Thin Film
Room 105A - Session TF-TuA
Thin Film Photovoltaics

Moderators: Eray Aydil, University of Minnesota, Colin Wolden, Colorado School of Mines

2:20pm **TF-TuA1 Perovskite Solar Cells: Material Synthesis, Device Operation and Charge Carrier Dynamics***, **Kai Zhu**,* National Renewable Energy Laboratory **INVITED**

Organic-inorganic hybrid halide perovskites have rapidly become a focal point of the photovoltaic (PV) community as a promising next-generation PV technology. Various perovskite absorbers (e.g., $CH_3NH_3PbI_3$ and $HC(NH_2)_2PbI_3$) and device architectures (e.g., mesoporous, planar, and mesoporous-planar hybrid cell configurations) have been examined with promising results by using either solution processing or thermal evaporation. The certified efficiency of a single-junction perovskite solar cell (PSC) has reached 22% after only a few years of active research. In addition to solar cell application, the fascinating optical and electronic properties of these perovskite systems have enabled their usage for various electronic devices including light emitting diodes, photodetectors, and transistors. Despite this remarkable progress associated with perovskites, there are still many fundamental questions to be addressed at both material and device levels. Further improvements are required to advance our understanding on the material effects on the fundamental physical and chemical processes that are important to device operations. In this presentation, I will present our recent studies toward a better understanding and control of perovskite nucleation, grain growth, and microstructure evolution using solution processing. The precursor chemistry and growth conditions are found to affect significantly the structural and electro-optical properties of perovskite thin films. Devices based on different grain sizes and film thicknesses were investigated to correlate the grain sizes with device performance. The impact of grain size on charge carrier dynamics was also studied. Tuning tolerance factor through solid state alloying is shown as an effective way for stabilizing perovskite structures. In addition, I will discuss briefly the role of grain boundary on charge carrier dynamics and device characteristics. These results and others will be discussed.

3:00pm **TF-TuA3 Perovskite Film Growth And Degradation Mechanisms In Graphene-Based Perovskite Solar Cells By In Situ Spectroscopy***, **Muge Acik**,* Argonne National Laboratory*; S.B.D. Darling,* Argonne National Laboratory, University of Chicago

High power conversion efficiency of perovskite-based solar cells offers promise for low-cost and scalable production of renewable energy. Hybrid organic-inorganic methylammonium lead halides, $MAPbX_3$ (X=I, Br, Cl)/mixed-halides ($I_{3-x}Cl_x$, $I_{3-x}Br_x$) have been reported as light harvesting layers with tunable bandgaps, long electron-hole diffusion lengths and high electron/hole mobility. Nevertheless, halide-based perovskites require *in situ* investigation for film growth mechanisms to overcome detrimental effects of incomplete lead precursor conversion, inconsistent crystallite formation/film uniformity, and weak cation-anion-solvent coordination (1). Graphene-derived hybrids has recently emerged as an ETL/HTL replacement in these devices. Graphene/perovskite structure-property relationships are, however, not well understood due to unclear chemistry at the ETL/perovskite/HTL interfaces. Moreover, effect of film thickness, lead content, stoichiometry control, overlayer/underlayer morphology/composition, and cation-anion electrostatic interactions ought to be examined for better charge transport at the graphene/perovskite interfaces. Stability factors also need to be studied for charge mechanisms to unravel device performance challenges. Indeed, underlayer ETLs (TiO_2/Al_2O_3) and overlayer HTLs (spiro-OMeTAD) were rarely studied with graphene. To address scalability and stability issues, we investigated 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 (≤600°C, Ar(g)) *in situ* spectroscopy (infrared absorption, micro-Raman, UV-vis-NIR, luminescence). Controlled perovskite formation was achieved at room temperature for bromide/chloride-based perovskites resulting in improved chemical stability with heat (vs. iodide derivative). Perovskite decomposition was observed at ~150°C. Oxygen-induced chemical reactions occurred at ≤150°C, eliminated hydroxyls/ carboxyls in RGO, and maintained ethers/epoxides upon perovskite decomposition (2). Poor perovskite formation was observed on RGO due to varying electron affinity and reactivity of precursor halides, resulting in film degradation in air (O_2, H_2O). Film morphology was explored by SEM, XRD, XPS, TEM, and AFM.

