

SYMPOSIUM ET04

Perovskite Solar Cells—Challenges and Opportunities
November 26 - November 30, 2018

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* Invited Paper

SESSION ET04.01: Interfaces I
Session Chairs: Wallace Choy and Kai Zhu
Monday Morning, November 26, 2018
Hynes, Level 3, Room Ballroom C

8:00 AM *ET04.01.01

Healing Defects of Perovskite and Improving Efficiency of Solar Cells by Over 900% Through a New Post-Device Ligand-Induced Modification Wallace C. Choy and Hong Zhang; University of Hong Kong, Hong Kong, China.

While perovskite solar cells (PVSCs) have drawn intense attention due to their high solar-to-power conversion efficiency (PCE), their practical application is hampered by the poor long-term stability against moisture. Although strategies have been reported to solve this issue, they are introduced during core-device fabrication processes which will increase the risk of introducing unexpected impurities during the fabrication.

In this work, we propose a new scheme of ligand-induced post-device (LPD) modification of perovskite on completely fabricated devices at room temperature to simultaneously improve the performance and stability of PVSCs [1]. The ligand vapors will induce chemical modification in the selected lateral regions particularly that of perovskite layer which prevent the diffusion of water molecules into the protected active perovskite region for enhancing PVSC stability. This post-device treatment could also passivate the surface defects of perovskites in active region for improving the PVSC performance. Interestingly, this LPD modification strategy shows a special 'stitching effect', namely repairing the as-fabricated 'poor devices' by healing the defects of perovskite in the operation region and significantly improve PCE by over 900%. The work greatly improves the production yield of PVSCs and their module performance as well as the reduction of lead-waste. It should be noted that the off-the-shelf treatment, completely separated from the fabrication process of common perovskite devices, provides a general strategy to improve the stability of different completed perovskite devices (e.g. solar cells, light-emitting diodes, and photodetectors) without introducing any undesirable impurities during device fabrication.

[1] H. Zhang, X. Ren, X. Chen, J. Mao, J. Cheng, Y. Zhao, Y. Liu, J. Milic, W.J. Yin, M. Grätzel, W.C.H. Choy*, "Improving the stability and performance of perovskite solar cells via off-the-shelf post-device ligand treatment", *Energy & Environmental Science*, 2018, DOI: 10.1039/C8EE00580J.

8:30 AM ET04.01.02

Understanding the Role of Surfaces on Halide Segregation in Mixed-Anion Perovskites Rebecca A. Belisle, Kevin A. Bush, Luca Bertoluzzi, Aryeh Gold-Parker, Michael F. Toney and Michael D. McGehee; Stanford Univ, Stanford, California, United States.

Photo-induced halide-segregation currently limits the perovskite chemistries available for use as high bandgap semiconductors for tandem solar cells. This is particularly problematic for perovskite-perovskite tandems, where semiconductors with bandgaps in excess of 1.8 eV are needed for optimal pairing with the low-bandgap tin-rich perovskites. And while the problem of halide-segregation is well documented in the literature, strategies to circumvent this problem are largely lacking. In this study we present a new method for hindering this process – surface modifications. By varying the surface chemistry of mixed-anion perovskites and monitoring the evolution of their photoluminescence and X-ray diffraction patterns under illumination, we link changes in the perovskite surface to changes in the rate of halide segregation. We observe that we can both reduce non-radiative recombination and dramatically slow the onset of halide segregation by applying specific post-deposition surface treatments to CH₃NH₃PbI₂Br films. Additionally we demonstrate that the surface sensitivity of halide segregation extends to perovskite/selective contact interfaces as well, and that halide segregation is suppressed at specific perovskite/selective contact heterojunctions. Finally, by using these observations and an in depth knowledge of the perovskite surface chemistry, we present a model by which tuning surface chemistry can prevent halide segregation in the bulk of the perovskite. In short, we propose carrier trapping at perovskite surfaces as the driver for halide migration and subsequent halide segregation, and that by reducing the trapping at surface states with targeted surface treatments this process can be abated if not completely stopped. Overall, this work presents both a deeper understanding of the halide-segregation process in perovskites as well as a pathway towards stable high bandgap perovskites for high efficiency perovskite tandems.

8:45 AM ET04.01.03

Effectively Transparent Top Contacts for Perovskite Solar Cells Michael Kelzenberg¹, Sisir Yalamanchili¹, Thomas Russell¹, Sophia Coplin¹, Qin Yang¹, Nina Vaidya¹, Pilar Espinet Gonzalez¹, Shujuan Huang², Jincheol Kim², Jianghui Zheng², Anita Ho-Baillie², Rebecca Saive³ and Harry A. Atwater¹; ¹California Institute of Technology, Pasadena, California, United States; ²University of New South Wales, Sydney, New South Wales, Australia; ³University of Twente, Twente, Netherlands.

Perovskite solar cells are of great interest due to their potential for low cost and high performance. One of the challenges to attaining high photovoltaic conversion efficiency, particularly for large-area cells, is the tradeoff between the optical and electrical performance of the top contact. Because perovskite absorbers and selective electrode materials provide very little lateral conductivity for current collection, a transparent conductive oxide (TCO) such as indium tin oxide (ITO) must be used for the front contact. However, TCOs offer a tradeoff between transparency and conductivity, resulting in cells that slightly compromise both their short-circuit current density due to optical losses, and their fill factor due to resistive losses. A solution is to increase the density of the grid fingers such that thinner TCOs can be used; however, this increases the shading losses.

Recently, a method to produce effectively transparent front contact grids has been described (Adv. Optical Mater. 4 (10), 1470-1474 (2016); Photovoltaic Specialists Conference (PVSC) IEEE 43rd, 3612-3615, (2016); Sustainable Energy and Fuels, 1 (3), 593-598, (2017)). This approach yields a relatively dense array of high-aspect-ratio, triangular-shaped front contact fingers, in which light striking the metal is reflected towards the cell. We previously described the application of this technique to produce effectively transparent superstrates for perovskite solar cells, which based on optical absorption measurements, is expected to increase the short-circuit current density of perovskite solar cells by ~1 mA/cm² (R. Saive, et al., PVSC 2018).

In the present work, we describe our efforts to integrate the effectively transparent superstrates with functional perovskite solar cells to realize the benefits of effectively transparent contacts (ETCs). We have investigated various combinations of perovskite absorbers and selective contact materials, and will report the results of our fabrication efforts. We are also investigating other approaches to integrate ETC technology with perovskite solar cells, including directly printing or transferring ETCs onto substrate-based perovskite cells topped with optimally thinned ITO layers.

9:00 AM ET04.01.04

Highly Efficient Thermally-Stable Perovskite Solar Cells via Cs:NiOx/CuSCN Double Inorganic Hole Extraction Layer Interface Engineering Sawanta S. Mali and Chang Kook Hong; Chonnam National Univ, Gwangju, Korea (the Republic of).

Obtaining long-term thermally stable via low-cost inorganic-hole extraction layer (i-HEL) is the best choice towards the commercialization of thermo-stable, low-cost perovskite solar cells (PSCs). In the present investigation we have developed a simple method for p-type cesium doped NiOx (Cs:NiOx) an active interfacial layer between perovskite and CuSCN i-HEL towards thermally stable low-cost PSCs. Cs:NiOx nanoparticles were synthesized by simple solution method followed by spin-coating between perovskite and CuSCN interface for mesoscopic regular (n-i-p) type PSCs. The developed method is not only protecting perovskite layer from polar diethyl sulfide solvent but also extract holes efficiently. The best efficiency based on Cs:NiOx/CuSCN double i-HEL devices exhibited 18.42% with >95% thermal stability over 1000 hours at 60 degree Celsius. Interestingly, NiOx/CuSCN and Cs:NiOx/CuSCN double i-HEL based devices are much stable either conventional spiro-MeOTAD or single i-HEL based PSCs due to perfect isolation of the perovskite layer from polar solvent.

9:15 AM ET04.01.05

Progress on Device Stability Enhancement of Perovskite Solar Cells via High Mobility P-Type Buffer Layer or Phthalocyanine Derivative with Long Carrier Lifetime Xiaolu Zheng¹, Yulong Wang², Hongwei Lei¹, Guang Yang¹, Zongxiang Xu² and Guojia Fang¹; ¹School of Physics and Technology, Wuhan University, Wuhan, China; ²Department of Chemistry, South University of Science and Technology of China, Shenzhen, China.

Organo-lead halide perovskite solar cells (PSCs) have attracted tremendous attention owing to their superior photovoltaic properties. However, despite the excellent power conversion efficiencies (PCEs) that have recently been achieved, the device stabilities are still a challenge for the commercialization of PSCs. Spiro-OMeTAD is a widely used hole transport layer (HTL) in conventional n-i-p PSCs, which has been reported to suffer degradation from the permeate of moisture due to the hygroscopic additive and the presence of pinholes. To fix the relatively low device stability of PSCs based on spiro-OMeTAD, numerous strategies have been developed and applied in PSCs.

One approach to diminishing these adverse effects introduced by the moisture permeate and ion migration is to insert a buffer layer. To avoid decreasing the device performance while improving the stability, this p-type semiconductor needs possess high conductivity and superior hole mobility besides hydrophobicity. Lead sulphide (PbS) is a traditional direct bandgap semiconductor with high hole mobility. We found that when inserting a thin layer of PbS between the metal electrode and spiro-OMeTAD, the PSCs with PbS buffer layer exhibited a better photovoltaic performance and significantly enhanced stability with respect to the reference cells. The superior hole mobility of spiro-OMeTAD/PbS bilayer was considered to be the dominated origin of the device performance improvement. And the hydrophobic nature and dense morphology of PbS enable it to provide an efficient permeation barrier against moisture and metal migration. The champion cell with PbS buffer layer displayed a PCE of 19.58% and maintained almost 100% of its initial PCE after 1000 h stored in ambient air. While in this structure the spiro-OMeTAD is still requisite.

Metallophthalocyanine (MPc) compounds that consist of an 18- π electron conjugated macrocycle skeletal structure are potential candidates for stable HTLs in PSCs. We reported a novel heavy atom Pc derivative, octamethyl-substituted palladium(II) phthalocyanine (PdMe₂Pc), which shows promise as an HTL in PSCs. The introduction of the heavy Pd atom endows the material with a long carrier lifetime and without dramatically reducing its mobility. This PdMe₂Pc exhibited a long carrier diffusion length (L_D) which is benefit to reducing the charge recombination. As a result, the devices based on PdMe₂Pc displayed a relatively high PCE of 16.28% and good long-term stability.

9:30 AM ET04.01.06

Environment-Induced Luminescence Hysteresis in Cs-FA Perovskites John M. Howard^{1,2}, Elizabeth Tennyson^{1,2}, Sabyasachi Barik^{2,7}, Rodrigo Szostak³, Edo Waks^{2,4}, Michael F. Toney⁵, Ana F. Nogueira^{5,3}, Bernardo Neves^{2,6} and Marina S. Leite^{1,2}; ¹Department of Materials Science and Engineering, University of Maryland, College Park, Maryland, United States; ²Institute for Research in Electronics and Applied Physics, University of Maryland, College Park, Maryland, United States; ³Institute of Chemistry, University of Campinas, Campinas, Brazil; ⁴Department of Electrical and Computer Engineering, University of Maryland, College Park, Maryland, United States; ⁵Stanford Synchrotron Radiation Lightsource, SLAC National Accelerator Laboratory, Menlo Park, California, United States; ⁶Department of Physics, Federal University of Minas Gerais, Belo Horizonte, Brazil; ⁷Department of Physics, University of Maryland, College Park, Maryland, United States.

Metal halide perovskites show great potential for a wide variety of optoelectronic devices, ranging from light-emitting diodes to photovoltaics. While the prototypical MAPbI₃ has relatively poor stability under ambient conditions, the addition of small amounts of Cs (10-20%) to FAPbI₃ has been shown to increase thermal, optical, and structural stability across the entire range of possible I/Br ratios. However, the influence of moisture, oxygen, and temperature on the optoelectronic properties of these Cs-FA perovskites remains unknown. To explore the individual and combined contributions of each of these parameters onto perovskites' optical behavior, we use micro-photoluminescence (micro-PL) with *in situ* environmental control on four relevant Cs_xFA_{1-x}Pb(I_yBr_{1-y}) compositions [1, 2]. We subject each sample to temporally identical humidity loops (< 5%, 15%, 35%, 55%, and < 5% rH) and identify

that humidity levels up to 35% rH increase the PL emission of all compositions considered by removing surface trap states. By contrast, we find that 55% rH reduces the overall PL emission for 38%-Br films, but sustains the PL enhancement from the prior 35% rH soak for the 17%-Br perovskites. The same 38%-Br films also show an appreciable and partially reversible red shift in their PL peak, correlated with the relative humidity level. Finally, upon completion of the humidity loop, all compositions except Cs-17%/Br-38% exhibit luminescence hysteresis; the extent of hysteresis is predominantly influenced by the Cs-Br ratio. We thus attribute the PL hysteresis to surface-limited degradation occurring throughout the 55% rH condition, where sufficient intercalation of the water into the perovskite lattice leads to the formation of FAI, FAPbBr₂, PbI₂, and PbBr₂. This degradation process leads to the formation of new sites for nonradiative recombination. Our environmental micro-PL method can be expanded to a range of emerging perovskite compositions and extended to include additional degradation factors. Finally, we will discuss how the control of each environmental parameter on perovskites degradation and recovery can be tackled by a machine-learning paradigm [3].

[1] J. M. Howard, et al., *Journal of Physical Chemistry Letters*, DOI: 10.1021/acs.jpcclett.8b01127 (2018)

[2] E. M. Tennyson, J. M. Howard, et al., *ACS Energy Letters* **2**, 1825 (2017) - Invited Perspective.

[3] J. M. Howard, et al., *Joule*, in preparation (2018) - Invited Perspective.

9:45 AM BREAK

10:15 AM ET04.01.07

Charge Injection from Excited CsPbBr₃ Nanocrystals into TiO₂ in Perovskite and Its Role in the Degradation of Perovskite Layer in Visible Light Prashant Kamat, Rebecca A. Scheidt and Elisabeth Kerns; University of Notre Dame, Notre Dame, Indiana, United States.

