Thin Films Division
Room 104B - Session TF-MoA

IoT Session: Thin Films for Photovoltaics
Moderators: Matthew Richard Linford, Brigham Young University, Mark Losego, Georgia Institute of Technology

1:20pm TF-MoA-1 Atomic Layer Deposition for Organic and Perovskite Solar Cells, *Thomas Riedl,* University of Wuppertal, Germany **INVITED**
Organic and perovskite based solar cells (OSCs / PSCs) provide an intriguing avenue for next-generation thin-film photovoltaics. Aside from the photo-active material, the choice of charge extraction layers (CELs) substantially impacts performance and lifetime. For OSCs, the use of ALD-grown tin-oxide (SnO_x) as electron extraction layer (EEL) mitigates two critical issues, i.e. light soaking[1] and photo-shunting[2], which frequently occur in case ZnO based EELs are used. In tandem OSCs, all-oxide recombination interconnects based on high work-function (WF) MoO_x and low-WF ALD grown SnO_x show ideal alignment of the conduction band of MoO_x and SnO_x and loss-free addition of the open circuit voltages of the two sub-cells.[3]

In the second part, I will show ALD-grown SnO_x as impermeable EEL for PSCs to enable impressive stability of the cell against heat and moisture. The SnO_x is positioned between the metal electrode and the perovskite. Its outstanding permeation barrier properties[4] protect the $MAPbI_3$ against the ingress of moisture or migrating metal atoms, while simultaneously the metal electrode is protected against leaking halide compounds. Thereby, PSCs with an efficiency of >20% and outstanding long-term stability can be achieved. They remain stable over 4500 hours at elevated temperatures as well as in ambient air. [5,6] ALD-grown SnO_x is also excellently suited to sandwich and protect ultra-thin metal layers (Ag or Cu) as cost efficient Indium-free semitransparent electrodes (SnO_x/metal/SnO_x) in PSCs. Using photoelectron spectroscopy, we unravel the formation of a PbI_2 interfacial layer between a SnO_x EEL and the perovskite. The resulting interface dipole between SnO_x and the PbI_2 depends on the choice of oxidant for ALD (water, ozone, oxygen plasma). SnO_x grown by using ozone affords hysteresis-free devices with a stable efficiency of 16.3% and a very high open circuit voltage of 1.17 V.[7] Ultimately, SnO_x grown by spatial-ALD at atmospheric pressure is presented. Its suitability to replace its low pressure analogues in PSCs is shown. [1, 2] This work paves the way towards roll-to-roll fabrication of stable, Indium-free PSCs.

[1] S. Trost et al., *Adv. Energy Mater.***2015**, *5*, 1500277.

[2] S. Trost et al., *Adv. Energy Mater.***2016**, *6*, 1600347.

[3] T. Becker et al., *Adv. Energy Mater.***2018**, *8*, 1702533.

[4] A. Behrendt et al., *Adv. Mater.***2015**, *27*, 5961.

[5] K. O. Brinkmann et al., *Nat. Comms.***2017**, *8*, 13938.

[6] J. Zhao et al., *Adv. Energy Mater.***2017**, *7*, 1602599.

[7] T. Hu et al., *Adv. Mater.***2017**, *29*, 1606656.

[8] L. Hoffmann et al., *J. Vac. Sci. & Technol. A***2018**, *36*, 01A112.

[9] L. Hoffmann et al., *ACS Appl. Mater. & Interf.***2018**, *10*, 6006.

2:00pm TF-MoA-3 Insights into ALD Al_2O_3 Growth on Hybrid Organic-Inorganic Perovskite, *Dibyashree Koushik*[1], Eindhoven University of Technology, The Netherlands, Netherlands*; L Hazendonk,* Eindhoven University of Technology, The Netherlands*; V Zardetto,* TNO-Solliance, The Netherlands, Netherlands*; W Kessels,* Eindhoven University of Technology, The Netherlands*; M Creatore,* Eindhoven University of Technology, The Netherlands, Netherlands
The need for environmentally stable perovskite solar cells (PSCs) has promoted the quest for moisture and thermal stress barrier layers that can adequately seal the perovskite absorber. Atomic layer deposited (ALD) metal oxides are widely acknowledged for their continuous and pinhole-free nature, derived from the self-limiting deposition process. We have recently shown that 10 cycles of ALD Al_2O_3 deposited directly on top of $CH_3NH_3PbI_{3-x}Cl_x$ perovskite are effective in delivering a superior PSC performance with 18% efficiency (compared to 15% of the Al_2O_3-free cell) and long-term humidity-stability of more than 60 days.[1,2] Motivated by these results, the present contribution focuses on the chemical modifications which the $CH_3NH_3PbI_{3-x}Cl_x$ perovskite undergoes upon growth of ALD Al_2O_3. Specifically, we couple *in situ* infrared spectroscopy studies