(1) M Acik, SB Darling. J. Mater. Chem. A (2016) Advance Article. Doi: 10.1039/C5TA09911K (2) M Acik, G Lee, C Mattevi, M Chhowalla, K Cho, YJ Chabal. Nature Mater. (2010) 9 (10), 840-845

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3:20pm **TF-TuA4 ALD Processing for Organo-Metal Halide Perovskite Solar Cells: Opportunities and Challenges***, V. Zardetto,* Eindhoven University of Technology, Netherlands*; F. di Giacomo, R. Andriessen,* Solliance/TNO, Netherlands*; T.M. Brown, A. di Carlo,* University of Rome “Tor Vergata”, Italy*; W.M.M. Kessels, **Mariadriana Creatore**,* Eindhoven University of Technology, Netherlands

Within the class of emerging photovoltaic technologies, organo-metal halide perovskite solar cells have exhibited a sky-rocketing conversion efficiency above 20% in just a few years. In this contribution we will address the opportunities which ALD offers to perovskite solar cells by highlighting its merits of low temperature processing and compatibility with 3D-structures.

Specifically, we will present two studies aimed at the suppression of charge carrier recombination processes at the complex interface ITO/mesoscopic TiO_2 scaffold/ mixed halide perovskite absorber.

In the first study we investigate the role of thin plasma-assisted ALD TiO_2 blocking layers on PET/ITO substrates, developed at a substrate temperature of 150°C [1,2]. The ALD TiO_2 layer is found to exhibit an excellent blocking behaviour towards charge carrier recombination at the above-mentioned interface, leading to open circuit voltage (V_{oc}) values as high as 900 mV (with respect to the pristine PV device exhibiting no rectifying behaviour with a V_{oc} of 50 mV) and superior device performance (9.2%) with respect to a sol-gel TiO_2 blocking layer (4%).

In the second example we carry out few ALD cycles of Al_2O_3 in a 250 nm-thick mesoscopic TiO_2 scaffold. Next to the conformality of the process, we demonstrate by means of electrochemical impedance spectroscopy that just one ALD cycle is sufficient to suppress the charge recombination processes. Specifically, the V_{oc} is found to increase from 860 to 960 mV upon 1 ALD cycle of Al_2O_3.

This contribution will end by discussing the challenges yet to be met by ALD processing directly on perovskite. In all these cases, a careful interface engineering needs to include several aspects potentially affecting the opto-chemical and morphological stability of the active components of the device. For example, methylammonium lead iodide perovskite solar cells already degrade under prolonged (i.e. few hours) annealing at 80°C, as witnessed by the appearance of a PbI_2-related peak in the XRD spectrum. However, when the Al_2O_3 plasma-assisted ALD process at 30°C is compared with the thermal process at 80°C, the plasma step is found to be responsible for abstraction of the methylammonium cation and the formation of iodate species. Instead, the thermal ALD process does not affect the chemistry of the perovskite. These selected examples point out that processing temperature and choice of reactant (moisture or plasma radicals) need to be carefully considered when dealing with processing of hybrid materials, such as perovskite solar cells.