The role of TiO₂ as an electron transport layer (ETL) that captures electrons from excited CsPbBr₃ seems to play an important role in delivering superior device performance. However, its role in perovskite solar cell is yet to be understood fully. By anchoring CsPbBr₃ nanocrystals onto mesoscopic TiO₂ film, we have probed the charge injection from excited perovskite into mesoscopic TiO₂ and other semiconductor oxides. The electron transfer rate constant in all these cases was found to be >10¹¹s⁻¹. When subjected to steady state irradiation with visible light in air, the injected electrons are scavenged away from the TiO₂, thus inducing oxidation of CsPbBr₃ nanocrystals. No such degradation is seen when CsPbBr₃ nanocrystals are coated on an inert support such as ZrO₂. We have also probed the charge recombination process in CsPbBr₃ deposited on FTO/TiO₂ films at different applied electrochemical bias and investigate the influence of electron charging effect in TiO₂ layer. Steady state and luminescence measurements that elucidate the role of TiO₂ in the solar cell operation will be discussed.

10:30 AM ET04.01.08

Exploring Bulk and Interfacial Degradation Effects in Perovskite and Perovskite-Inspired Absorbers for Solar Cells Azat Akbulatov², Lyubov Frolova^{1,2}, Olga Yamilova^{2,1}, Sergey Luchkin¹, Moneim Elshobaki¹, Sergey Tsarev¹, Alexandra Sveshnikova¹, Keith Stevenson¹ and Pavel Troshin^{1,2}; ¹Skoltech, Moscow, Russian Federation; ²ICPC RAS, Moscow, Russian Federation.

The emerging perovskite solar cells have demonstrated impressive power conversion efficiencies exceeding 22%, while their practical application is restricted mainly by poor operation stability. We have reported recently that hybrid MAPbX₃ (X=I, Br, I+Br, I+Cl) perovskites undergo facile thermal and photochemical degradation even under anoxic conditions without exposure to oxygen and moisture, while their all-inorganic counterparts CsPbX₃ proved to be significantly more stable [1].

Here we will discuss our the most recent results coming from a systematic study of the intrinsic stability of a broad range of materials represented by various lead-based perovskites as well as lead-free complex halides of tin, germanium, bismuth and antimony. The revealed pathways of thermal, photochemical and electrochemical degradation processes will be presented and a conclusion on the potential of different groups of materials for practical application in PV technology will be drawn.

We will also analyze the interface degradation effects occurring between the electrodes, charge transport layer materials and the photoactive layer induced by electric field, elevated temperatures, solar light or a combination of these stress factors [2-3]. Finally, it will be shown that reaching any commercially interesting operation lifetimes for perovskite solar cells requires a considerable shift from the currently used device design paradigms as well as a comprehensive multiparametric optimization of all used materials and functional components.

1. A. F. Akbulatov, K. J. Stevenson, P. A. Troshin et al., *J. Phys. Chem. Lett.* **2017**, *8*, 1211

2. S.Yu. Luchkin, P. A. Troshin, K. J. Stevenson et al., *ACS App. Mater. Interfaces* **2017**, *9*, 33478

3. A. F. Akbulatov, K. J. Stevenson, P. A. Troshin et al., *Adv. Energ. Mater.* **2017**, *7*, 1700476

10:45 AM ET04.01.09

Transport Layers Limit the Efficiency of Perovskite Solar Cells—An Experimental and Theoretical Study Vincent Le Corre¹, Lorena Perdígón Toro², Markus Feuerstein², Martin Stolterfoht², Dieter Neher² and Lambert Jan Anton Koster¹; ¹Zernike Institute for Advanced Materials, University of Groningen, Groningen, Netherlands; ²Institute of Physics and Astronomy, Universität Potsdam, Potsdam, Germany.

Perovskite solar cells (PSCs) are the current rockstar of photovoltaic research attracting more and more attention. With efficiency now reaching up to 23% PSCs are on the way of catching up with classical inorganic solar cells. However, PSCs have not reached their full potential yet. In fact, their efficiency is limited, on the one hand, by non-radiative recombination, mainly via trap states located either at the grain boundaries or at the interface between the perovskite and the transport layers. On the other hand, it is limited by losses due to the poor transport properties of the commonly used transport layers. Indeed, state-of-the-art transport layers (e.g. TiO₂, PCBM and Spiro-OMeTAD...) suffer from rather low mobilities, typically within 10⁻⁴ – 10⁻² cm² V⁻¹ s⁻¹, when compared to the high mobilities, 1 – 10 cm² V⁻¹ s⁻¹, measured for perovskite using field-effect transistors or space-charge-limited-current measurement.

In this work, the effect of the mobility, thickness and doping density of the transport layers was investigated by means of a combined experimental and modeling analysis. For the experiment, two sets of devices made of a triple-cation perovskite were studied, including *n-i-p* and *p-i-n* structures demonstrating efficiencies of up to 20%. For the two structures, the thickness and doping density of one of the transport layers were varied in order to understand their effect on the performance and especially on the FF. In addition, we performed a transient extraction experiment to look at the influence of the transport layers properties on the rate of extraction. The experimental results were then reproduced using drift-diffusion simulations to explain how and by how much every single parameter influences the extraction and the performance. A new and simple formula was also introduced to easily calculate the amount of doping necessary to counterbalance the low mobility of the transport layer.

In conclusion, this work presents a comprehensive analysis of the effects of the different properties of a transport layer on the efficiency of PSCs. We also present general guidelines on how to optimize a transport layer to avoid losses.

11:00 AM ET04.01.10

Strategically Construct Bilayer SnO₂ as Electron Transport Layer in Perovskite Solar Cells Liangyou Lin^{1,2}, Jacob Tse-Wei Wang¹, Timothy Jones¹ and Gregory J. Wilson¹; ¹CSIRO Energy, Newcastle, New South Wales, Australia; ²Huazhong University of Science and Technology, Wuhan, China.

The highly diverse and adaptable architectures of the PSCs is also one of the key steps that leading PSCs to the forefront of the emerging PV technologies. Among various device configurations, the “n-i-p” planar structure without secondary mesoporous layers has attracted lots of attention due to its simple device fabrication process; where n-type metal oxides have been widely applied as the first layer on top of the FTO or ITO. TiO₂ is the most commonly used electron transport material in the PSCs due to its mature development in the field of DSSCs, however, several studies have pointed out that TiO₂ may not be the best candidate to carry PSCs toward commercialization due to its unfavorable properties, including UV instability, high-temperature sintering process, large energy level offset, etc. On the contrary, SnO₂ emerged as an ideal n-type layer for PSCs recently, with advantages of higher electron mobility, low-temperature process, and UV-stabled properties. However, SnO₂ behaves quite differently while prepared by different methods. In this work we devised a facile strategy to combine the strength of two different SnO₂. Interestingly, we found the bilayer displays better energy level alignment with perovskite, faster charge extraction, and lower trap-density. As a result, the photovoltaic devices based on this electron transport layers demonstrate a superior power conversion efficiency up to 20.5% with V_{oc} close to 1.2 V and negligible J-V hysteresis in the device.

11:15 AM ET04.01.11

Argon Plasma Treatment to Tune Perovskite Surface Composition for High Efficiency Solar Cells and Fast Photodetectors Xun Xiao¹, Chunxiong Bao², Yanjun Fang², Jun Dai³, Benjamin R. Ecker⁴, Yuze Lin², Shi Tang², Ye Liu², Yehao Deng^{2,1}, Xiaopeng Zheng², Yongli Gao⁴, Xiao Cheng Zeng³ and Jinsong Huang^{1,2}; ¹University of North Carolina at Chapel Hill, Chapel Hill, North Carolina, United States; ²Mechanical and Materials Engineering, University of Nebraska–Lincoln, Lincoln, Nebraska, United States; ³Department of Chemistry, University of Nebraska–Lincoln, Lincoln, Nebraska, United States; ⁴Department of Physics and Astronomy, University of Rochester, Rochester, New York, United States.

The surface composition of perovskite films is very sensitive to film process and can deviate from optimal, which generates unfavorable defects and results in efficiency loss in solar cells and slow response speed in photodetectors. An argon plasma treatment is introduced to modify the surface composition by tuning the ratio of organic and inorganic component ratio as well as defects type before deposition of passivating layer and form an ultra-thin n type self-doping layer. It efficiently enhanced the charge collection across the perovskite-electrode interface by suppressing charge recombination. Therefore, perovskite solar cells with argon plasma treatment yield enhanced efficiency to 20.4% and perovskite photodetectors can reach their fastest respond speed which is solely limited by the carrier mobility.

11:30 AM ET04.01.12

From Thin-Film to Single Crystals—Probing the Intrinsic Anisotropy and Instability in Cubic Lead Perovskites Shijing Sun², Federico Brivio¹, Fengxia Wei⁴, Yue Wu⁵, Zeyu Deng¹, Gregor Kieslich³, Paul D. Bristowe¹, Tonio Buonassisi² and Anthony K. Cheetham¹; ¹University of Cambridge, Cambridge, United Kingdom; ²Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; ³Technische Universität München, Munich, Germany; ⁴A*Star, Singapore, Singapore, Singapore; ⁵National University of Singapore, Singapore, Singapore.

The commercialization of perovskite solar cells (PSCs) have been hindered by their chemical, structural and thermal instability. There is an increasing interest in compositional tuning of perovskites to improve their intrinsic stability. In this study, extrinsic and intrinsic strain in cubic perovskites, methylammonium (MA) and formamidinium (FA) lead bromide were examined in thin-film, powder and single crystal forms to investigate the role of A-site cations on the structural-property relationships. Based on laboratory and synchrotron X-ray diffraction and density functional theory (DFT), our quantitative analysis reveal the presence of anisotropic strain in the cubic perovskites, where the lattice strain is the highest on {111} and lowest on {100}. Comparative studies on FAPbBr₃ and MAPbBr₃ showed that the cation dynamics and hydrogen bonding of FA contributes to the higher strain as well as more compliant bulk properties. Our results shed light on the rational perovskite compositional design to minimize strain induced decomposition.

11:45 AM ET04.01.13

Thermally Driven Evolution of Ferroelectric Domains in Perovskite Solar Cells Holger Röhm, Tobias Leonhard, Alexander Schulz, Michael J. Hoffmann and Alexander Colmann; Karlsruhe Institute of Technology, Karlsruhe, Germany.

Every perovskite solar cell undergoes changes in temperature during operation and most fabrication routes include one or more thermal annealing steps. For methylammonium lead iodide (MAPI), the archetype of metal halide perovskite solar cells, both the formation and growth of the crystals are strongly interlinked with the phase transition temperature at 328 K. At this temperature, the crystal changes from a polar tetragonal to a non-polar centrosymmetric cubic structure. To date, the majority of research related to the thermal treatment of perovskite solar cells focuses on the growth of crystals from precursor chemicals during layer formation or the thermal decomposition at elevated temperatures. So far, the influence of temperature on the formation of the microstructure within perovskite grains such as formation and evolution of polar domains remains unclear. Here, we study the effects of annealing temperature and duration on the formation and transformation of ferroelectric domains and show the influence of domain patterns on the optoelectronic microstructure and macroscopic device performance of solar cells. Annealing of MAPI layers at 100°C yields flat grains with an average diameter of > 1 μm. After fast grain growth in the first few minutes, further annealing does not change the layer morphology anymore. However, ferroelectric domains as revealed by piezoresponse force microscopy (PFM) show vastly different orientations and domain shapes during this thermal treatment. The investigation of the corresponding solar cells elucidates the influence of changes in the sub-grain microstructure on the JV-characteristics, power conversion efficiencies and the hysteretic behavior of solar cells.

SESSION ET04.02: Device Physics and Characterization
Session Chairs: Juan-Pablo Correa-Baena and Antonio Guerrero
Monday Afternoon, November 26, 2018
Hynes, Level 3, Room Ballroom C

1:30 PM *ET04.02.01

Light-Induced Processes in Organohalide Perovskites—Defects and Polarons Filippo De Angelis; CNR-ISTM, Perugia, Italy.

We illustrate the results of ab initio molecular dynamics simulations coupled to first principles electronic structure calculations on the effect of light absorption on the electronic and dynamical properties of lead-halide perovskites. The role of the organic cation dynamics and of ion/defect migration is

analyzed in relation to photoinduced structural transformations and solar cell operation. Iodine defects, such as vacancies and interstitials, undergo a light-induced dynamical transformation leading to their mutual annihilation, accounting for the observed enhanced photoluminescence quantum yield following light irradiation. We also show how most of perovskites unusual properties in terms of defects and trapping dynamics can be explained by the close similarity between the perovskite properties and the photochemistry of iodine, both for 3D and 2D materials. Along with the unusual defect chemistry, the role of large polarons in screening charge carriers from recombination is finally illustrated based on quantitative models that allow us to estimate the extent and size of polaron distortion in various perovskites from first principles. The combination of unusual defect chemistry and of polaron screening of the charge carriers largely contributes to the outstanding optoelectronic properties of lead-halide perovskites.

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2:00 PM *ET04.02.02

Perovskite Material and Solar Cell Research by Surface Science and Advanced Characterization Yabing Qi; Okinawa Institute of Science and Technology, Okinawa, Japan.

Perovskite solar cell research has been continuously advancing in various fronts. To fabricate high performance stable perovskite solar cells, it is of paramount importance to obtain a better understanding of fundamental aspects with the help of surface science and advanced characterization. My group at OIST is making concerted efforts to investigate these materials and devices and to develop innovative strategies to improve their performance. In this talk, I will present our research progress on the improvement of perovskite solar cell stability and development of upscalable processes to fabricate perovskite solar cells and modules.

2:30 PM ET04.02.03

Perovskite Solar Cells—The Role of Ions, Density of States and Device Structure Nir Tessler¹ and Yana Vaynzof²; ¹Technion-Israel Institute of Technology, Haifa, Israel; ²Universität Heidelberg, Heidelberg, Germany.

Preventing hysteresis and enhancing stability remain key challenges that could be resolved with the aid of judicious device design. We report numerical study of a solar cell model system that is based on a mixed electron-ion conducting perovskite active layer having various device configurations. In the full picture we allow for both mobile ions and the polarizability due to the easy-rotational methylammonium (MA). We then compare with cells where the MA rotation is frozen and/or the ions are non-existing. Several insights, resulting from these detailed simulations, will be presented.

