Thin Films Division
Room 20 - Session TF-WeM
Thin Film for Photovoltaics

Moderators: Mariadriana Creatore, Eindhoven University of Technology, The Netherlands, Virginia Wheeler, U.S. Naval Research Laboratory

8:00am **TF-WeM-1 Stable Perovskite Solar Cells by 2D/3D Interface Engineering**, ***Mohammad Khaja Nazeeruddin***, *G Grancini, C Roldán-Carmona, I Zimmermann, Y Lee,* Ecole Polytechnique Fédérale de Lausanne (EPFL), Switzerland **INVITED**

Metal halide perovskite solar cells (PSCs) have received global attention because of their excellent photovoltaic performance and ease of fabrication. However, much of the focus in perovskite solar cell advance has been on improved device efficiency through trial and error recipe modification. Despite the impressive photovoltaic performances, perovskite solar cells are poorly stable under operation, failing by far the requirements for a widespread commercial uptake.[1-3] Various technological approaches have been proposed to overcome the instability problem, which, while delivering appreciable improvements, are still far from a market-proof solution.[4-5] In this talk we demonstrate stable perovskite devices by engineering an ultra-stable 2D/3D $HOOC(CH_2)_2NH_3)_2PbI_4/CH_3NH_3PbI_3$ perovskite junction. The 2D/3D composite delivers an exceptional gradually organized multidimensional structure that yields 13% photovoltaic efficiency in a low cost, hole-conductor free architecture and 20% in standard mesoporous solar cells. To demonstrate the up-scale potential of this technology we fabricate 10x10 cm^2 solar modules by a fully printable, industrial-scale process delivering 11% efficient devices which are stable for >10,000 hours with zero efficiency loss measured under controlled standard conditions. This innovative architecture will likely enable the timely commercialization of perovskite solar cells.

References

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8:40am **TF-WeM-3 Single-step, Atmospheric CVD of Methylammonium Bismuth Iodide Perovskite Thin Films**, *X Chen,* Washington University in St. Louis; *Y Myung,* Sejong University, Republic of Korea; *A Thind, Z Gao, B Yin, B Sadtler, R Mishra,* ***Parag Banerjee,*** Washington University in St. Louis

Synthesis of methylammonium bismuth iodide ($(CH_3NH_3)_3Bi_2I_9$) is achieved through a single step, atmospheric pressure, chemical vapor deposition (CVD) process. The precursors used are powders of bismuth iodide (BiI_3) and methylammonium iodide (CH_3NH_3I). These precursors are sublimated inside a tube furnace reactor with a well-controlled and predetermined temperature profile. The sublimated vapors are transported via Ar carrier gas to the cooler parts of the tube furnace, where simultaneous condensation and reaction between the two precursors leads to the formation of high quality $(CH_3NH_3)_3Bi_2I_9$ films on the wafer surface.

Structural and compositional information is obtained via grazing incidence X-ray diffraction (GI-XRD), SEM, TEM and XPS which confirm the $(CH_3NH_3)_3Bi_2I_9$ phase. Band-edge information is obtained via a combination of cyclic voltammetry and UV-vis spectroscopy. The band gap is revealed to be 1.9 eV. Temperature-dependent Hall measurements detect the recently observed [1] ferrielectric phase transition at ~150K via changes to the slope in the concentration vs. temperature and mobility vs. temperature curves. A room temperature electron concentration of 1.48 x 10^{19} cm^{-3} and mobility of 7.13 cm^2/V.sec is obtained for $(CH_3NH_3)_3Bi_2I_9$ films with good crystallinity.

Reference:

[1] Kamminga, M. E.; Stroppa, A.; Picozzi, S.; Chislov, M.; Zvereva, I. A.; Baas, J.; Meetsma, A.; Blake, G. R.; Palstra, T. T. M., Polar Nature of $(CH_3NH_3)_3Bi_2I_9$ Perovskite-Like Hybrids. *Inorganic Chemistry* 2017, 56, 33-41.