[1] F. Di Giacomo *et al*., Adv. Energy Mat. 5, 1401808 (2015)

[2] V. Zardetto *et al*., ECS Transactions 69 (7), 15 (2015)

4:20pm **TF-TuA7 Identification of Critical Defects in Thin Film CdTe Solar Cells Deposited by Magnetron Sputtering***, P.M. Kaminski, A. Abbas, S. Yilmaz, **John Walls**,* Loughborough University, UK

The exceptional uniformity of deposition provides magnetron sputtering with important advantages as a deposition technique for some applications of thin film cadmium telluride (CdTe) solar cells. Efforts to develop a viable sputtering process for CdTe have been conducted in many laboratories around the world. These efforts have been moderately successful but the conversion efficiency achieved has not matched that obtained using lower energy deposition techniques such as Close Space Sublimation or Vapour Transport Deposition. In particular, sputtered CdTe is less tolerant to the cadmium chloride activation process. Delamination of the films at the cadmium sulphide junction is often observed. Catastrophic void formation within the CdTe layer has also been reported. This behaviour has often been attributed to film stress even though this can be mitigated in the as-deposited films. Using state-of-the-art High Resolution Transmission Electron Microscopy, we will report on the identification of the nanoscale defects that are responsible for the poor response of sputtered CdTe films to the cadmium chloride treatment. Identification of the atomic scale mechanisms at work provides a way to significant process improvement.

4:40pm **TF-TuA8 Solar Energy Conversion Properties and Defect Physics of $ZnSiP_2$**, ***Aaron Martinez***, Colorado School of Mines*; E.L. Warren, P. Gorai,* National Renewable Energy Laboratory*; K.A. Borup,* Aarhus University, Denmark*; D. Kuciauskas, P.C. Dippo,* National Renewable Energy Laboratory*; B.R. Ortiz,* Colorado School of Mines*; R.T. Macaluso,* University of Texas at Arlington*; S.D. Nguyen,* University of Northern Colorado*; A.L. Greenaway, S.W. Boettcher,* University of Oregon, Eugene*; A.G. Norman,* National Renewable Energy Laboratory*; V. Stevanovic, E.S. Toberer,* Colorado School of Mines*; A.C. Tamboli,* National Renewable Energy Laboratory

Implementation of an optically active material on silicon has been a persistent technological challenge. For tandem photovoltaics using a Si bottom cell, as well as for other optoelectronic applications, there has been a longstanding need for optically active, wide band gap materials that can be integrated with Si. $ZnSiP_2$ is a stable, wide band gap (2.1 eV) material that is lattice matched with silicon and comprised of inexpensive elements. From bulk single crystal growth, we have demonstrated the first $ZnSiP_2$ photovoltaic device, and shown that $ZnSiP_2$ has excellent photoresponse and high open circuit voltage of 1.3 V, as measured in a photoelectrochemical configuration. The high voltage and low band gap-voltage offset are on par with much more mature wide band gap III–V materials. Photoluminescence data combined with theoretical defect calculations illuminate the defect physics underlying this high voltage, showing that the intrinsic defects in $ZnSiP_2$ are shallow and the minority carrier lifetime is 7 ns. The favorable results obtained from characterization of bulk material encourage the development of $ZnSiP_2$ as a photovoltaic absorber material. To pursue this development, we have constructed a thin film growth reactor. This reactor employs a combination of ultra high vacuum chemical vapor deposition, using silane and phosphine as precursor gases, and physical vapor deposition, using an effusion cell to evaporate elemental Zn. The preliminary results of the first stages of thin film growth will be presented in addition to an overview of our characterization of bulk $ZnSiP_2$.

5:00pm **TF-TuA9 Controlling the Composition of Zn(O,S) Alloys Grown by Atomic Layer Deposition**, ***Diane K. Lancaster***, *H. Sun,* University of Colorado, Boulder*; S.M. George,* University of Colorado at Boulder