during film growth, with XPS analysis of the ALD Al_2O_3/perovskite interface. The IR-active signature of NH_3^+ stretch mode (asymmetric at 3179 and symmetric at 3132 cm^{-1}) of the perovskite undergoes minimal changes upon exposure to ALD cycles, indicating no diffusion of the ALD precursors (TMA and H_2O) into the bulk of the perovskite. The exclusion of H_2O infiltration is evident also from the absence of two well-defined peaks at 3500 and 3450 cm^{-1}. These conclusions are supported by Doppler broadening-positron annihilation spectroscopy studies, revealing no changes in the open volume of 'bulk' perovskite upon deposition of Al_2O_3. Analysing the differential IR spectra (Absorbance (perovskite + Al2O3)-Absorbance (pristine perovskite)) with increasing ALD cycles, the abstraction of NH_3^+ from the perovskite surface is discerned, with the appearance of negative N-H stretch and bend modes. In parallel, the growth of ALD Al_2O_3 on perovskite is witnessed by the characteristic IR-active Al-O-Al phonon and (OH)-Al=O stretch modes. Based on the XPS analysis, a plausible growth mechanism of ALD Al_2O_3 on top of perovskite is discussed. During the first half- cycle, TMA reacts with perovskite via the interaction of one of its methyl groups with one of the H atoms of $CH_3NH_3^+$ of perovskite. This interaction weakens the hydrogen-bonds between $CH_3NH_3^+$ and I$^-$ of the perovskite, resulting in breakdown of the organic moiety from the inorganic framework. CH_3NH_2 and CH_4 are released as byproducts, leaving behind an adduct comprising of PbI_3-Al(CH_3)$_2$. In the next half-cycle of H_2O dosage, the H_2O molecule can react with the PbI_3-Al(CH_3)$_2$ adduct and generate the −OH surface sites necessary to promote the growth of Al_2O_3.

1. D. Koushik *et al.*, *Energy Environ. Sci*, **2017**, *10*, 91.

2. D. Koushik *et al.*, *Adv. Mater. Inter.*, **2017**, *4,* 1700043*.*

2:20pm TF-MoA-4 Single Junction GaAs Thin Film Solar Cells on Flexible Metal Tapes for Low Cost Photovoltaics, *Devendra Khatiwada*[2], *M Rathi, P Dutta, S Sun, Y Yao, Y Gao, Y Li, S Pouladi, J Ryou, V Selvamanickam,* University of Houston
III-V semiconductor materials like GaAs that have a high absorption coefficient in the relevant energy range for photovoltaic absorbs most of the sunlight within small range beneath the surface. Highest efficiencies have been reported in III-V solar cells based on GaAs wafer. However, its application has been very limited due to high cost of these wafers. We develop a technology to provide high quality epitaxial semiconductor thin films on low-cost flexible metal tapes by roll to roll fabrication to overcome the wafer cost .

Herein, we introduce high quality epitaxial semiconductor thin film on low cost flexible metal (Hastelloy) to provide flexibility and overcome the wafer cost with roll to roll processing. Firstly, polycrystalline to single crystalline like material were grown on the flexible metal tape over which biaxially textured Germanium (Ge) thin film were grown. Finally, epitaxial (Al) GaAS semiconductor thin films were grown on the biaxially textured Ge thin films using Metal Organic Chemical Vapor Deposition (MOCVD). The device were further processed for contact deposition via photolithography process.

