:20am **EH-MoM6 Nanoscale Characterization of Defects and Interfaces in Thin Film Solar Cells**, *Mowafak Al-Jassim*, NREL

Thin-film solar cells based on polycrystalline CdTe, Cu(In,Ga)Se₂ (CIGS), and Cu₂ZnSnSe₄ (CZTSe) have demonstrated high solar-to-electricity conversion efficiencies. Typically, polycrystalline thin-film solar cells are expected to exhibit poor performance compared to their single-crystalline counterparts, due to the existence of unavoidable structural defects such as dislocations and grain boundaries (GBs). It is surprising, therefore, that CdTe-, CIGS-, and CZTSe-based polycrystalline thin-film solar cells have achieved higher efficiencies than their single-crystalline counterparts.

Here, we present our results on the study of the atomic structure and electronic properties of structural defects including stacking faults, twins, dislocations, and GBs in CdTe, CIGS, and CZTSe using a combination of

aberration-corrected scanning transmission electron microscopy (STEM) and first-principles density-functional theory calculation. Polycrystalline CdTe thin films were grown by closed-space sublimation, whereas CIGS and CZTSe thin films were deposited by co-evaporation. Atomic resolution scanning transmission electron microscopy (STEM) images were acquired with Nion UltraSTEM 100 and 200 microscopes. We found that intrinsic GBs in CdTe, CIGS, and CZTSe create deep levels mainly due to the anion-anion "wrong" bonding. However, these deep levels can be removed through extrinsic and/or intrinsic passivation. In addition to high resolution structural and chemical characterization, we will present data on the electrical and optoelectronic properties of defects obtained by a correlative approach that involves STEM, cryogenic cathodoluminescence defect spectroscopy and electron beam induced current imaging.

10:40am **EH-MoM7 Two-Step Thermal Annealing Improves the Morphology of Spin-Coated Films for Highly Efficient Perovskite Hybrid Photovoltaics**, *ChihPing Chen*, Ming Chi University of Technology, Taiwan, Republic of China

We describe the relationships between the morphologies and the power conversion efficiencies (PCE) of perovskite photovoltaics having a conventional p-i-n heterojunction structure, indium tin oxide (ITO)/poly(3,4-ethylenedioxythiophene):polystyrenesulfonate (PEDOT:PSS)/CH₃NH₃PbI_{3-x}Cl_x/PC₆₁BM/Al. The PCE of such a device is highly dependent on the morphology of the perovskite film, which is governed by the concentrations of its precursors and the annealing conditions. A two-step annealing process allowed sufficient crystallization of the perovskite material, with a high coverage at a high precursor concentration. Relative to the device prepared using a one-step process (90 °C for 30 min), we observed a 60% increase in PCE for this optimized device. We observed a PCE of 10% of our optimized cells. Corresponding devices exhibited extremely high stability after long-term storage (>1368 h) in the dark in a N₂-filled glove box, with consistently high PCEs (AM 1.5G, 100 mW cm⁻²).

11:00am **EH-MoM8 Charge Transport in PbS Quantum Dot Arrays for Photovoltaic Applications**, *Miquel B. Salmeron*, Lawrence Berkeley Lab, USA **INVITED**

New forms of matter can be designed by combining nanoscale building blocks to create artificial solids with novel functionalities for device applications, such as field effect transistors, solar cells, photodetectors, and light emitting diodes. Artificial atoms or quantum dots (QDs) are ideal elements for this purpose since their electronic properties can be tuned through control of their size, shape and composition, while charge transport through QD assemblies can be engineered by controlling the hopping barrier between neighboring dots. However, fabrication of the QDs comprised of hundreds to thousands of atoms is inevitably imperfect and defects and impurities are always present. The nature of the defect states is unknown and the microscopic mechanisms of charge transport are far from being understood. In this presentation we show, by means of nanoscale imaging, spectroscopy, and density functional theory (DFT), that charge transport takes place in PbS QD arrays following percolation pathways that are spatially different for electrons and holes, electrons via in-gap states (IGS) instead of conduction band states, and holes via valence band states. This novel and exotic transport phenomenon is explained by the measured electronic structure and energy level alignment of the individual QDs. In contrast with previous hypothesis that surface stoichiometry and ligands are responsible for IGS, we found that the IGS are induced by adsorbed oxygen molecules whose p* states hybridize with QD valence band states, thus enabling inter-particle coupling and electron transport. We demonstrate that chemical treatments can be used for surface impurity engineering to achieve tunable electronic structure and transport properties.

11:40am **EH-MoM10 The Effect of n and p Delta Doping on InAs/GaAs Quantum Dot Solar Cell**, *W.J. Choi, HoSung Kim, S.H. Kim, J.D. Song*, Korea Institute of Science and Technology, Republic of Korea, *J.H. Park*, Korea University, Republic of Korea

The efficiency of single junction solar cells (SJSCs) is limited by Shockley-Queisser limit and intermediate band solar cell (IBSC) concept has been introduced in order to overcome the efficiency limit of conventional SJSC. For IBSC model, low dimensional semiconductor structures such as quantum wells and quantum dots (QDs) have been applied to the SJSC. Especially, self-assembled InAs QDs have been frequently applied to GaAs/AlGaAs SJSCs because QDs provide quantum confined states that lower the average band gap of the SJSCs to absorb longer wavelength light beyond GaAs band edge of 870 nm. Theoretical studies of QDSCs have suggested a maximum efficiency of 45 % under 1 sun and 63 % under 1000X concentration. Contrary to their expectations,

actual QDSC devices suffer from photocurrent loss due to inhomogeneous distribution in QD sizes and high carrier confinement of QDs. In order to solve these problems, n delta doping techniques on QDs have been investigated. Here, we introduce the result of QDSCs with n and p delta doping on QDs.

For this study, two types of SC samples were grown on N-GaAs substrate and P-GaAs substrate respectively by molecular beam epitaxy. The undoped and delta-doped QDSCs with doping density of $1 \times 10^{12} \text{ cm}^{-2}$ were prepared and every SC samples has spacer layer with thickness of 20 nm between InAs QD layer and delta doping layer. SC samples grown on N-GaAs and P-GaAs substrate were delta doped with Si and Be respectively. The InAs QDs were grown by modified Stranki-Krastanov growth method. With this growth technique, the QD size and density can be controlled by using the repetition period of a cycle.

The efficiency of QDSCs with and without Si delta doping are 13.6 % and 11.4 % respectively. The enhancement of the efficiency of QDSCs with Si delta doping is due to the increase of J_{sc} . This increase of J_{sc} is due to the n-delta doping and this enhances electron transitions in QDs and increase the carrier lifetime in QDs. The efficiency of QDSCs with and without Be delta doping are 8.45 % and 10.9 % respectively. Compare to the result of QDSCs grown on N-GaAs substrate, the efficiency of QDSCs with Be delta doping has been decreased. This could be attributed to the P delta doping. The Be delta doping induces suppression of the photocarrier generation in the radiative QDs because intentionally doped holes are strongly localized in the radiative QDs. We will present the result of the time-resolved photoluminescence of the QDSCs with Si and Be delta doping.

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