For example: Even when there is no indication of hysteresis and the device's characteristics can be modelled using ionic free model, the actual electron and hole distributions may be vastly different to the predictions by ionic free model. The low effective DOS promotes higher Voc but makes it more difficult to overcome energy level mismatch. These are related to the fact that the ionic motion is not only causing the hysteresis, it also allows for large deviations between electron and hole densities. Also, when a large energy mismatch exists between the BL and the perovskite the charge density distribution self-adapt to create an effective dipole at the interface. Such self-induced dipole can compensate for 0.4eV mismatch and thus prevent any loss in Voc. In this context formamidinium is preferred to MA.

We also found that while the use of doped BLs is effective to reduce serial resistance and potential S shapes it also results in a relatively pronounced ionic motion. We note that even in hysteresis-free cells the ions still redistribute as a function of bias. We show that by keeping a certain level of resistivity, as in undoped BL, the ionic motion is significantly reduced. We expect this to have significant impact on device long term stability.

2:45 PM ET04.02.04

Structural Origins of Light-Induced Phase Segregation in Organic-Inorganic Halide Perovskite Photovoltaic Materials Rachel E. Beal^{1,2}, Hans Steinrueck², Nanna Zhou Hangström⁴, Michael F. Toney² and Ana F. Nogueira³; ¹Stanford University, Stanford, California, United States; ²Materials Sciences Division, Stanford Sychotron Radiation Lightsource, Stanford, California, United States; ³Institute of Chemistry, University of Campinas, Campinas, Brazil; ⁴Stockholm University, Stockholm, Sweden.

Organic-inorganic perovskite materials offer a promising route to reducing the dollars-per-watt cost of solar energy due to their ease of deposition and favorable optoelectronic properties. A wide range of perovskite compositions can be solution processed with relative ease where changing the stoichiometry of the material allows for the preparation of materials with bandgaps tailor-made for specific tandem and single-junction applications. Early work showed that varying the Br:I ratio in (CH₃NH₃)Pb(Br_xI_{1-x})₃ tunes the bandgap between 2.3 and 1.6 eV, but photo-induced phase segregation leads to the formation and I-enriched regions in materials with $x \geq 0.2$ that trap carriers and pin the voltage of photovoltaic devices. Materials with a combination of formamidinium (FA) and cesium of the A-site in the general ABX₃ stoichiometric formula have demonstrated improved stability to this phenomenon, but the fundamental and mechanistic underpinnings of photo-induced phase segregation are not well understood. We have studied the structural origins of photo-induced phase segregation by coupling synchrotron X-ray diffraction with photoluminescence experiments. We examine materials with a range of FA:Cs and Br:I ratios and show that optical stability is observed at the phase boundary between Br-poor cubic and Br-rich tetragonal compositions, with material compositions farther from the boundary demonstrating a greater extent of segregation. Ours is the first study to examine materials in the FA:Cs phase space with bandgaps relevant for high-efficiency device applications. By mapping out the phase boundary, we provide a roadmap for compositional selection for photostable devices.

3:00 PM BREAK

3:30 PM *ET04.02.05

'Life' of Halide Perovskite—Evolution From the Solution and Degradation in the Environment Yuanyuan Zhou; Brown University, Providence, Rhode Island, United States.

Halide perovskites have recently emerged as a new family of semiconducting materials that are revolutionizing the field of photovoltaics. The rapid development of perovskite-based solar cells is being led by advances in microstructural/compositional engineering of perovskite thin films. In this context,

understanding the 'life' of halide perovskite: evolution/crystallization from the solution and degradation in the environment, and developing new strategies for the 'life-lengthening' (stabilization) of perovskites are becoming the most significant research directions.

In this talk, first, I will look at fundamental phenomena pertaining to nucleation & grain growth and grain-boundary evolution involved in the thin-film crystallization of perovskites from a materials-science perspective. Established scientific principles that govern these phenomena will be invoked in the context of specific examples of perovskite thin films. Based on these fundamentals, I will present a set of new synthetic strategies that have been recently developed in our group for scalable processing of high-performance large-area perovskite thin films and devices. Second, I will discuss the key role of grain boundaries in the degradation processes of perovskites, and show our recent progress in the grain-boundary tailoring of perovskite thin films that endow perovskites with new functionalities and enhances the perovskite stability. Finally, I will discuss the challenges and opportunities in the advanced characterization (high-resolution and *in-situ/operando* TEM, etc.) of perovskites for not only gaining a deep understanding of defects/microstructures, but also elucidating classical and non-classical phenomena pertaining to the crystallization, degradation, and stabilization of perovskites. The overall goal is to gain a deterministic control over the perovskite thin films with engineered microstructures/compositions for efficient PSCs that are also highly durable under environmental (heat/moisture/light) stresses.

4:00 PM ET04.02.06

How Does the Chemical Reactivity of Mobile Ions Trigger Reversible Performance Losses at Reverse Bias in Lead Halide Perovskite Solar Cells? Luca Bertoluzzi¹, Kevin A. Bush¹, Rohit Prasanna¹, Brian O'Regan² and Michael D. McGehee³; ¹Stanford University, Stanford, California, United States; ²Sunlight Scientific, Berkeley, California, United States; ³Department of Chemical Engineering, University of Colorado Boulder, Boulder, Colorado, United States.

Enhancing the stability of perovskite solar cells is currently one of the main preoccupations of the perovskite research community. Environmental degradation triggered by moisture, oxygen, UV light and thermal stress, is being efficiently tackled by the concomitant engineering of the device architecture and encapsulation.¹ However, multiple groups have pointed out that different conditions of light and applied voltage can also lead to partially reversible efficiency losses. We recently reported partially reversible performance losses caused by reverse bias.² Other groups remarked that devices placed outdoor loose part of their efficiency during the day and partially recover during the night.³ Finally, since these processes are not fully reversible, it is important to understand and stop them for reliability reasons.

Mobile ions within the active material have been suspected to trigger these processes. We have recently proposed a drift-diffusion model to examine the role of such ions at reverse bias.² We concluded that while ion migration can explain the reverse bias leakage current, ionic transport alone cannot explain the reversible performance losses we measured. Instead, we suggested that a reversible electrochemical reaction involving these ions is likely to take place. In a different study, Maier and coworkers showed that iodide vacancies can be created under prolonged illumination due to the oxidation of iodide into iodine, which subsequently migrate to interstitial sites.⁴

While growing evidence suggests that ionic chemistry is triggering partially reversible losses, it is crucial to understand and stop ionic reactivity. In this talk, we will discuss the nature of the ionic reaction triggered by prolonged reverse bias by resorting to different electrochemical techniques for strategically chosen perovskite compositions and contacts. In addition, we use a drift-diffusion model to explain a mechanism for how such a reaction can lead to partially reversible performance losses.

¹Cheacharoen R. et al., *Energy Env. Sci.*, 2018, 11, 144-150

²Bowring A. et al. *Adv. Energy Mater.*, 2017, 8, 1702365

³Domanski K. et al. *Energy Env. Sci.*, 2017,10, 604-613

⁴Maier J. et al *Nat. Mater.*, 17, 2018, 445-449

4:15 PM ET04.02.07

Deposition of Halide Perovskite Thin Films and Solar Cells Using the RIR-MAPLE Technique Wiley A. Dunlap-Shohl¹, E. T. Barraza², Andrew Barrette³, David J. Dirkes⁴, Wei You⁴, Kenan Gundogdu³, Adrienne D. Stiff-Roberts² and David Mitzi^{1,5}; ¹Mechanical Engineering and Materials Science, Duke University, Durham, North Carolina, United States; ²Electrical and Computer Engineering, Duke University, Durham, North Carolina, United States; ³Physics, North Carolina State University, Raleigh, North Carolina, United States; ⁴Chemistry, University of North Carolina at Chapel Hill, Chapel Hill, North Carolina, United States; ⁵Chemistry, Duke University, Durham, North Carolina, United States.

Although many techniques have been developed for the deposition of high-quality halide perovskite thin films, the dominant solution- and vapor-deposition methods often possess some undesirable attributes, such as the challenges associated with drenching potentially sensitive substrates in solvents, or with controlling fluxes of volatile and thermally unstable organic salts. These obstacles constrain the range of possible device architectures used in halide perovskite optoelectronics. Thus, it is desirable to explore novel perovskite thin film deposition methods that might help to circumvent these challenges. In this work, we use the resonant infrared matrix-assisted pulsed laser evaporation (RIR-MAPLE) technique, wherein a frozen solution of the precursors is evaporated by a laser whose energy is resonant with chemical bonds in the solvent, to deposit various hybrid halide perovskite thin films and explore their morphological, compositional, and optoelectronic characteristics.¹ We demonstrate, for the first time, perovskite solar cells with absorber deposited by RIR-MAPLE, which reach stabilized power conversion efficiency of over 12%.² The technique is also extended to consider layered or two-dimensional perovskites with more complex organic structure.

(1) Barraza, E. T.; Dunlap-Shohl, W. A.; Mitzi, D. B.; Stiff-Roberts, A. D. Deposition of Methylammonium Lead Triiodide by Resonant Infrared Matrix-Assisted Pulsed Laser Evaporation. *J. Electron. Mater.* **2018**, *47*, 917-926.

(2) Dunlap-Shohl, W. A.; Barraza, E. T.; Barrette, A.; Gundogdu, K.; Stiff-Roberts, A. D.; Mitzi, D. B. MAPbI₃ Solar Cells with Absorber Deposited by Resonant Infrared Matrix-Assisted Pulsed Laser Evaporation. *ACS Energy Lett.* **2018**, *3*, 270-275.

4:30 PM ET04.02.08

Trapped-Charges as the Core Origin for Degradation of Perovskite Crystals Namyoung Ahn, Min-cheol Kim, Kwisung Kwak and Mansoo Choi; Seoul National University, Seoul, Korea (the Republic of).

At the current state of perovskite photovoltaics field, it is no exaggeration to say that the most important issue is their stability upon real operation. To find out engineering ways on long-term stability with commercially-viable level, it is more urgent to seek the root origin of decomposition of perovskite crystals than any other. Therefore, we have explored what decisively destroys these hybrid perovskite crystals from experiments and theoretical approaches. From all our studies, we conclude that trapped-charges induce irreversible degradation of perovskite crystals as the core origin. First, a novel experimental set-up utilizing the deposition of ions with different polarity via a corona discharger revealed that perovskite materials irreversibly degrade along grain boundaries where ion charges trapped in the presence of either water or oxygen. In the case of light-illuminated perovskite films, such degradation was observed mainly along grain boundaries where provide a lot of trap states for photo-generated electrons and holes, which was also evidenced by Kelvin probe force microscopy (KPFM) measurements. Additionally, *ab initio* molecular dynamics (AIMD) simulation based on density functional theory (DFT) strongly supports trapped-charge driven degradation of perovskite crystals from the theoretical viewpoint, by showing that CH₃NH₃PbI₃ crystals surrounded by

either water or oxygen molecules break down with trapped-charges (localized at one crystal), whereas the decomposition never takes place without trapped-charge. These simulations not only uncover atomistic mechanisms for trapped-charge driven degradation but also bring out the observation of the deprotonation of organic cation (CH_3NH_3^+) for the first time. Finally, we obtain more powerful evidence to support trapped-charge driven degradation through light-induced degradation test of $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite films coated on different charge-selective layers. The test results showed that the polarity of localized charges inside $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite films determines degradation speed and pathways depending on the kind of surrounding gaseous molecules. Based on these experimental results and additional calculations, we discovered the effect of polarity-dependent localized charges on the degradation of $\text{CH}_3\text{NH}_3\text{PbI}_3$ crystals through close observations on real operation of $\text{CH}_3\text{NH}_3\text{PbI}_3$ -based photovoltaics

[1] N. Ahn, K. Kwak, M. S. Jang, H. Yoon, B. Y. Lee, J.-K. Lee, P. V. Pikhitsa, J. Byun, and M. Choi, "Trapped-charge driven degradation of perovskite solar cells", *Nature Communications*, (2016)

[2] K. Kwak, E. Im, N. Ahn, J. Heo, K. Bang, M. Kim, S. Kim, and M. Choi, "Atomistic mechanism of trapped-charge driven degradation of perovskite solar cells", *arXiv:1709.04130* (2017)

4:45 PM ET04.02.09

Facile Recrystallization Process for Efficient Triple-Cation Mixed-Halide Planar-Structure Perovskite Solar Cells Jacob Tse-Wei Wang¹, Liangyou Lin¹, Timothy Jones¹, Mihaela Grigore³, Andre Cook¹, Dane W. deQuilettes⁴, Roberto Brenes⁴, Benjamin Duck¹, Kenrick Anderson¹, Noel W. Duffy⁵, Vladimir Bulović⁴, Jian Pu², Jian Li², Bo Chi² and Gregory J. Wilson¹; ¹CSIRO Energy, Newcastle Energy Centre, Mayfield West, New South Wales, Australia; ²Center for Fuel Cell Innovation, School of Materials Science and Engineering, Huazhong University of Science & Technology, Wuhan, China; ³CSIRO Energy, North Ryde, New South Wales, Australia; ⁴Research Laboratory of Electronics, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; ⁵CSIRO Energy Clayton Laboratories, Clayton, Victoria, Australia.

The state-of-the-art PSCs use mixed-cation and mixed-halide perovskite compositions due to the superior qualities over the archetypal MAPbI_3 . Adding Cs^+ to perovskite has been shown to improve qualities including thermal stability, reproducibility, and suppression of phase segregation. In general, controlling the precise stoichiometry in a perovskite is critical for meeting its desired properties. However, it has been found purposely introduced excess PbI_2 in the perovskite causes significant influence on the intrinsic perovskite qualities. The few percent excess PbI_2 predominantly resides at grain boundaries, providing benefits of prolonged carrier lifetime, enhanced charge carrier injection, suppressed ion migrations and hysteresis, leading to improved overall device performance. Theories have been proposed to explain these beneficial effects, including the better energy level alignments, grain boundary passivation, and superior crystal quality and crystallinity. Nevertheless, there are also reports showing the residual PbI_2 can lead to degradation and fragile film structure with long-term device stability concerns. Nonetheless, with most of the best performing cells still incorporating slight excess PbI_2 , it is important to investigate this indefinite property function for further improving device performance and stability.