Zn(O,S) alloys are promising conduction band buffers for solar cells. The tunable conduction band of Zn(O,S) alloys improves electron transfer between electron absorber and electron transport materials. Zn(O,S) alloys are produced with atomic layer deposition (ALD) by alternating between ZnO ALD and ZnS ALD using diethylzinc (DEZ) and H_2O or H_2S as the reactants. However, controlling the composition of Zn(O,S) alloys is complicated by an efficient exchange reaction between H_2S and ZnO to produce H_2O and ZnS. This H_2S + ZnO -> H_2O + ZnS exchange reaction dramatically increases the sulfur content of the Zn(O,S) alloys. Because of this exchange reaction, the growth temperature and the H_2S exposure have an effect on the Zn(O,S) alloy composition that is nearly equivalent to the ratio between the alternating numbers of ZnO ALD and ZnS cycles. For example, the exchange reaction is much more efficient at higher temperatures. Increasing the growth temperature from 100°C to 225°C changed the composition for films grown with an alternating sequence of 3 ZnO ALD cycles and one ZnS ALD cycle from 65% ZnS to 90% ZnS, respectively. To overcome the complexity of the exchange reaction, we have developed a new method of growing Zn(O,S) alloy films that avoids alternating between numbers of ZnO ALD and ZnS ALD cycles. This new growth method exposes the H_2O and H_2S simultaneously in sequence with the DEZ exposures. The simultaneous H_2O and H_2S exposures allow competition between the forward exchange reaction (H_2S + ZnO -> H_2O + ZnS) to produce ZnS and the reverse exchange reaction (H_2O + ZnS -> H_2S + ZnO) to recreate ZnO. Film composition using this method was determined by the mole fraction of the H_2S in the dosing mixture. The bandgaps of the Zn(O,S) alloys were measured versus film composition. Composition determined the bandgaps of the Zn(O,S) alloys regardless of growth conditions. Controlling the Zn(O,S) band gap was also much more reproducible using the simultaneous H_2O/H_2S exposures. Bandgaps varied linearly from 3.06 eV to 3.39 eV for H_2S mole fractions in the H_2O/H_2S dosing mixture from 0.03 to 0.39, respectively. We are now able to prepare tunable conduction band buffers for solar cell applications.

5:20pm **TF-TuA10 ALD Ta-doped ZnO Transparent Conducting Oxide**, ***Zhengning Gao***, *Y. Myung, R. Mishra,* Washington University in St. Louis*; R. Kanjolia,* SAFC, Sigma*; J. Park,* Korea University, Republic of Korea*; P. Banerjee,* Washington University in St. Louis

ZnO based transparent conducting oxides (TCOs) offer earth abundant alternatives to conventional indium tin oxide (ITO) films. At the same time, ALD enables discretized doping of substitutional cations at a monolayer level, providing fine and exquisite control over dopant concentration and resultant properties. In this work, we present the ALD of tantalum (Ta) doped ZnO (TZO) films. Compared to dopants such as Ga^{3+} and Al^{3+}, a Ta cation exists in +5 oxidation state and thus, can ideally transfer 3 electrons by substitutionally doping a Zn^{2+} site. We show that 30 nm TZO films with 2 at% Ta provides a minimum resistivity of 4 mW.cm and optical transmissivity of > 86% in the visible range.

The precursors used for Zn, O and Ta are diethyl Zn (DEZ), H_2O and pentakis-dimethylamido Ta (PDMAT). The targeted % Ta is varied from 2 to 20% by introduction of PDMAT pulse between DEZ and H_2O pulses. Downstream quadrupole mass spectrometry (QMS) tracks the interaction chemistry of the PDMAT with Zn-ethylated surface and the DEZ with a Ta-dimethyl amido saturated surface. Electron concentration and mobility are measured using Hall measurements. A minimum resistivity of 4 mW.cm with carrier density of $9.0x10^{19}$ cm^{-3} and a mobility of 17.7 cm^2/V-sec is observed at 2 at% Ta. UV-Vis spectroscopy indicates a monotonic increase in bandgap of ZTO from 3.2 to 3.4 eV upon addition of Ta. Photoluminescence (PL) shows a quenching of the green band emission of ZnO associated with oxygen defects upon the addition of 2 at% Ta. Upon further Ta addition, a red shifted defect peak appears which is attributed to formation of new Zn vacancies. This data is supported by X-ray photoelectron spectroscopy (XPS), showing removal of O vacancies and a clear Ta-O-Zn bond formation for higher Ta doping. The results provide a clear understanding on the mechanism of Ta doping in ZnO and its direct impact on vacancies and resulting electronic and optical properties.