9:00am **TF-WeM-4 Atomic Layer Deposition of TiO_2 Charge Recombination Blocking Layer and SnO_2 Electron Transport Layer for Perovskite Solar Cells**, *Y Kuang,* Eindhoven University of Technology, Netherlands; *V Zardetto,* Solliance Solar Research, Netherlands; *R van Gils,* Eindhoven University of Technology, Netherlands; *F di Giacomo,* Solliance Solar Research, Netherlands; *G Lucarelli,* University of Rome Tor Vergata, Italy; *W Kessels,* Eindhoven University of Technology, Netherlands; *T Brown,* University of Rome Tor Vergata, Italy; ***Mariadriana Creatore,*** Eindhoven University of Technology, Netherlands, The Netherlands

Within the class of emerging photovoltaic technologies, 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 atomic layer deposition (ALD) offers to perovskite solar cells [1] by highlighting the following merits: control on charge carrier transport and recombination processes at complex interfaces [2,3] and compatibility with low-temperature processing [3]. Specifically, two case studies will be presented:

· Plasma-assisted ALD amorphous TiO_2 (cycles consisting of $Ti(Cp^{Me})(NMe_2)_3$ and O_2 plasma exposure steps) has been adopted in $MeNH_3PbI_3$ perovskite solar cells in a mesoscopic configuration [2], with the purpose of suppressing charge recombination processes at the ITO/mesoscopic scaffold/perovskite interface. The superior performance of 10 nm thick ALD TiO_2 layers (i.e. up to 16% cell efficiency under 1000/m^2 illumination and 24% under indoor illumination) with respect to conventionally adopted spray pyrolysis TiO_2, is explained by a lower reverse dark current measured for ALD TiO_2. This result points out the superior blocking character of the ALD TiO_2 layer toward electron-hole recombination, which is also confirmed by the evaluation of the electron lifetime from open circuit voltage decay analysis. Since ALD TiO_2 is carried out at temperatures below 150°C, flexible perovskite solar cells built on PET/iTO substrates are also tested, exhibiting a conversion efficiency of 10.8% under indoor illumination, comparable to the one of flexible dye-sensitized solar cells and exceeding the one of flexible a-Si:H solar cells.

· Ultra-thin (15 nm) plasma-assisted ALD amorphous SnO_2 (cycles consisting of $Sn(NMe_2)_4$ and O_2 plasma exposure steps) is adopted as electron transport layer in a $Cs_x(MA_yFA_{1-y})_{1-x}Pb(I_z,Br_{1-z})_3$ perovskite solar cell in an n-i-p thin film configuration. The solar cell efficiency reaches the value of 15.9±0.5%, while the same solar cell configuration with an electron-beam deposited TiO_2 electron transport layer reaches an efficiency of just 10 ±0.5%. UPS analysis shows that the higher efficiency achieved by SnO_2 (with respect to TiO_2) is due to a better energy level alignment between the SnO_2 and perovskite conduction bands, promoting electron transport. Hole transport, instead, is efficiently blocked because of the misalignment between the SnO_2 and perovskite valence bands.

References

[1] V. Zardetto et al., Sustainable Energy and Fuels 1,30 (2017)

[2] F. Di Giacomo et al., Nano Energy 30, 460 (2016)

[3] V. Zardetto et al., Solar Energy, accepted (2017)

9:20am **TF-WeM-5 The Reaction Between Pyridine and $CH_3NH_3PbI_3$ Surface-Confined Reaction or Bulk Transformation?**, ***XiaoZhou Yu,*** University of Alabama; *H Yan, Q Peng,* University of alabama

Abstract

The Methyl amine lead iodide perovskite ($CH_3NH_3PbI_3$) shows great potential in solar cells, light-emitting diodes, lasers, and chemical sensors. Base on the surface chemical properties of $CH_3NH_3PbI_3$, many chemicals with Lewis base group, for instance: pyridine, tetra-ethyl ammonium, were used to enhance the photovoltaic, optoelectronics performance and the stability in ambient environment. However, people found contradict results that Pyridine molecules not only passivate the surface Pb^{2+} sites of $CH_3NH_3PbI_3$, but also to bleach and recrystallize $CH_3NH_3PbI_3$. Surface passivation demands the confinement of the reaction at the surface region but recrystallizing and bleaching require the transformation of bulk $CH_3NH_3PbI_3$. The underlying mechanism for these seemly contradicting results are not well-understood. Our results show, at 25 ºC, partial pressure of pyridine vapor is a determining factor for its reaction behaviors with $CH_3NH_3PbI_3$: one can modify just the surface of $CH_3NH_3PbI_3$ by using pyridine vapor of the pressure less than 1.15 torr, but can transform the whole bulk $CH_3NH_3PbI_3$ film with a pyridine vapor of 1.3 torr or higher. The results indicate, for the first time, that a small change of free energy of pyridine vapor (~ 0.3 kJ/mol) can cause the transition from surface-confined reaction to bulk transformation. It is interesting that in all pressure ranges, pyridinium ions is the main product from the reaction between pyridine and $CH_3NH_3PbI_3$. The bulk transformation is probably due to the formation of a liquid-like film, which increases the mobility of species to catalyze the reaction between pyridine and $CH_3NH_3PbI_3$. These findings provide a guidance for designing experiments in applying pyridine and probably other amines to functionalize and transform $CH_3NH_3PbI_3$ and other hybrid halide perovskites.