In this study, we use the $\text{Cs}_{0.05}(\text{FA}_{0.85}\text{MA}_{0.15})_{0.95}\text{Pb}(\text{Br}_{0.15}\text{I}_{0.85})_3$ stoichiometric perovskite structure as a platform to demonstrate a simple yet effective recrystallization method for PbI_2 -rich perovskite crystals with a series of recrystallization agents. Surprisingly, for the first time, through the Grazing Incidence X-ray Diffraction (GIXRD), we found not only the excess PbI_2 in the film can be successfully removed, the perovskite had a profound recrystallization throughout the bulk, showing enhanced PL emission/lifetime, charge collection efficiency, reduced defects at grain boundaries (GBs) as well as superior device performance over 20% PCE.

SESSION ET04.03: Poster Session I
Monday Afternoon, November 26, 2018
8:00 PM - 10:00 PM
Hynes, Level 1, Hall B

ET04.03.01

NH_4SCN -Induced Recrystallization Engineering for $\text{CH}_3\text{NH}_3\text{PbI}_3$ Film and Its Application in Highly Efficient Inverted Planar Heterojunction Perovskite Solar Cells Jie Xu, Hua Dong, Ting Lei, Jinfei Dai, Yifei Shi, Xiaoyun Liu and Zhaoxin Wu; Key Laboratory for Physical Electronics and Devices of the Ministry of Education & Shaanxi Key Lab of Information Photonic Technique School of Electronic and Information Engineering Xi'an Jiaotong University, Xi'an, China.

High crystallinity and compactness of the active layer is essential for metal-halide perovskite solar cells. Here, a simple pseudohalide (NH_4SCN)-induced film retreatment technology is developed as the passivation for preformed perovskite film. It is found that the retreatment process yields a controllable decomposition-to-recrystallization evolution of the perovskite film. Corresponding, it remarkably enlarges the grain size of the film in all directions, as well as improving the crystallinity and hindering the trap density. Meanwhile, owing to an intermediate catalytic effect of the pseudohalide compound (NH_4SCN), no crystal orientation changing and no impurity introduction in the modified film. By integrating the modified perovskite film into the planar heterojunction solar cells, a champion power conversion efficiency of 19.44% with a stabilized output efficiency of 19.02% under 1 sun illumination is obtained, exhibiting a negligible current density–voltage hysteresis. Moreover, such a facile and low-temperature film retreatment approach guarantees the application in flexible devices, showing a best power conversion efficiency of 17.04%.

ET04.03.02

High-Efficient and Low-Temperature Perovskite Solar Cells by Employing a Bi-Hole Transport Layer Consisted of Vanadium Oxide and Copper Phthalocyanine Ting Lei, Yifei Shi, Hua Dong, Jie Xu, Feijie Wei and Zhaoxin Wu; Xi'an Jiaotong University, Xi'an, China.

In our work, an inorganic-organic bilayer hole transport layer (B-HTL) was designed and utilized in planar perovskite solar cells. Here the B-HTL is consist of the inorganic VO_x matrix and copper phthalocyanine (CuPc) buffer layer, providing the excellent resistance of moisture as well as the alignment of the interfacial energy level. Benefiting from this typical HTL, enlarged built-in potential and charge extraction can be achieved in PSCs simultaneously. Correspondingly a champion device with B-HTL shows a 16.85% efficiency with negligible hysteresis, which is superior to the PSC based on PEDOT:PSS HTL. Meanwhile, significantly prolonged stability of the PSCs with B-HTL can be observed, exhibiting an only 10% efficiency loss after 350 hours in the ambient air. Moreover, such an entire low-temperature ($\leq 60^\circ\text{C}$) fabrication process of this typical PSCs exhibits its successful application in flexible devices.

Inorganic-organic bilayer hole transport layer : the B-HTL is consist of the inorganic VO_x matrix and copper phthalocyanine (CuPc) buffer layer, with excellent resistance of moisture as well as the alignment of the interfacial energy level ;

Considerable improvement of the PCE: nearly 20% PCE enhancement of the PSCs based on B-HTL compared with the device with PEDOT (from

14.31% to 16.85%);

Facile and low temperature fabrication process for the whole device: The fabrication process of B-HTL operates at Room temperature; the highest temperature requirement of the fabrication is only 60C, which is under the glass transition temperature (T_g) of most polymers used as the matrix of the flexible electrodes, such as PET PEN PS and PC

Considerable stability: Maintain 90% PCE over 350h in ambient air. (40% RH).

DOI:10.1039/C8CC03672A

ET04.03.03

Boosting the Performance and Stability of Quasi-Two-Dimensional Tin-Based Perovskite Solar Cells Using a Formamidinium Thiocyanate Additive [Hongki Kim](#)¹, Yoon Ho Lee¹, Taecheon Lyu², Jong Heun Yoo¹, Taiho Park¹ and Joon Hak Oh¹; ¹Chemical Engineering, Pohang University of Science and Technology, Pohang-si, Korea (the Republic of); ²Chemistry, Pohang University of Science and Technology, Pohang-si, Korea (the Republic of).

Organic-inorganic hybrid lead-based perovskite solar cells have shown tremendous growth in power conversion efficiency (PCE) over recent years. Despite remarkable strides in performance, one of the biggest barriers to commercialization is the toxicity of lead. Therefore, there has been a growing interest in implementing high performance solar cells based on lead-free perovskites with lower toxicity and outstanding optoelectronic properties. In this regard, tin-based perovskite solar cells have been spotlighted because they show suitable optical band gap, high absorption coefficient and high charge carrier mobility. However, self-p-doping by the oxidation of Sn²⁺ to Sn⁴⁺ in tin-based perovskite solar cells has been a critical issue for achieving high performance tin-based perovskite solar cells. Therefore, essential strategies that take into account tin chemistry are required to mitigate the intrinsic instability and improve the performance of tin-based perovskite solar cells. Based on the chemical nature of tin, N-, S-, O-based electron donors can coordinate with tin halides (SnX₂, X = halide anions) by donating a lone pair electron to the empty orbital in the valence shell of divalent tin. Accordingly, it is expected that coordination between Sn²⁺ ions and appropriate ligands could block the reaction of Sn²⁺ ions with oxygen, resulting in effective suppression of the oxidation of Sn²⁺ to Sn⁴⁺.

Taking this into account, herein we fabricated quasi-two-dimensional (quasi-2D) tin-based perovskite solar cells with greatly enhanced performance and stability compared to conventional three-dimensional (3D) formamidinium tin iodide (FASnI₃) perovskite solar cells, by employing an additional formamidinium thiocyanate (FASCN) additive into the quasi-2D tin-based perovskites. The incorporation of the FASCN additive greatly prevented quasi-2D tin-based perovskites from oxidation during film formation, through the strong chemical interactions with tin component (Sn²⁺). Moreover, it resulted in a coarser perovskite grain and a higher degree of crystallinity in the out-of-plane direction, leading to enhanced optoelectronic performance of the quasi-2D tin-based perovskites. As a result, we achieved reproducible high-performance tin-based perovskite solar cells with improved stability, reaching the highest PCE up to 8.17% compared to that of 3D FASnI₃ device (1.84%), and retaining over 90% of its initial efficiency after 1000 hours aging in a nitrogen-filled glove box. These results demonstrate a versatile, yet simple methodology that can be applied to other lead-free perovskites suffering from poor oxidative stability.

ET04.03.04

Plasmonic Enhancement for High Efficient and Stable Perovskite Solar Cells by Employing "Hot Spots" Au Nanopyramids [Feijie Wei](#), Hua Dong, Jie Xu, Ting Lei and Zhaoxin Wu; Xi'an Jiaotong University, Xi'an, China.

Metal plasmonic effect is one promising way for improving the performance and stability of the perovskite solar cells via optical-electrical behalves, and the ability is in proportion to the enhanced local electromagnetic fields induced by metal nanostructures. In our work, unique gold nanopyramids (Au NBs) structures were explored and incorporated in the hole transport layer of planar heterojunction PSCs. This typical "bipyramid-like" metal nanostructure with sharp tips has the multiple and strong plasmonic absorption properties from visible to the NIR, exhibiting high plasmonic-induced probability. In addition, generated "hot spots" around Au NBs provided much stronger EM fields enhancements than conventional Au nanoparticles, hence enhanced light harvesting and improved interfacial charge dynamic process can be achieved simultaneously. As for the further investigation of the electrical property, hot holes injection induced by Au NBs effectively filled in the interfacial traps under operation condition, contributing to the improvement of the open circuit voltage, the elimination of the hysteresis effect and the long-term stability. Accordingly, the best PSC incorporated with Au NBs showed the PCE of 18.84% whereas the reference device just showed the PCE of 16.02%. Our work demonstrated that plasmonic metal nanostructures possessing the feature of "hot spots" offered a great potential to further expand the performance limitation and operation tolerance of the PSCs.

ET04.03.05

Theoretical Investigation of Water-Resistant Halide Perovskites [Hiromitsu Takaba](#), Tatsuya Hongo and Junna Takahashi; Kogakuin Univ, Tokyo, Japan.

Organic / inorganic perovskite compound is capable of highly efficient energy conversion and halide perovskites are important issue for its practical application in a solar cells. However most perovskite of APbI₃ has a problem that the structure is distorted and degraded by invasion or diffusion of water molecules or the existence of defect in the crystal. Therefore, it is necessary to search for structures having energetically stable and high water resistance. In this study, energetically stability and water resistance for various virtual halide perovskites containing fluoride in A-ion site were investigated by density functional theory and molecular dynamics. Dynamics of bond dissociation or water adsorption as well as the electronic structure, e.g. band gap and light adsorption spectrum, of various compounds were systematically investigated and then the novel composition for durable halide perovskite was theoretically suggested. Our simulation results indicate that fluoride halide perovskite is stable and a little bit wide band gap compared to CH₃NH₃PbI₃ (MAPbI₃) perovskite. The calculated adsorption energy of water molecule on the surface of fluoride halide perovskite is smaller than that on MAPbI₃. The reaction barrier for 2(Pb-I)_{perovskite} + H₂O = -PbO + 2HI was estimated and it is confirmed the presence of fluoride molecule at A-ion site prevent from the reaction showing higher reaction barrier than that for MAPbI₃. This would be due to the interaction with negatively charged atoms of F. We also investigated the combination of fluoride and other A-site ion to tune the band gap suitable for the application to solar cell.

H. Takaba, S. Kimura, Md. K. Alam, *Chem. Phys.*, **2017**, 485-486, 22.

ET04.03.06

Highly Efficient and Stable Tandem Solar Cells Based on Halide Perovskites [Ik Jae Park](#), [Jae Hyun Park](#), Su Geun Ji, Min Ah Park and Jin Young Kim; Seoul National University, Seoul, Korea (the Republic of).

The tandem configuration consisting of two or more solar cells is practically the only approach to overcome the Shockley-Queisser limit. From theoretical calculation shows that the combination of a top cell with a large bandgap energy (1.5~1.7 eV) and a bottom cell with a low bandgap energy (1.0~1.1 eV) can lead to a conversion efficiency higher than 30%. Given that the bandgap energy of most commercial single junction solar cells is around 1.1 eV, the perovskite solar cell with a bandgap energy around 1.6 eV must be a very promising candidate for the top cell of tandem solar cells. In this presentation, I

will discuss the essential requirements for preparing highly performing perovskite top cells of tandem solar cells. Firstly, the strategies for improving the performance of the p-i-n type planar perovskite solar cell will be introduced. After a series of interfacial engineering procedures to the charge extraction layers, a conversion efficiency as high as 19% could be achieved. Secondly, strategies for fabricating transparent perovskite solar cells with a TCO top electrode layer will be discussed. Finally, some of the recent results on the highly efficient (> 23%) tandem solar cells incorporating the transparent perovskite top cell will be introduced.

ET04.03.07

Enhancing Stability for Organic-Inorganic Perovskite Solar Cells by Atomic Layer Deposited Al₂O₃ Encapsulation Eun Young Choi², Jincheol Kim¹, Sean Lim¹, Ekyu Han², Anita Ho-Baillie¹ and Nochang Park²; ¹University of New South Wales, Sydney, New South Wales, Australia; ²Korea Electronics Technology Institute, Seongnam-si, Korea (the Republic of).

In this work, we employed atomic layer deposition (ALD) to form Al₂O₃ layer as an encapsulant for perovskite solar cells (PSCs). Al₂O₃ layer deposited at temperature as low as 95°C achieved excellent water vapour transmission rate (WVTR) of 1.84×10^{-2} g/m²/day at 45°C-100 %RH when thermal ALD (Th-ALD) was used. In order to test the moisture barrier capability of Al₂O₃ layer for PSCs, mesoporous perovskite devices, with spiro-OMeTAD or PTAA as hole transport layer (HTM) encapsulated by 50 nm Al₂O₃ film, were exposed to 65°C-85 %RH for 350 hours and their stabilities were monitored. We found that the colour of perovskite did not change after 350 hours of exposure regardless of the type of HTM used. With regards to Th-ALD encapsulated devices, PTAA based PSCs experienced a smaller power conversion efficiency (PCE) drop than spiro-OMeTAD based PSCs after thermal stress at 65°C. This is due to the presence of pinholes within spiro-OMeTAD layer after thermal stress which were not observed in PTAA. Finally, we have successfully achieved excellent durability test results for mesoporous (HC(NH₂)₂PbI₃)_{0.85}(CH₃NH₃PbBr₃)_{0.15}/PTAA devices encapsulated by 50nm Al₂O₃ with less than 4% drop in PCE after 7500 hours (>10 months) of exposure to 50 %RH under room temperature.

ET04.03.08

Planar Perovskite Solar Cells with High Open-Circuit Voltage Containing a Supramolecular Iron Complex as Hole Transport Material Dopant Yasemin Saygili¹, Silver-Hamill Turren-Cruz^{1,2}, Selina Olthof³, Ilknur Bayrak Pehlivan⁴, Michael Saliba⁷, Klaus Meerholz³, Tomas Edvinsson⁴, Shaik Mohammed Zakeeruddin¹, Michael Graetzel¹, Juan-Pablo Correa-Baena⁵, Anders Hagfeldt¹, Marina Freitag⁶ and Wolfgang Tress¹; ¹Institute of Chemical Sciences and Engineering, Ecole Polytechnique Federale de Lausanne, Lausanne, Switzerland; ²Benemerita Universidad Autonoma de Puebla, Puebla, Mexico; ³Department of Chemistry, University of Cologne, Cologne, Germany; ⁴Department of Engineering Sciences, Solid State Physics, Uppsala University, Uppsala, Sweden; ⁵Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; ⁶Department of Chemistry Angstrom Laboratory, Uppsala University, Uppsala, Sweden; ⁷Adolphe Merkle Institute, Fribourg, Switzerland.