The fabricated thin film III-V solar cells showed promising photovoltaic efficiency under A.M 1.5G with front illumination geometry. Photon conversion efficiency greater than 11% was observed under A.M 1.5 (1 sun) with open circuit voltage (V_{OC}) of 642mV, short circuit current density (J_{SC}) of 25mA/cm^2 and fill factor (FF) of 70% . Further improvement in device efficiency is achieved with new device architectures, optimization of the growth and improving fabrication processes.

This work was partially funded by the U.S. Department of Energy Sunshot Initiative.

2:40pm TF-MoA-5 New Insights into the Microstructure and Composition of New Generation CdSeTe/CdTe/MZO Photovoltaic Devices, *T Fiducia, A Abbas,* Loughborough University, UK*; K Li, C Grovenor,* University of Oxford, UK*; A Munshi, K Barth, W Sampath,* Colorado State University*; John Walls,* Loughborough University, UK
Thin film polycrystalline Cadmium Telluride solar cells are the lowest cost solar technology. Recent improvements in the device architecture have increased device conversion efficiency and lowered costs still further. The traditional semi-absorbing cadmium sulphide window layer has been replaced with higher band gap alternatives such as magnesium-doped zinc-oxide (MZO). Also Selenium has been added to the near-junction interface region in the CdTe absorber layer which becomes graded during the cadmium chloride activation process and increases carrier lifetime. In this paper we report on microstructural and composition studies using STEM and EDX on device cross-sections along with the use of Nano-SIMS to

---

[1] **TFD James Harper Award Finalist**

[2] **TFD James Harper Award Finalist**

provide 3-Dimensional chemical maps of the cells at high resolution and sensitivity. These microstructural analyses are correlated with electrical measurements from the devices. The analysis of chlorine and selenium in these cells reveals the different types of diffusion modes involved in 3 dimensions. It provides new insights into the passivation mechanisms at work in grain boundaries. It also provides the first direct evidence for passivation of incoherent twin facets and incorporation of chlorine and selenium in grain interiors. Improved understanding of the ways these new devices work will determine how they may be improved still further.

3:00pm TF-MoA-6 Schottky Barrier Metal-Insulator-Silicon Photovoltaics: Influence of Fixed Charge and Dipoles in Atomic Layer Deposited Alumina, *Nicholas Strandwitz,* Lehigh University

Metal-insulator-semiconductor Schottky barriers are a potentially low-cost photovoltaic configuration. The PV figures of merit are strongly influenced by the interface composition and structure. Our group has used atomic layer deposition (ALD) to create well-defined alumina-based insulators in which the thickness, fixed charge, and composition can be well-controlled. Based on a simple electrostatic model, fixed charge in the insulator can be used to modify barrier heights, and the fixed charge at ALD alumina-silicon interfaces can be tuned over a range of approximately $5E12$ cm^{-2}, making this system an ideal test-bed to understand the role of fixed charge experimentally. We find little to no influence of the fixed charge characteristic of the alumina-silicon interface in our experiments, and that barrier heights appear to be dominated by interface dipoles. We relate our results to previous experimental and theoretical work that relates dipole strength to differences in oxygen areal densities at the silicon oxide-aluminum oxide interface. We also report preliminary PV figures of merit for our well-controlled MIS junctions.

3:40pm TF-MoA-8 Sulfur Vacancies as the Origin of *n*-type Doping in Pyrite FeS$_2$ Single Crystals, *B Voigt, W Moore, J Walter, D Ray, M Manno,* University of Minnesota; *J Jeremiason,* Gustavus Adolphus College; *L Gagliardi, **Eray Aydil**, C Leighton,* University of Minnesota