9:40am **TF-WeM-6 GaN-stabilized Ta_3N_5 Thin Film as a Photoanode for Solar Water Splitting**, ***Taro Yamada***, *Y Sasaki,* The University of Tokyo, Japan*; S Suzuki,* Shinshu University, Japan*; M Zhong,* The University of Tokyo, Japan*; K Teshima,* Shinshu University, Japan*; K Domen,* The University of Tokyo, Japan

Tritantalum pentanitride (Ta_3N_5), a visible-light absorbing material (<600 nm), was formed into a thin layer and tested as a photoelectrode in electrolytic solution under simulated solar light. By the aid of cobalt phosphate catalyst (CoPi), the electrode surface evolved O_2 at a substantial efficiency for photon energy conversion. By inserting a GaN layer between the catalyst and Ta_3N_5, the electrode exhibited an improved stability and durability for O_2 evolution in aqueous electrolytic solution.

The Ta_3N_5 film was prepared by high-temperature (1000-1300 K) nitridation of sputtered Ta film on Ta metallic substrate in NH_3 flow at the atmospheric pressure. Ta sputtering was performed in a RF magnetron setup with a Ta metal target at 4 Pa of purified Ar introduction pressure. The gas impurities were minimized and a trace amount of O_2 was introduced for sputtering. The formed Ta film is amorphous with a thickness approximately 500nm. After nitridation, the formed Ta_3N_5 is a transparent, orange-colored film with a visible light absorption cutoff at xxx nm. The CoPi catalyst was deposited by simulated solar irradiation in $Co(NO_3)_3$ solution in neutral phosphate buffer.

The O_2 evolution performance was examined in pH 13 K_3PO_4 buffer under potentiostatic control with a Pt counter electrode and a Ag/AgCl reference electrode. At 1.23 V vs RHE of the anodic potential, The photocurrent by a solar simulator at AM1.5G (1 kWm^{-2}) reached 7 $mAcm^{-2}$ or higher, however rapidly decay in 1 hour. This was due to Ta_3N_5 oxidation, and we introduced a GaN overlayer (thickness ~ 50 nm) by NH_3-nitridation of evaporated Ga_2O_3 layer (electron-beam heating, largely metallized). The same photoelectrochemical test exhibited a photocurrent higher than 8 $mAcm^{-2}$, lasting for more than 10 hours, with slow deactivation afterwards. Microscopic observation of the GaN layer showed fine grains (<50 nm in diameter) of GaN, blocking Ta_3N_5 oxidation. The faradaic O_2 evolution was confirmed by anther setup.

The semiconductive properties of Ta_3N_5 and the GaN/Ta_3N_5 junction are currently investigated. Both Ta_3N_5 and GaN in the present case are polycrystalline and contain influential amounts of impurities, reflecting in the resistivity and other transportation properties.

The photoelectrochemical performance of the present GaN/Ta_3N_5 electrode matches nearly 5 % of solar-to-H_2 energetic conversion as a free-run water photo-splitting device by assembling a with H_2 evolving photocathode. By improving the quality of the layers of Ta_3N_5 and the GaN in terms of crystallinity and purity, we can gain a good control for the performance of the photoelectrodes towards efficient solar energy recovery.

11:20am **TF-WeM-11 A Viable Magnetron Sputtering Process for Thin Film CdTe Solar Cells**, ***John Walls***, *F Bittau, R Greenhalgh, A Abbas, S Yilmaz,* Loughborough University, UK

The exceptional uniformity of deposition provides magnetron sputtering with potentially important advantages for the production of thin film CdTe solar cells. For example, the thickness of the absorber layer could be reduced to ~1um saving on material cost. The uniformity is also essential for glazing applications such as power producing semi-transparent windows. Efforts to develop a viable process for the deposition of thin film CdTe solar cells by magnetron sputtering have been hampered for many years by the formation of surface blistering following the cadmium chloride activation process. Delamination of the films at the cadmium sulphide junction is often observed and catastrophic void formation within the CdTe layer and at the junction has also been reported. As a result, the conversion efficiency of sputtered devices has not matched that obtained using lower energy deposition techniques such as Close Space Sublimation or Vapour Transport Deposition. We have discovered that blistering is caused by argon trapped in the CdTe layer during the sputtering process. High Resolution Transmission Electron Microscopy reveals that argon gas bubbles are formed by diffusion during the high temperature device activation process. The bubbles then coalesce to cause surface blistering. Here we report on the development of a viable sputtering process by replacing argon with xenon as the magnetron working gas. Using xenon avoids gas bubble and blister formation. The microstructural integrity of the devices is retained resulting in increased performance of sputtered thin film CdTe photovoltaic devices.