Finally, ALD TZO is deposited on flexible glass substrates and inside nanoporous anodic alumina templates to demonstrate formation of transparent conducting electrodes, conformally on a variety of platforms of relevance to photovoltaic research.

5:40pm **TF-TuA11 Leveraging Small Molecules to Control Interfacial Stability of Transparent Conductive Oxides**, ***Ina Martin***, *R. Matthews, E.B. Pentzer, T.J. Peshek,* Case Western Reserve University

Transparent conductive oxide (TCO) degradation is a known failure mode in thin-film photovoltaic (PV) devices through mechanisms such as resistivity increase and delamination. Degradation studies encompassing accelerated aging of the individual TCO, material combinations (e.g. the TCO interacting with an encapsulant) and full devices are necessary to elucidate the complicated mechanistic pathways of degradation that occur in thin-film PV devices. We have previously demonstrated quenching of the damp-heat-induced degradation of Al:ZnO (AZO), used as a front contact in CIGS modules, by depositing a mere 1 nm of a silane modifier, 3-aminoproplytriethoxysilane (APTES). Here we present results on the effect of the application of thin interfacial modifiers on AZO degradation, for thin films and within full CIGS ($Cu(In,Ga)Se_2$) thin film PV devices. Accelerated aging was performed under damp-heat (DH) and thermal-cycling protocols (from the IEC 61646 testing protocol for PV modules), ASTM G155 and outdoor testing. Modifiers include a monofunctional amine terminated silane (APDMES, 3-aminopropyldimethlyethoxysilane), and a trifunctional amine terminated silane (APTES, 3-aminopropyltriethoxysilane).

6:00pm **TF-TuA12 Thickness Dependence of Electro-optical Properties of $Pb_{0.95}La_{0.05}Zr_{0.54}Ti_{0.46}O_3$ Thin Films for Photovoltaic Applications**, ***Vaishali Batra***, *S. Kotru,* The University of Alabama

Exploring the viability of alternate materials to increase efficiency of the solar cells, and to decrease the fabrication cost, has gained momentum in the past decade. Ferroelectric materials are one of those materials which have become a subject of intense research for future energy applications.

These materials are well established in memory and MEMS industry and nowadays are being investigated to design photovoltaic (PV) devices. These materials show PV effect without a need of p-n junction as required in semiconductor devices. Additionally they exhibit bulk PV effect due to internal electric field originating from electric polarization. Of all the materials, lanthanum doped lead zirconate titanate ($Pb_{0.95}La_{0.05}Zr_{0.54}Ti_{0.46}O_3$/PLZT) of perovskite type crystalline structure is considered to be promising ferroelectric material for solar cell applications. The practical realization of these devices requires high PV response which is still a challenge. In this work, an innovative method based on orientation control of PLZT thin films is used to improve the PV response.

Promoting (001) orientation and suppressing (110) orientation in the PLZT films is observed to improve the electrical and optical properties of these films. This work focusses on effect of varying thickness of PLZT films on their electrical and optical properties. The reflectance and band gap energies strongly depend on film thicknesses and are found to be in the range of 3.30-3.57 eV. AFM demonstrates the change in morphology and improvement in roughness with respect to orientation. The roughness in the films is observed to increase with the increase in film thickness in the range of 2.92 nm to 4.06 nm. Raman spectroscopy reveals the shift in longitudinal and transverse optical modes with the change in film thickness suggesting the change in ferroelectric phases and crystallinity in the films. The electrical properties were studied using the model for metal-ferroelectric-metal (MFM) heterostructures with Schottky contacts using Pt electrodes. High polarization, free carrier concentration and higher photovoltaic properties are obtained from thicker PLZT films. The photovoltaic efficiency is observed to increase by ~4-10 times by controlling the orientation of the films.

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