Pyrite FeS_2 is an ideal photovoltaic material for low-cost and sustainable thin film solar cells because it is composed of earth-abundant, non-toxic, inexpensive elements, has a suitable band gap well-matched to the solar spectrum, and absorbs light so strongly that a 100 nm thick film is adequate to absorb over 90% of all photons with energies above the band gap. While pyrite FeS_2 was pursued vigorously in the 1980's as a potential solar cell material, efficiencies never exceeded 3 %. One of the fundamental problems was a lack of control over doping. Recently, rigorously phase-pure pyrite FeS_2 single crystals and thin films were shown to be exclusively *n*-type, with a universal dependence of electron mobilities in both thin films and crystals on Hall coefficient suggesting that a common dopant is responsible for this *n*-type behavior. This dopant, however, has not been identified. We have amassed the strongest evidence to date that sulfur vacancies are this common dopant. Single crystals with experimentally indistinguishable lattice parameters, mosaic spread, and nominal stoichiometry, grown via chemical vapor transport under different sulfur vapor pressures, show significantly different electron densities and mobilities. Specifically, crystals grown under high sulfur vapor pressure exhibit semiconducting behavior and temperature-dependent electron densities with an activation energy of 225 meV. Decreasing the sulfur vapor pressure during crystal growth decreases this activation energy, increases the electron density and mobility, and triggers metal-like conduction observed in temperature-dependent resistivity measurements. This is consistent with higher concentrations of sulfur vacancies in pyrite crystals grown under decreased sulfur vapor pressure. These trends are independent of transition metal impurity concentrations and, importantly, electron densities are too large to be explained by trace amounts of transition metal impurities. All evidence thus implicates sulfur vacancies as the ubiquitous *n*-type dopant in pyrite FeS_2.

4:00pm TF-MoA-9 Strong Effect of Reaction Temperature on the Nucleation of Atomic Layer Deposition of Al$_2$O$_3$ on Methylamine Lead Perovskite, *Xiaozhou Yu, H Yan, Q Peng,* University of Alabama

Hybrid perovskite solar cells have attracted tremendous attention due to the low cost and high-power conversion efficiency. The biggest barrier to its commercialization is the poor stability in the outdoor environment.Al_2O_3 atomic layer deposition (ALD) has shown great promise in improving the environmental stability of hybrid perovskites, however, the nucleation of ALD Al_2O_3 on perovskite has not yet been understood, especially the reaction between tri-methyl aluminum (TMA), a strong Lewis acid, and fresh hybrid perovskites. In our work, the growing behavior and surface reaction mechanism of Al_2O_3 ALD (Trimethyl Aluminum (TMA) and H_2O chemistry) on $CH_3NH_3PbI_3$ perovskite is studied systematically by *in situ* quartz crystal microbalance(QCM) and *in situ* quadrupole mass spectrometers (QMS).We find that the reaction temperature is the key parameter affecting the nucleation of Al_2O_3 ALD on $CH_3NH_3PbI_3$. At 25°C, TMA can accumulate mass onto the surface of a fresh $CH_3NH_3PbI_3$ substrate through substrate site-limited reactions. The surface passivation provided by TMA adsorption at 25°C improves the ambient stability of $CH_3NH_3PbI_3$. In contrast, at 75°C, TMA etches $CH_3NH_3PbI_3$ by the formation of volatile products, which will degrade $CH_3NH_3PbI_3$ to PbI_2.

4:20pm TF-MoA-10 Synthesis of Gas Barrier Coatings for Hybrid Halide Perovskites by Atomic Layer Deposition, *X Yu, H Yan, **Qing Peng**,* University of Alabama

Atomic layer deposition of oxide film on shows a great promise to dramatically improve the ambient stability of hybrid halide perovskite. The nucleation of an ALD oxide on PCBM ([6,6]-phenyl-C61 butyric acid methyl ester) is critical to reliably apply this strategy. In this paper, we present the first study of the nucleation behavior of ALD oxides, including Al_2O_3 and ZnO on PCBM. We find PCBM film acts a gas diffusion barrier blocking the ALD reactants (diethyl zinc) from etching the underlying $CH_3NH_3PbI_3$. However, ZnO is not able to nucleate on PCBM. We further identify that trimethyl aluminum, a strongly Lewis acid, reacts readily with C=O on PCBM to generate a seeding layer for nucleating ZnO ALD. This new chemical route is highly reliable and can be used to synthesize ALD ZnO coatings over PCBM. The synthesized PCBM/Al_2O_3-ZnO dramatically improves the stability of $CH_3NH_3PbI_3$ against the ambient and even against liquid water. The result signifies the importance of understanding of nulceation of ALD in enabling reliable barrier coatings for hybrid halide perovskite.

Author Index

Bold page numbers indicate presenter