In perovskite solar cells (PSCs), the most commonly used hole transport material (HTM) is spiro-OMeTAD, which is typically doped by metalorganic complexes, for example, based on Co, to improve charge transport properties and thereby enhance the photovoltaic performance of the device. In this study, we report a new hemicage-structured iron complex, 1,3,5-tris(5'-methyl-2,2'-bipyridin-5yl)ethylbenzene Fe(III)-tris(bis(trifluoromethylsulfonyl)imide), as a p-type dopant for spiro-OMeTAD. The formal redox potential of this compound was measured as 1.29 V vs. the standard hydrogen electrode, which is slightly (20 mV) more positive than that of the commercial cobalt dopant FK209. Photoelectron spectroscopy measurements confirm that the iron complex acts as an efficient p-dopant, as evidenced in an increase of the spiro-OMeTAD work function. When fabricating planar PSCs with the HTM spiro-OMeTAD doped by 5 mol % of the iron complex, a power conversion efficiency of 19.5 % (AM 1.5G, 100 mW cm⁻²) is achieved, compared to 19.3 % for reference devices with FK209. Open circuit voltages exceeding 1.2 V at 1 sun and reaching 1.27 V at 3 suns indicate that recombination at the perovskite/HTM interface is low when employing this iron complex. This work contributes to recent endeavors to reduce recombination losses in perovskite solar cells.

ET04.03.09

Two-Dimensional Perovskites with Short Interlayer Distance for High Performance Solar Cell Chunging Ma, Dong Shen, Xiao Cui, Ming-Fai Lo and Chun-Sing Lee; Center of Super-Diamond and Advanced Films (COSDAF) and Department of Chemistry, City University of Hong Kong, Hong Kong, Hong Kong.

Two-dimensional (2D) perovskites have emerged as one of the most promising photovoltaic materials owing to their excellent stability compared to their three-dimensional (3D) counterparts. However, in typical 2D perovskites, the highly conductive inorganic layers are isolated by large organic cations leading to quantum confinement and thus inferior electrical conductivity across layers. To address this issue, the large organic cations are replaced with small propane-1,3-diammonium (PDA) cations to reduce distance between the inorganic perovskite layers. As shown by optical characterizations, quantum confinement is no longer dominating in the PDA-based 2D perovskites. This leads to considerable enhancement of charge transport as confirmed with electrochemical impedance spectroscopy, time-resolved photoluminescence and mobility measurements. The improved electric properties of the interlayer-engineered 2D perovskites yield a power conversion efficiency (PCE) of 13.0%. Furthermore, environmental stabilities of the PDA-based 2D perovskites are improved. PDA-based 2D perovskite solar cells (PSCs) with encapsulation can retain over 90% of their efficiency upon storage for over 1,000 h and PSCs without encapsulation can maintain their initial efficiency at 70°C for over 100 h, which exhibit promising stabilities. These results reveal excellent optoelectronic properties and intrinsic stabilities of the layered perovskites with reduced interlayer distance.

ET04.03.10

Direct Observation of Cation-Exchange in Liquid-to-Solid Phase Transformation in FA_{1-x}MA_xPbI₃ Based Perovskite Solar Cells Yuemín Xie, Xiuwen Xu, Menglin Li, Yuhui Ma and Sai-Wing Tsang; City University of Hong Kong, Hong Kong, Hong Kong.

As one of the emerging photovoltaic technologies, the high performance and ease of fabrication of organometal halide perovskite based solar cells (PVSCs) draw tremendous attention in the photovoltaic community. Recently, formamidinium (FA) dominating mixed-organic-cation FA_{1-x}MA_xPbI₃ perovskites are attracting intensive attention for their extended optical absorption range (reduced optical bandgap) and high photovoltaic performance. However, FA_{1-x}MA_xPbI₃ based perovskite usually has undesired yellow-colour non-perovskite phase (δ -phase) leading to a compromised efficiency, and a facile strategy to achieve pure-phase FA_{1-x}MA_xPbI₃ is rarely reported. Here, we demonstrate a facile approach to form δ -phase free FA_{1-x}MA_xPbI₃ using non-stoichiometric precursor solution. It is found that even a small amount of excessive methylammonium iodide (MAI) added in the precursor solution has a profound effect on perovskite crystallization during the liquid-to-solid phase transformation. In contrast to previous reports, using an in-situ photoluminescence spectroscopy measurement, it is directly observed that the organic-cation-exchange process is in fact occurred in the early stage of film formation during the liquid-to-solid phase transition, which can promote the formation of FA_{1-x}MA_xPbI₃ and pure-phase perovskite film can be achieved. By controlling the amount of cation ratio in the precursor solution optimized pure-phase FA_{1-x}MA_xPbI₃ is achieved. The champion perovskite solar cell exhibits an encouraging power conversion efficiency (PCE) of 17.40%. This study demonstrates a facile method to achieve high performance FA dominating mixed-organic-cation perovskite devices while providing insight into the ion-exchange process during perovskite crystallization.

Publication: Direct observation of cation-exchange in liquid-to solid phase transformation in FA_{1-x}MA_xPbI₃ based perovskite solar cells, Yue-Min Xie et

al, J. Mater. Chem. A, 2018, 6, 9081-9088.

ET04.03.11

Heat Treatment for Regenerating the Degraded Low Dimensional Perovskite Solar Cells Chunqing Ma, Dong Shen, Ming-Fai Lo and Chun-Sing Lee; Center of Super-Diamond and Advanced Films (COSDAF) and Department of Chemistry, City University of Hong Kong, Hong Kong, Hong Kong.

Organolead halide perovskite devices are reported to be susceptible to thermal degradation, which is resulted from heat-induced fast ion diffusion and structural decomposition. In this work, it is found that performances of degraded low dimensional perovskite solar cells can be considerably improved (e. g. power conversion efficiency shows ~ 10% increase over the fresh device) by a short time heat treatment (85°C, 3 mins). Capacitance-Frequency, X-ray diffraction and ionic diffusion calculation results suggest that heat treatment can enhance the crystallinity of the degraded low dimensional perovskite and minimize the detrimental effects caused by the water molecules, leading to improved performances. Our results indicate that the heat treatment does not necessarily lead to the accelerated degradation, but can also regenerate the degraded low dimensional perovskite.

ET04.03.12

High-Performance MAPbI₃ and Cs_{0.15}FA_{0.85}PbI₃ Perovskite Solar Cells Made in a Humid Air with a Relative Humidity of 70% Xiuwen Xu, Yucmin Xie, Menglin Li, Yuhui Ma and Sai-Wing Tsang; City University of Hong Kong, Hong Kong, Hong Kong.

Understanding air-processing limitations and developing facile strategies to fabricate high-performance air-processed perovskite solar cell (PSC) is appealing yet challenging for the low-cost industrial deployment. Here, we demonstrate that besides the general wisdom of the moisture effect, oxygen induces a de-wetting behavior during the spin-coating of PbI₂ precursor solution, both of which leads to the failure of desirable PbI₂ deposition in air. Interestingly, by simply preheating the substrate and PbI₂ solution, uniform PbI₂ films can be deposited in air with a relative humidity (RH) of 70%. This is probably due to the rapid solvent evaporation at high temperature, reducing the ingress of oxygen and moisture. With the preheating approach, PSCs based on MAPbI₃ achieves an encouraging power conversion efficiency (PCE) of 18.11%. More importantly, it is found that the combination of preheating and a PbI₂-(CsI)_{0.15}-(FAI)_x intermediate complex can unlock the processing limitation and facilitate the growth of high-quality FA based perovskite films in humid air (RH: 70%). With the coupled method, a low-temperature air-processed planar Cs_{0.15}FA_{0.85}PbI₃ PSCs achieves a high PCE of 15.56% with superior thermal-stability and photo-durability. Our work not only reveals the origin of the detrimental effects on perovskite formation in humid air, but also provides practical strategies for high-efficiency air-processed MA or FA based PSCs for future commercialization.

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ET04.03.13

ZnO/SnO₂ Double Electron Transport Layer Guides Improved Open Circuit Voltage for Highly Efficient CH₃NH₃PbI₃-Based Planar Perovskite Solar Cells Duo Wang; School of Physics, Peking University, Beijing, China.

The electron transport layer (ETL) is a very important component of planar perovskite solar cells (P-PSCs), and it can effectively extract photon-generated electrons from perovskites and convey them to the cathode. By this token, its properties directly determine the photovoltaic performances of P-PSCs. Herein, we developed ZnO/SnO₂ as a double electron transport layer for CH₃NH₃PbI₃-based P-PSCs, achieving a high open circuit voltage (V_{OC}) of 1.15 V with the power conversion efficiency (PCE) of 19.1% when the controlled devices have a V_{OC} of 1.07 V and a PCE of 18.0%. To the best of our knowledge, up to now, this is the highest V_{OC} obtained by using an inorganic electron transport layer for pure CH₃NH₃PbI₃-based P-PSCs. Moreover, a higher E_F and E_{CBM} of ETL are believed to drive a larger V_{OC} and a better PCE. These indicate that it is a very significant method to achieve a higher V_{OC} for P-PSCs by matching ETLs with a higher E_F and E_{CBM}.

ET04.03.14

High Crystallization of Perovskite Film by a Fast Electric Current Annealing Process Wei Luo; School of Physics, Peking University, Beijing, China.

High efficiency organic-inorganic hybrid perovskite solar cells have experienced rapid development and attracted significant attention in recent years. Crystal growth as an important factor would significantly influence the quality of perovskite films and ultimately the device performance, which usually requires thermal annealing for 10 min or more.

We demonstrate a new method to get high crystallization of perovskite film by electric current annealing for just 5 s. Two strip electrodes were clipped onto the opposite sides of the FTO/SnO₂/coated perovskite film, and subsequently applied with a direct voltage of 30 V for 5 s. The coated perovskite film was annealed quickly by the joule heat of current flowing through the FTO layer. In contrast to conventional thermal annealing, a homogeneous perovskite film was formed with larger grains and fewer pinholes, leading to a better performance of the device with higher open-circuit voltage and fill factor. The average PCE consequently improved to 17.02% from 16.05% with the conventional thermal annealing (100 °C for 10 min). In addition, the annealing time is significantly shortened to a few seconds and the heating area is relatively concentrated to the only film. This facile electric current annealing process with less energy loss and time consumption shows great potential in the industrial mass production of photovoltaic devices.

ET04.03.15

Solution-Processed Cu₉S₅ as Hole Transport Doping Layer for Efficient and Stable Perovskite Solar Cells Dong Han; School of Physics, Peking University, Beijing, China.

In recent years, perovskite solar cells have drawn widespread attention. We believe that investigation of long-term stability of perovskite solar cells is a critical issue and necessary to be solved for its commercialization. As a hole transport material (HTM), 2,2',7,7'-tetrakis(N,N-di-p-methoxyphenylamine)-9,9'-spirobifluorene (Spiro-OMeTAD) is widely used in n-i-p perovskite solar cells (PVSCs). However, it suffers a severe degradation from the permeation of moisture due to the doping of lithium bis(trifluoromethyl)sulfonylamide (Li-TFSI), which has strong hygroscopicity. In this paper, we propose a method which offers a new way to reduce the hysteresis and improve the stability of n-i-p perovskite solar cells by employing nitrogen-doped SnO₂ (N:SnO₂) electron transport layer (ETL) and Spiro-OMeTAD/Cu₉S₅ hole transport layer (HTL) without Li-TFSI doping. Cu₉S₅ is a p-type transport material with favorable energy level matching with Spiro-OMeTAD. Furthermore, since there is no Li-TFSI doping in HTL, it can avoid devices suffering a severe degradation from the permeation of moisture. In the meantime, the LUMO of SnO₂ can be tuned from -4.33 eV to -3.91 eV by implanting nitrogen ions into the SnO₂, which exactly match the LUMO of CH₃NH₃PbI₃ (-3.90 eV) and thus help to reduce the hysteresis. The modified n-i-p perovskite solar cells achieve maximum PCE of 17.10% and remain about 96 % of PCE after 1200 hours stability test in air atmosphere with no encapsulation.

ET04.03.16

Impact of SnF₂ and Pyrazine Additives in Formamidinium Tin Iodide Perovskite Solar Cells Simon Sanders¹, Dominik Stümmler¹, Pascal Pfeiffer¹, Florian Schimkat¹, Peter Baumann², Gintautas Simkus^{1,3}, Michael Heuken^{1,3}, Andrei Vescan¹ and Holger Kalisch¹; ¹Compound Semiconductor Technology, RWTH Aachen University, Aachen, Germany; ²APEVA SE, Herzogenrath, Germany; ³AIXTRON SE, Herzogenrath, Germany.

Due to a steep rise in efficiency, organic-inorganic halide perovskite solar cells have attracted wide research interest in the past few years. The achievement of a power conversion efficiency (PCE) of 22.7 % in 2017 using a lead halide perovskite makes these devices a promising alternative to the established thin-film and wafer-based solar cell technologies. Nevertheless, the toxicity of Pb remains as a major issue for the commercialization of perovskite photovoltaics. So far, Sn-based perovskites showed the most promising results in Pb-free perovskite solar cells with efficiencies up to 9.0 %. However, Sn-based perovskite layers typically suffer from poor layer quality (coverage and homogeneity issues) and fast degradation caused by the instability of the Sn²⁺ ion which easily oxidizes to Sn⁴⁺.

In this work, we present formamidinium tin iodide (FASnI₃) perovskite solar cells which are processed by spin-coating under inert nitrogen atmosphere, employing a standard non-inverted stack composed of compact and mesoporous TiO₂, the perovskite layer and Spiro-MeOTAD sandwiched between fluorine-doped tin oxide (FTO) and evaporated gold contacts. Morphological and structural characterization of processed layers and devices is carried out by scanning electron microscopy. Photovoltaic measurements are performed in nitrogen atmosphere under simulated AM1.5 sunlight of 100 mW/cm² illumination. Absorption spectra measurements are conducted in the wavelength range of 300 - 1000 nm.