11:40am **TF-WeM-12 Hybrid Single Layer Organic Solar Cell Based on Polyvinyl Alcohol and Zinc Oxide Nanoparticles**, ***Monas Shahzad,*** Forman Christian College (A Chartered University), Pakistan

Organic solar cell technology is very low cost, reliable and efficient technology. In this work, we have studied the performance of single layer hybrid organic solar cell, which is based on polyvinyl alcohol (PVA) doped with Camellia sinensis (Black Tea) solution and Zinc Oxide (ZnO) as plasmonics nanoparticles to scatter more light into active layer of solar cell. The broad absorption spectra of the composite material (PVA and tea solution) with various concentrations ranged from UV to visible region. Its energy gap was measured which allowed trapping a large portion of the incident solar light. The band gap is reduced upon the addition of Camellia sinensis (Black Tea) because the addition of Camellia sinensis (Black Tea) caused PVA to get more ordered structure. Characterization of ZnO nanoparticles using XRD and SEM confirmed the hexagonal wurtzite structure and spherical surface morphology of nanoparticles. Six solar cells were fabricated based on various concentrations of PVA doped with Camellia sinensis (Black Tea) solution using silver paste/graphite as counter electrodes, with and without ZnO nanoparticles thin film. The current-voltage (IV) characteristics curves of the fabricated organic solar cells were measured. The IV curves were studied of all soar cells that gave the following efficiencies 0.0216%, 0.0364%, 0.34%, 0.42%, 0.564 and 0.729%. The maximum energy conversion efficiency was calculated to be 0.7%, for an organic solar cell having high concentration of camellia sinensis, with ZnO nanoparticles thin film and silver paste as a counter electrode.

Key Words: Hybrid organic cell, polyvinyl alcohol, Camellia Sinensis, ZnO nanoparticles.

12:00pm **TF-WeM-13 Phase Stability and Cation Site Distribution during Thermal Annealing of CZTS Nanoparticle-Coatings**, ***Stephen Exarhos***, *E Palmes, R Xu, L Mangolini,* University of California, Riverside

Cu_2ZnSnS_4 (CZTS), a potential low-cost, earth-abundant absorber material, has been under intense investigation for prospective use in thin film photovoltaic (PV) devices. Its high optical absorption coefficient and variable band gap also have potential applications in other areas including photocatalysis, thermoelectrics, and energy storage. Theoretically predicted physical properties, however, have not been realized to date owing to the lack of control over chemical and microstructural heterogeneity and grain size and grain boundary chemistry. Using a modified aerosol spray pyrolysis technique, we have grown phase-pure 25 nm CZTS nanoparticles having no organic ligand contaminant. This is desirable in that grain boundary chemistry is known to degrade both optical and electrical response. Many applications demand that these nanoparticles be consolidated into relatively thick, large grain size films by means of a high temperature annealing treatment that drives impurities to interfaces thereby degrading properties. For PV applications, large grains are required to significantly reduce exciton recombination at grain boundaries. While the particles produced here do not sinter uniformly into polycrystalline thin films, we have shown that introducing a thin amorphous oxide to the surface of the particles does indeed promote uniform grain growth to create thin films with the optimal morphology for absorber layers in PV devices. The improvement is attributed to an increased retention of volatile SnS, a byproduct of CZTS decomposition, which occurs at high temperature. We have also controlled grain growth by incorporating Na_2S into the film prior to annealing by means of a facile dipping technique – sodium is known to enhance grain growth in this material, though its incorporation is generally uncontrolled. Additionally, we present data from *in situ* Raman spectroscopy measurements designed to simulate the standard CZTS thin film annealing process. Using this approach, we have characterized the time/temperature effects on the vibrational spectrum of annealed CZTS films at high temperature in static variable atmospheres of sulfur vapor with and without a thin surface oxide interfacial coating. This technique is also used to monitor the cation site exchange process (copper and zinc) in the lattice that appears to be dependent on the rate of cooling following high temperature annealing.

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