To increase the area covered with the perovskite film, we examine the influence of using different amounts of toluene as anti-solvent initiating a rapid crystallization. It was determined that 1 ml of toluene is sufficient for 80 µl perovskite solution to produce closed films. To suppress Sn²⁺ oxidation and to obtain smooth perovskite films, pyrazine and SnF₂ were added into the perovskite precursor solution. By varying the ratio of additives in this solution, their impact on layer morphology and on cell performance are investigated. A pyrazine/SnF₂ ratio of 0.2 M / 0.1 M has proven to be the optimum leading to smooth layers and a maximum PCE of 2.1 %. We highlight that layers with higher concentrations of additives suffer from delayed crystallization and therefore reduced coverage. However, we found that these layers exhibit additional light absorption for wavelengths above 650 nm and still provide reasonable photocurrents.

ET04.03.17

High Efficiency Perovskite Solar Cells with Molecular Passivated NiO_x Charge Extraction Layer Menglin Li; Materials Science and Engineering, City University of Hong Kong, Hong Kong, Hong Kong.

Developing low cost and stable metal oxide charge extraction layer is attractive yet challenging for fabricating long-term stable high-performance perovskite solar cells (PSCs). Here, it is found that the solution processed NiO_x based PSCs surface suffers from strong recombination with interfacial defects. We have found that continuous light soaking is required in the NiO_x based PSCs to recover the built-in potential and consequently open-circuit voltage (V_{oc}). Interestingly, we have found that n-butylamine molecular monolayer can effectively passivate those defects in the NiO_x layer. The device power conversion efficiency (PCE) with molecular passivated NiO_x as the hole transport layer is increased from 13.5% to 18.0%. Further molecular dynamic simulation reveals auto-decomposition process at as-prepared NiO_x/MAPbI₃ interface, which can be eliminated by surface passivation.

ET04.03.18

Understanding the Crucial Design of Amorphous Hole Transport Materials in Perovskite Solar Cell Kun-Han Lin, Antonio Prlj and Clémence Corminboeuf; Institute of Chemical Sciences and Engineering, Ecole polytechnique fédérale de Lausanne (EPFL), Lausanne, Switzerland.

Within the last nine years, the power conversion efficiency of perovskite solar cell (PSC) has soared to 22.7% [1]. Among recently proposed high-performance PSCs, hole transport layers have proved to be essential components for these devices [2]. A promising HTM should possess a suitable ionization potential (IP) to enlarge the open-circuit voltage (V_{oc}); meanwhile, it should transport charge carriers efficiently from the perovskite/HTM interface to the electrode [3]. In contrast to this well-known design principle, a comprehensive understanding of the structure-property relationship remains lacking, especially for the challenging relationship between molecular structure and mobility. The discrepancy of knowledge in these two aspects hampers the discovery pace of promising HTMs. As a result, investigating the non-trivial structure-mobility relation with the aid of computer simulations at a molecular level would be beneficial. Our recent work on a prototype HTM, TPAC-3M [4], demonstrated that increasing the number of “carbazole side arms” (mono- to tri- arm) attached to a triphenylamine (TPA) core enhances the mobility by approximately 5 times by lowering the reorganization energy and the energetic disorder. Further optimization of the IP of the high-mobility tri-arm HTM by substituting methoxy groups with various other electron-withdrawing groups results in HTMs with desirable energy alignments with the perovskite materials. Care should be taken, however, as an enormous molecular dipole moment can result from IP-tuning, which magnifies the energetic disorder and leads to a mobility loss of more than one order of magnitude. After a thorough investigation, we propose a new tri-arm molecule containing pyridine substitutions, that possesses enhanced hole mobility and a suitable IP. Moreover, the pyridine moiety can also serve as a Lewis base that passivates the surface defects of perovskite, which reduces charge recombination at the perovskite/HTM interface [5].

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ET04.03.19

Effect of Fabrication Methods of Metal Oxide Layers on the Carrier Transport Properties of Perovskite Solar Cells II Takamasa Takeuchi, Hiroya Kiuchi, Kazunori Ito, Masato Gocho, Toshiya Kobayashi, Yuki Fukazawa and Hironori Ogata; Hosei University, Koganei, Japan.

Perovskite solar cells are an important photovoltaic technology with high efficiencies exceeding 20% due to their optimal band gap, large absorption coefficient, and high charge mobilities. We focused on the electron transport layer (ETL) in perovskite solar cells, which is one of the important parts for high performing perovskite solar cells. Focusing attention on the fabrication method of ETL, the electrodeposition method, the spray pyrolysis method and the spin coating method were reported so far. However, there are no detailed reports that systematically investigate and compare the effects of these preparation methods on the crystallinities, interface structures, interface levels and charge transport properties. In this study, we have used titanium oxide as the electron transport layer and compared the morphologies, defect structures, the interface structure, the interface state and the electron transporting properties and photovoltaic properties of the titanium oxide thin film fabricated by different production method by changing various controlling parameters. Furthermore, their film thickness dependences were systematically investigated.

ET04.03.20

Charge Transport Properties of Doped Tin Oxides Layers in Efficient Perovskite Solar Cells Hiroya Kiuchi, Takamasa Takeuchi, Kazunori Ito, Masato Gocho, Toshiya Kobayashi, Yuki Fukazawa and Hironori Ogata; Hosei University, Tokyo, Japan.

In the process of manufacturing perovskite solar cells, the electron transport layers prepared by low-temperature process are desired for large-scale production of perovskite solar cells. In general perovskite solar cells, titanium oxide is widely used as the electron transport layers (both compact layer and mesoporous layer). However, high temperature treatment is necessary for the fabrication of TiO₂ layer. On the other hand, SnO₂ can be fabricated at lower temperature than TiO₂. In addition, SnO₂ has a wide band gap energy, high electron mobility and is considered to be one of promising electron transport layers in perovskite solar cells. Perovskite solar cells using SnO₂ as electron transport layer have been reported so far. However, their conversion efficiencies are lower than those using TiO₂. Further improvement of solar cell characteristics is expected by doping to SnO₂ layer. There are several reports on doped SnO₂ ESLs through replacing Sn⁴⁺ ions with suitable dopant elements such as Mg, Li, Y, and Nb for applications in PSCs. In this study, we have fabricated perovskite solar cells by combination of various hole blocking layers and doped SnO₂ electron transporting layer and investigated their charge transport properties and solar cell performances systematically. Detailed experiment results will be presented.

ET04.03.21

Thermal Stability of Polycrystalline Hybrid Perovskite Thin Films Dominated by Grain Boundary Ruihan Yang, Yafei Wang and Shibin Li; University Of Electronic Science And Technology Of China, Chengdu, China.

Perovskite solar cells (PSCs) have been developed rapidly with power conversion efficiencies (PCE) rushing from 3.8% to a certified 22.1%. Accompanied with the improvement of PCE, the stability of perovskite has become a focus recently. Thermal instability of hybrid perovskite thin films is one of the important issues that must be overcome on the way to commercialization of PSCs, and then it's essential to deeply understand the degradation mechanism of perovskite thin films caused by thermal instability.

In this work, we studied the dependence of thermal stability of CH₃NH₃PbI₃ (MAPbI₃) crystals on grain size. We fabricated MAPbI₃ films by anti-solvent one-step deposition method and increased the grain size by IPA solvent annealing. According to the SEM, XRD and UV-Vis absorption measurements, it was demonstrated the thermal stability of polycrystalline hybrid perovskite thin films dominated by grain boundaries (GBs). The grain size plays a key role in the thermal degradation of the MAPbI₃. It was found that degradation rates of MAPbI₃ films in thermal environment are sensitive to the grain size and temperature. MAPbI₃ films with larger grain sizes and less GBs have a better resistance to heat-transfer. To further understand the degradation mechanism of perovskite crystals, a molecular model was put forward. The dangling bonds in GBs were considered to promote the process of thermal decomposition. Thus MAPbI₃ films with less GBs exhibit higher thermal stability. Meanwhile, solar cell devices with a structure of FTO/TiO₂/meso-TiO₂/MAPbI₃/PTAA/Au were fabricated and J-V curves of PSCs were measured to compare the photovoltaic performance of PSCs. The highest efficiency of PSCs increased from 16.87% to 18.56% with the increase of grain size. The results indicate that the reduction of GBs of perovskite is a feasible way to improve the thermal stability of PSCs.

ET04.03.22

Multi-Layered Thin Film Encapsulation for Perovskite Solar Cells via Low-Temperature Plasma-Enhanced Atomic Layer Deposition Seong Hyun Lee¹, Jung Wook Lim^{1,2}, Gayoung Kim^{1,2} and Man Gu Kang^{1,2}; ¹ICT Material Research Group, Electronics and Telecommunications Research Institute, Daejeon, Korea (the Republic of); ²Department of Advanced Device Engineering, University of Science and Technology (UST), Daejeon, Korea (the Republic of).

The performance of perovskite solar cells (PSCs) has dramatically improved over half a decade, and a record efficiency of 22.7% for a cell with an active area of less than 0.1 cm² has been achieved. However, the stability against moisture is essential for viability in the commercial market. Many efforts have been devoted to modifying the stability of either the perovskite material itself or the electron and hole transport layers but the fundamental solutions have not been found to date. Therefore, the encapsulation technologies have received a considerable amount of attention for the long-term stability of PSCs. In this study, we investigated the multi-layered encapsulation thin films deposited by low-temperature plasma-enhanced atomic layer deposition (PEALD). The multi-layered encapsulation films consist of Al₂O₃ and SiO₂ layer which have high moisture barrier properties. We optimized the thickness of each layers and the number of layer interfaces of the encapsulation layers to reduce the water vapor transmission rate (WVTR). Through the MOCON test, it was demonstrated that the WVTR of Al₂O₃/SiO₂ multi-layered encapsulation film with a 100 nm-thick is lower than that of Al₂O₃ and SiO₂ single-layered encapsulation film with the 100 nm-thick. And, in the case of multi-layered encapsulation, it was indicated that the number of Al₂O₃/SiO₂ interfaces strongly affects the values of WVTR.

Based on above results, we applied the multi-layered encapsulation to PSCs and investigated the moisture stability of the PSCs with respect to the process temperature, film thickness and process sequences of the multi-layered encapsulation thin films. And we explored the effect of plasma damage on the performance and moisture stability of the PSCs during the PEALD process. Furthermore, we will discuss the performance degradation of large-scale PSC modules with the Al₂O₃/SiO₂ multi-layered encapsulation under damp heat conditions consisting in 85 °C and 85 % relative humidity, during a period of 1000 hours. This work would pave the way for the commercialization of the practical PSC modules in the near future.

ET04.03.23

Interconnection Optimizations for Efficient Perovskite Solar Modules Zhen Li^{2,1}, Mengjin Yang¹, Donghoe Kim¹, Talysa Klein³, Maikel van Hest³ and Kai Zhu¹; ¹Chemistry and Nanoscience Center, National Renewable Energy Laboratory, Golden, Colorado, United States; ²State Key Laboratory of Solidification Processing, Center for Nano Energy Materials, School of Materials Science and Engineering, Northwestern Polytechnical University and Shaanxi Joint Laboratory of Graphene (NPU), Xi'an, China; ³Materials Science Center, National Renewable Energy Laboratory, Golden, Colorado, United States.

Small area perovskite solar cells (PSCs) have achieved power conversion efficiency (PCE) comparable to other thin film solar cells. Pushing PSC technology toward commercialization requires developing large-area perovskite solar modules with fully scalable deposition approaches. A fully scalable deposition scheme for perovskite module fabrication was demonstrated using spray coating for TiO₂ electron transport layer (ETL) and blade coating for both perovskite absorber layer and spiro-OMeTAD hole transport layer (HTL). It is found that the interconnections between sub-cells in the PSC modules are important for achieving high performance and reliability. Due to the difficulty of removing TiO₂ layer by scribing, the interconnection between sub-cells contains a TiO₂/metal junction. The TiO₂/metal junction shows a schottky diode or ohmic contact behavior, depending on the thickness of the TiO₂ layer. Optimization of the interconnection contact achieves better module performance, mainly contributed from improved fill factor. Finally, we demonstrated a highly efficient 4-cell MA_{0.7}FA_{0.3}PbI₃ perovskite module with a stabilized PCE of 15.6% measured from an aperture area of ~10.36 cm², corresponding to an active-area PCE of 17.9% with a geometric fill factor of ~87.3%.

ET04.03.24

The Abnormal Synergetic Effect of Organic and Halide Ions on the Stability and Optoelectronic Properties of Mixed Perovskite via *In Situ* Characterizations Mingzhu Long, Tiankai Zhang and Jianbin Xu; Chinese University of Hong Kong, Hong Kong, China.

The mixed cation lead mixed halide perovskite (MLMP) $\text{Cs}_x\text{FA}_{1-x}\text{PbI}_3\text{Br}_{3-y}$ is one of the most promising candidates for both single-junction and tandem solar cells applications due to its high efficiency and remarkable stability. However, the composition effect on thermal stability and photovoltaic performances has not yet been comprehensively investigated. Therefore, the interplay between composition, crystal structure, morphology and optoelectronic properties under heat stress, were systematically elucidated here through a series of *in situ* characterizations. It is revealed for the first time that the FA and Br would release synchronously at first even under mild annealing. This release leads to serious FA- and Br-deficiency issue, with only 88.3% of Br and 90.2% of FA retained after annealing at 100 °C, which significantly magnifies the hysteresis, phase segregation and instability issues of the MLMP solar cells. Finally, a trace amount of FA^+ and Br^- in tert-butanol was introduced onto the post-annealed MLMP surface to compensate for the deficiency through a vacancy filling process. The degradation lifetime to 80% of the initial efficiency (t_{80}) is remarkably improved and the hysteresis issue is also well resolved. This work highlights the importance of the synergetic composition effect of the organic cation and halide anion on stability and efficiency optimization for long-term applications.

ET04.03.25

Acetamidinium Substituted Methyl Ammonium Perovskite Cells with Higher Open-Circuit Voltage and Improved Intrinsic Stability Pallavi Singh, Rudra Mukherjee and Sushobhan Avasthi; Indian institute of Sciences Bangalore, Lucknow, India.

Methylamine lead halide perovskites suffer from a high degradation rate of $>0.1\% \text{ h}^{-1}$. Some of this degradation is extrinsic, e.g. exposure to humidity, which can be minimized via device encapsulation. However, perovskite is also intrinsically unstable, even in completely encapsulated conditions hybrid perovskite degrade at the temperatures $>80^\circ\text{C}$, mainly due to the organic component i.e., methyl ammonium ion (MA). In this work, we report a novel mixed-cation perovskite with 40% acetamidinium (AA) cation in the MAPbI_3 matrix. Unlike MA cation, the AA cation has a restricted C-N bond rotation due to delocalized π -electron cloud over N-C-N bond. This results in stronger hydrogen bonding that enhances the intrinsic stability of the lattice. $\text{MA}_x\text{AA}_{1-x}\text{PbI}_3$ thin-films with 5%, 10%, 20% and 40% AA are synthesized in the same manner as MAPbI_3 with AAI precursor added to the precursor solution in the stoichiometric ratio. Spin-coated films are annealed at 100°C to obtain black coloured $\text{MA}_x\text{AA}_{1-x}\text{PbI}_3$ films. The XRD pattern shows a monotonic shift in 2θ peak from 14.24 to 14.02 when we increase the AA% in perovskite matrix from 0 to 20%, however, we see the presence of some other secondary phases like AAPbI_3 when AA% is $>10\%$. Further, post-treatment of the as deposited film with methylamine vapor suppresses the secondary phases. In addition, it also improves the grain sizes from about 200 nm needles to 1-2 μm grains with complete surface coverage in accordance with a literature. The improvement in the film quality also reflects in the increase in the carrier lifetimes to 37 μs for 10% AA substituted films compared to 25 μs for the standard MAPbI_3 films. Further, 12 devices with $\text{FTO}/\text{c-TiO}_2/\text{m-TiO}_2/\text{MA}_{0.9}\text{AA}_{0.1}\text{PbI}_3/\text{Spiro-OMeTAD}$ structure were fabricated. An increase in the open-circuit voltage was observed for the AA substituted devices having V_{oc} in the range of 1.04 – 1.08 V against 0.96 – 1.01 V of the standard MAPbI_3 devices. Also, the fill-factors of the AA cells increased to 0.73 – 0.75 against 0.67 – 0.69 of the MAPbI_3 devices. But the short-circuit currents of the AA devices fell to 15 – 19 mA/cm^2 from 21 – 22.5 mA/cm^2 of the standard devices. The thicknesses and absorption spectra of the films are currently under investigation to account for the decrease in the J_{sc} . The overall PCE of the AA devices came out to be 13.2% against 14.53% of the standard devices. Increasing the thickness of the AA substituted films will increase the J_{sc} of the devices possibly without affecting the V_{oc} owing to their higher carrier lifetimes, thus providing scope for higher PCE's. Also, thermal degradation measurement shows that as expected, AA substituted films are more stable than pure MAPbI_3 films. While pure films lose their color and luster in just 32 hours at 120°C , $\text{MA}_x\text{AA}_{1-x}\text{PbI}_3$ films retain the black phase. The thermal stability measurements of the fabricated devices are underway.

SESSION ET04.04/ET02.05: Joint Session: Perovskite and Silicon Solar Cells

Session Chairs: Antonio Abate and Stefaan De Wolf

Tuesday Morning, November 27, 2018

Hynes, Level 3, Room Ballroom C

8:00 AM ET04.04.01/ET02.05.01

Light Management in Perovskite/Silicon-Heterojunction Tandem Solar Cells—Influence of Texture Position on Efficiency and Energy Yield Marko Jošt¹, Eike Köhnen¹, Benjamin Lipovsek², Amran Al-Ashouri¹, Klaus Jäger¹, Anna B. Morales-Vilches¹, Janez Krc², Lars Korte¹, Marko Topic², Bernd Rech¹, Bernd Stannowski¹ and Steve Albrecht¹; ¹Helmholtz-Zentrum Berlin, Berlin, Germany; ²LPVO, University of Ljubljana, Ljubljana, Slovenia.

Monolithic perovskite/silicon-heterojunction (SHJ) tandem solar cells have already shown that efficiency-wise they can compete with high efficiency silicon single junction cells; just recently a result with efficiency above 25% has been certified and published [1]. To further increase the tandem device performance to a level well above the best silicon single junctions at 26.7%, optical optimizations as well as a detailed device understanding of this advanced tandem architecture need to be developed. The highest potential for the tandem design is to utilize a textured silicon bottom cell, however, wet chemical processing of the perovskite topcell on top of the textured surface is challenging [1]. A solution could be in applying a textured foil onto a flat top-cell (or frontside) to improve light management as we have recently shown for perovskite single junctions [2]. Here we present how light trapping from textured surfaces changes the optics and with that the efficiency and also energy yield of monolithic tandem solar cells. By implementing a textured foil on a planar tandem solar cell front, we enabled a power conversion efficiency above 25.0%. This experimental achievement was realized by photocurrent enhancements due to light-trapping and -incoupling. The experimental results were verified with optical simulations to validate the correctness of the simulations. Based on the simulations we show the influence of the texture position and their respective efficiency differences also under non-ideal illumination conditions, such as high angle of incident light. Interestingly, we find that a planar front side with textured foil shows $< 1\%$ absolute less efficiency under STC conditions. To enable a high energy yield at all angles of illumination, we find that it is important to utilize textured front surfaces either by textured wafers or textured foils and we give guidelines to optical optimization of perovskite/silicon tandem devices.

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8:15 AM ET04.04.02/ET02.05.02

Towards CIGS Perovskite Tandem Cells Jesper Jacobsson¹, Adam Hultqvist², Håkan Rensmo² and Gerrit Boschloo¹; ¹Chemistry, Uppsala University, Uppsala, Sweden; ²Uppsala University, Uppsala, Sweden.

Perovskite solar cells will have a hard time to reach competitiveness with respect to conventional PV-technologies; unless they are integrated in tandem-architectures that possibly could outperform single junction silicon cells. One interesting potential perovskite tandem companion is CIGS, $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$, which is a commercial thin film technology with record efficiencies above 22 % and a variable band gap. In this project, we strive for constructing efficient 2-terminal CIGS-perovskite tandem cells. We will here discuss progress and challenges connected to recombination layers, perovskite engineering, and transparent top contacts in CIGS-perovskite tandem architectures.

8:30 AM ET04.04.03/ET02.05.03

Thermal, Oxidative, and Operational Stability in Low Band Gap Tin-Lead Perovskite Solar Cells for Robust All-Perovskite Tandems [Rohit Prasanna](#)¹, Tomas Leijtens¹, Aryeh Gold-Parker¹, Eli Wolf¹, James A. Raiford¹, Stacey F. Bent¹, Michael F. Toney¹ and Michael McGehee^{1,2}; ¹Stanford University, Stanford, California, United States; ²Chemical Engineering, University of Colorado Boulder, Boulder, Colorado, United States.

Low gap ABX_3 perovskites tin and lead at the B-site are a breakthrough that have enabled fabrication of efficient all-perovskite tandem solar cells. However, tin is susceptible to oxidation to the 4+ state, a degradation pathway unique to tin-containing perovskites. Suppressing this oxidation reaction is essential to ensure that highly efficient all-perovskite tandem solar cells are also stable against long term environmental stressors. We identify the specific chemical mechanism by which pure tin-based perovskites undergo oxidation using a combination of chemical methods including thermogravimetric analysis and solvent extraction of degradation products. We find that the oxidation reaction depends on a cooperative mechanism that involves simultaneous oxidation of multiple adjacent tin iodide octahedra. Critically, the most favorable oxidation pathway is blocked by substitution of 50% or more of the B-site with lead because this significantly lowers the chances of there being multiple adjacent tin octahedra that can facilitate the cooperative mechanism. As a result, the stability of tin perovskites toward oxidation is improved by orders of magnitude upon alloying with lead. The resulting guideline is that low band gap perovskites can be designed to have significantly enhanced oxidative stability by keeping the tin fraction at 50% or below.

We proceed to design solar cells to withstand aging under elevated temperatures in air. We probe the thermal stability of high-performing low band gap solar cells by aging at 85 C in air. Encouragingly, there is no measurable change in the bulk absorption of the perovskite absorber under thermal aging in air, indicating that the strategy of suppressing oxidation by using a mixed tin-lead perovskite successively avoids oxidative breakdown. However, the fill factor drops due to the formation of an S-kink after 100 hours of aging. We develop a treatment of the tin-lead perovskite film by exposure to methylammonium chloride vapour that results in significant grain growth and healing of cracks between grains. This post-treatment drastically improves the thermal stability of the full solar cells. Using an MAI-vapour-treated low gap perovskite with 50% tin, capped with a sputtered Indium Tin Oxide (ITO) top electrode, we successfully demonstrate a solar cell that maintains its full power conversion efficiency for 150 hours in air at 85 C, and remains above 85% of initial PCE for over 300 hours. In addition, we demonstrate stable operation of a tin-lead solar cell at maximum power point under 1-sun illumination for over 100 hours with no drop in performance. These measurements are a huge improvement upon any thermal stability results reported for tin-containing perovskites. The fact that good thermal stability in air is achieved with no encapsulation represents a major step toward proving the long-term stability of tin-lead low band gap perovskite solar cells, and of efficient all-perovskite tandem solar cells.

8:45 AM ET04.04.04/ET02.05.04

What Makes an Economically Successful Tandem? [Ian Marius Peters](#), Sarah Sofia and Tonio Buonassisi; Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

Two conflicting characteristics compete where the commercial viability of one-sun tandem solar cell is concerned: On the one hand, tandem solar cells have fundamentally higher efficiencies than single junction solar cells. On the other hand, tandem solar cells are intrinsically more complex than single junction solar cells and require more fabrication steps, which makes them more expensive. Only if the benefit from the additionally generated energy outweighs the higher fabrication cost can tandem solar cells be successful.

The question under which conditions the last sentence is true is a multilayered one. The value of efficiency is highest when considering the integrated PV system, which makes it necessary to explore system level aspects. These aspects include, among others, economic considerations as well as topics from material science; for example degradation.

In this work we attempt to provide an overview of what is needed to make tandem solar cells economically successful. Central to our findings is the concept of a “marriage of equals”, which states that the sub cells in a tandem should be similar, as well as enable high efficiencies. We will take a look at different material pairings, including perovskite on silicon, III-V on silicon and thin-film on thin-film tandems and investigate how these tandems compare to single junction solar cells in various types of systems and various locations.

We find that under the right circumstances one-sun tandem solar cells can outperform single junction solar cells economically. Yet more than techno-economic considerations are needed to make these types of solar cell a wide-spread reality. As an outlook we hope to offer a perspective of future opportunities for this technology.

9:00 AM *ET04.04.05/ET02.05.05

Designing Metal Halide Perovskites Solar Cells to be Stable for High Efficiency Tandems [Michael D. McGehee](#); Department of Chemical Engineering, University of Colorado Boulder, Boulder, Colorado, United States.

The talk will begin by showing what we have done to make perovskite on silicon tandem solar cells with 25 % efficiency and how 30 % efficiency can probably be obtained in the coming years. Then the challenge of making solar panels with metal halide perovskite semiconductors that will last for more than 25 years will be addressed. We will show that packaged solar cells can survive industry standard reliability tests such as 1000 hrs at 85°C and 85% humidity, 200 temperature cycles between -40°C and 85°C, and ultraviolet exposure. The strategies for making stable perovskite cells include choosing perovskite compositions that have higher thermal and oxidative stability, managing stress during the formation of the film to prevent buckling that makes subsequent processing difficult, minimizing tensile stress in the final film since it appears to make bonds weaker, using solution processing of the top contact layer to fill in gaps at grain boundaries so that a sputtered transparent conducting oxide layer can form a superb barrier layer, using polyolefin as the encapsulant since it does not chemically react with the perovskite and has an ideal elastic modulus, using butyl rubber edge seals and using glass on glass packaging.

9:30 AM BREAK

10:00 AM *ET04.04.06/ET02.05.06

High Efficiency Perovskite/Silicon Tandem Solar Cells [Kylie Catchpole](#); Australian National University, Acton, Australian Capital Territory, Australia.

Combining perovskites with well-established photovoltaic materials such as silicon or CIGS is an attractive option for producing cheap, high efficiency and high voltage solar cells. Perovskite-based tandem solar cells can potentially achieve over 30% tandem efficiency. We demonstrate a 4-terminal tandem

perovskite-silicon configuration in which the efficiency is as high as 26%. We also demonstrate a two-terminal monolithic tandem device with a perovskite top subcell and a high-temperature tolerant homojunction c-Si bottom subcell, with an efficiency of over 22%, and a perovskite/CIGS tandem with an efficiency of over 23%, which is the highest efficiency that has been reported for this configuration. We describe the optical and electronic factors that have been instrumental in reaching these efficiencies. We also show that interface passivation can lead to open circuit voltages over 1.2V for a 1.6eV bandgap perovskite, and that semi-transparent cells can achieve high stability under combined heat and light. These results show the clear potential of perovskites in practical high efficiency tandem devices.

10:30 AM *ET04.04.07/ET02.05.07

Optimizing Interfacial Layers on Silicon Heterojunction Bottom Cells for Perovskite/Silicon Tandem Solar Cells with 25% Power Conversion Efficiency and Beyond Lars Korte, Anna B. Morales-Vilches, Luana Mazzarella, Eike Köhnen, Philipp Tockhorn, Lukas Kegelmann, Ganna Chistiakova, Mathias Mews, Bernd Stannowski and Steve Albrecht; Helmholtz-Zentrum Berlin, Berlin, Germany.

With open circuit voltages (V_{oc} s) above 730 mV, silicon heterojunction (SHJ) solar cells are promising candidates for the bottom cells in organic-inorganic lead halide perovskite/silicon tandem solar cells. Using simulation studies, we have shown that under realistic assumptions, power conversion efficiencies up to 30% should be achievable with such devices [1]. To attain this goal, starting from first devices with moderate stabilized efficiencies of 18.1% [2] we carefully optimized the optical and electrical properties of the device in order to achieve low parasitic absorption and reflection, photocurrent matching between the two sub-cells and lowly resistive current transport across the internal tunnel-recombination junction.

In this presentation, I will discuss how we were recently able to demonstrate certified 25% efficient perovskite/SHJ tandem cells [3] by addressing these issues. I will focus on the silicon bottom cell and contact stack optimization: Starting from a rear junction SHJ cell design on double side textured wafers with 22.6% power conversion efficiency ($j_{sc} = 38.3$ mA/cm², $V_{oc} = 731$ mV, FF = 80.6 %) [4], we developed a rear side only-textured SHJ cell, which allows to process the perovskite top cell using conventional spin-coating methods. Optimizing film thicknesses at the perovskite/SHJ interface and tuning the refractive index of the nc-SiO₂:H film used as front surface field in the SHJ to an intermediate value of ~2.6 (at 800 nm) were instrumental in achieving 25% efficient cells with photocurrents above 17.8 mA/cm². On this basis, I will briefly discuss the potential to further enhance device performance using alternative deposition methods, such as plasma-enhanced ALD for tin oxide interlayers, and alternative materials such as tungsten oxide alloys for carrier selective contacts.

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11:00 AM *ET04.04.08/ET02.05.08

Progress on Si Tandems Anita Ho-Baillie¹, Hamid Mehrvarz¹, Jianghui Zheng¹, Fajun Ma¹, Chuq Yi¹, Stephen Bremner¹, Shujuan Huang¹, Hidenori Mizuno² and Tyler J. Grassman³; ¹Australian Centre for Advanced Photovoltaics, The University of New South Wales, Sydney, New South Wales, Australia; ²Fukushima Renewable Energy Institute, National Institute of Advanced Industrial Science and Technology, Fukushima, Japan; ³The Ohio State University, Columbus, Ohio, United States.

Tandem solar cell is a promising approach for achieving high efficiencies for photovoltaics [1]. The challenge is to find an efficient, economical and stable technology for each cell stack to realize true savings in the system's levelised cost of energy. Nevertheless, substantial progress has been made in the demonstrations of two-terminal Si tandem cells. The advantage of 2-terminal over 4-terminal configuration is the reduced complexity in wiring and packaging [2]. The challenge lies in the integration of the cell stacks without electrical and optical losses.

Recently, a simple perovskite/Si tandem cell structure has been reported [3]. It does not require additional interface layer for the integration of perovskite and Si cells. Instead, the electron transport layer in the perovskite top cell serves as the recombination layer between the top and bottom sub cells. The lack of lateral conductivity in this recombination layer means undesirable shunts are effectively localized. Another advantage of this structure is its compatibility with homo-junction Si cells – the most common choice for incumbent commercial Si photovoltaic technology. Recent optimizations have improved cells' performance from 20.5% to 22.7% on 4cm².

Great progress has been made on 2-terminal III-V/Si and III-V/Si tandems via wafer bonding and direct growth. Many of these tandem cell structures require smooth interface negating the use of textured Si bottom cell. This means external measures are required for anti-reflection and light trapping. Strategies for improving the optical performances of InGaP/GaAs/Si tandem by SmartStack [4] and monolithic epitaxial GaAs/Si tandem [5] will be presented in this talk.

[1] S. Bremner, C. Yi, I. Almansouri, A. Ho-Baillie, M. Green, *Solar Energy* 2016, 135, 750.

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11:30 AM *ET04.04.09/ET02.05.09

Textured Monolithic Perovskite/Crystalline Silicon Tandem Solar Cells with >25% Power Conversion Efficiency Jeremie Werner¹, Florent Sahli¹, Brett Kamino², Matthias Bräuninger¹, Raphaël Monnard¹, Gizem Nogay¹, Philippe Wyss¹, Andrea Ingenito¹, Bertrand Paviet-Salomon², Loris Barraud², Laura Ding², Juan Diaz Leon², Gianluca Cattaneo², Arnaud Walter², Soo-Jin Moon², Terry Chien-Jen Yang¹, Peter Fiala¹, Fan Fu¹, Mathieu Boccard¹, Matthieu Despeisse², Bjoern Niesen², Sylvain Nicolay², Quentin Jeangros¹ and Christophe Ballif^{1,2}; ¹Photovoltaics and Thin-Film Electronics Laboratory (PV-Lab), Ecole Polytechnique Fédérale de Lausanne (EPFL), Neuchâtel, Switzerland; ²PV-Centre, CSEM, Neuchâtel, Switzerland.

As crystalline silicon (c-Si) solar cells are approaching their efficiency limit of 29%, novel solutions must be found to increase the competitiveness of Si photovoltaics compared to conventional energy sources. One of the most promising approaches lies in combining c-Si solar cells with a low-cost wide-bandgap top cell to form a tandem device. Organic-inorganic halide perovskite solar cells are particularly attractive candidates for top cells, showing high efficiencies with simple and potentially cost-effective device fabrication. Calculations have shown that the practical efficiency potential of perovskite/c-Si tandem solar cells is beyond 30%.

Here, we present perovskite/silicon tandem devices featuring fully textured bottom cells, through a careful control of the top cell deposition conditions and

hence of the optoelectronic properties and interfaces of the different materials. These cells were employed as a platform to address the most crucial questions for tandem development:

- **Reaching maximal performance:** fully conformal perovskite top cells were developed and optimized, enabling the use of industrially viable textured bottom cells for maximal optical performance given the reduced reflection losses and enhanced light trapping. This enabled current-matching conditions with >20 mA/cm² in both the perovskite and silicon subcells (excluding metallization-induced shadow losses). Parasitic absorption was minimized thanks to the development of highly transparent charge transport layers and electrodes. This optical optimization of the tandems led to a certified steady-state efficiency of 25.2% for an aperture area of >1 cm².

- **Up-scaling:** a nanocrystalline silicon intermediate recombination layer was developed to increase the shunt resistance and enable large-area tandem devices, achieving 13-cm² cells with a steady-state efficiency above 20%.

- **Silicon bottom cell technology:** we tested our process with different bottom-cell technologies (silicon heterojunction or tunnel oxide passivated contact) and reached $>25\%$ efficiencies on both cell types for an aperture area of >1 cm².

- **Industrially viable metallization:** a screen-printed silver (Ag) metallization method was developed for the front grid. It employs a low-temperature Ag paste that can be cured without affecting the perovskite properties.

- **Encapsulation and cell reliability:** an encapsulation process involving a glass/glass configuration with a butyl rubber edge sealant was developed. Encapsulated tandems were subjected to standard reliability testing conditions, including damp heat at 85 °C/85%RH and light soaking for 1000 hours.

Overall, these results suggest a path in the development of monolithic perovskite/silicon tandem solar cells with realistic efficiency potential $>30\%$ on large area with enhanced stability.

SESSION ET04.05/ET05.05: Joint Session: The Past, Present and Future of Halide Perovskites

Session Chairs: Michael Saliba and Yuanyuan Zhou

Tuesday Afternoon, November 27, 2018

Hynes, Level 3, Room Ballroom B

1:30 PM *ET04.05.01/ET05.05.01

Hybrid Halide Perovskite Semiconductors—An Historical Perspective David B. Mitzi; Duke University, Durham, North Carolina, United States.

Organic-inorganic perovskites enable a combination of useful organic and inorganic properties within a single molecular-scale composite and have attracted substantial interest for use within organic-inorganic electronic devices [1], in part due to the high carrier mobilities, long minority carrier lifetimes, tunable structures/band gaps, relatively benign defects and grain boundaries, and facile processing for systems based on Group 14 metals (e.g., Ge, Sn and Pb). Most recently, these materials have enabled unprecedented rapid improvement in performance within single junction photovoltaic (PV) devices, from an initial demonstration in 2009 [2] to levels with $>20\%$ power conversion efficiency and open circuit voltages >1 V [3]. This talk will provide an historical perspective on foundational work related to the organic-inorganic perovskite semiconductors, including discussion of crystal structure flexibility, semiconducting properties, film deposition approaches and electronic device applications of the three-dimensional and lower-dimensional perovskite structures [4,5]. Recent trends in the field, as they relate to application in photovoltaics and related devices, will also be coupled into this discussion.

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2:00 PM *ET04.05.02/ET05.05.02

Photovoltaics of Halide Perovskites and Perspectives of Extensive Applications from the Ground to the Universe Tsutomu Miyasaka; Toin University of Yokohama, Yokohama, Japan.

Lead halide perovskite absorbers have achieved high photovoltaic performance exceeding the efficiency of CIGS and CdTe and their long term stability against heat, moisture, and light are being improved by compositional engineering of perovskite and surrounding carrier transport materials. For industrial applications, thermal stability of perovskites and carrier transport materials is a critical issue in comparison with thermally highly strong inorganic solar cell (Si, CdTe, etc.). Metal oxide electron transport layers (ETLs) generally have advantage in higher thermal stability than organic ETLs. We have been working with TiO₂ ETL-based multi-cation perovskite cells, which yielded efficiency over 21% by ambient air solution processes.¹ Light intensity dependence of Voc shows ideality factor low enough ($n < 1.4$) for the perovskite solar cell to work as a high voltage power source even under weak light. Such merit meets a requirement in solar cell application to space satellite missions, which needs high photovoltaic performance even under very weak sunlight (Mars and Jupiter). We have examined the durability of perovskite solar cells which have thermally stable compositions comprising FA-based perovskites, TiO₂ ETL, and P3HT as hole transport layer (HTL). These cells exhibit good stability against thermal impact between temperature range between -80°C and $+100^{\circ}\text{C}$. We also confirmed very poor thermal stability of spiro-OMeTAD as a reference HTL. On exposure to high energy electron and proton radiations as accelerated conditions simulating long term space irradiations, the perovskite cells demonstrated high stability and tolerance, which are superior to those of Si and GaAs solar cells.² Space applications also require fabrication of lightweight flexible devices. Thin film substrate-based perovskite solar cells were fabricated by low-temperature multilayer coating methods using amorphous TiO_x as ETL, which yield efficiency up to 18%. Future perspectives of industrialization of perovskite photovoltaic devices will be discussed focusing on the durable composition of perovskite devices and advantage of lightweight thin film device.

References

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2:30 PM BREAK

3:00 PM *ET04.05.03/ET05.05.03

Perovskite Photovoltaics—History, Progress and Perspective [Nam-Gyu Park](#); Sungkyunkwan University, Suwon, Korea (the Republic of).

Since the first report on the high efficiency, stable solid-state perovskite solar cell (PSC) in 2012 by our group, following two seed works on perovskite-sensitized liquid junction solar cells in 2009 and 2011, PSC demonstrated its power conversion efficiency (PCE) of 22.7% in 2017. According to Web of Science, publications on PSC increase exponentially since 2012 and total number of publications reaches about 9,000 as of May, 2018, which is indicative of a paradigm shift in photovoltaics. Although high photovoltaic performance was achieved, current-voltage hysteresis has been issued because it is related to stability of PSC. In this talk, methodologies to remove hysteresis are described. Interlayers at heterojunction are found to play important role in reducing hysteresis and improving stability. Manipulation of Frenkel defect is a universal approach toward hysteresis-free PSC. We have discovered novel methods for large-area perovskite coating and phase transformation in perovskite, which will be discussed in detail. In addition to photovoltaics, perovskite can be used to other applications. Long charge diffusion length and high energy stability of organic-inorganic halide perovskite are suitable for low-dose, high resolution X-ray imaging. We demonstrated X-ray image using millimeter thick perovskite film based on multicrystalline perovskite crystal with single-crystal-like optoelectronic properties. For heading toward Shockley–Queisser limit, research direction in PSC is proposed in this talk.

3:30 PM *ET04.05.04/ET05.05.04

Compositional Engineering for Efficient and Durable Perovskite Solar Cells [Anders Hagfeldt](#); Laboratory of Photomolecular Science, Swiss Federal Institute of Technology Lausanne (EPFL), Lausanne, Switzerland.

In our work on perovskite solar cells (PSC) we have achieved efficiencies above 20% with a mixed composition of iodide/bromide and methyl ammonium/formamidinium [1]. For cells larger than 1 cm² we have obtained 19.6% [2], replacing the anti-solvent step in the perovskite film formation with a vacuum flash treatment. With the use of SnO₂ compact underlayers as electron acceptor contacts we have constructed planar perovskite solar cells with a hysteresis free efficiency above 20% [3]. The cation mixing strategy has been developed further by including the Cs in a so-called ‘triple cation’ composition, i.e. Cs/FA/Ma as well as Rb in a quadruple cation mixture. Larger grains grown in a monolithic manner are observed and for example reproducibility and device stability are improved [4]. At the meeting we will discuss our follow up works [5] and present our champion data; up to 22% efficiency with an external electroluminescence of 4%, and an outstanding open-circuit voltage of 1.24 V at a band gap of 1.63 eV entailing one of the smallest loss-in-potential of 0.39 V ever measured for any solar cell material. Furthermore, we will report promising stability at 85 °C for 500 h under full solar illumination and maximum power point tracking (during which 95% of the initial performance was retained). Recently, we have also commented on the standardization of PSC aging tests [6].

Keywords: Perovskite, composition, stability

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4:00 PM *ET04.05.05/ET05.05.05

Perovskite Solar Cells—The Path to a Printable Terawatt-Scale Technology [Kai Zhu](#); National Renewable Energy Laboratory, Golden, Colorado, United States.

Perovskite solar cells (PSCs) have become a competitive photovoltaic (PV) technology with rapid progress of efficiencies reaching to about 23%. Uniquely, PSCs have the highest efficiencies when they are solution processed, so one can envision solar cells printed in a similar manner and scale as newspapers. In addition, the bandgap tunability through perovskite composition engineering can enable high-efficiency multijunction devices, including perovskite/perovskite, perovskite/silicon, or perovskite/thin-film absorber (e.g., CIGS). Thus, PSCs are suited to helping address the challenge of terawatt-scale, PV-based electricity production that can power the future world. In this talk, I will discuss our recent progress in two areas: (1) scalable fabrication of high-efficiency, large-area perovskite solar cells and modules; (2) development of perovskite-based tandem devices. I will discuss our recent studies toward better control of film formation across the device stack at large scales by improving the precursor chemistry to better match the processing methods. The precursor chemistry and growth conditions affect significantly the physical and optoelectronic properties of perovskites. The challenges associated with perovskite solar module fabrication will be discussed. I will show the impact of interconnections on the performance of perovskite solar modules fabricated by scalable depositions. Toward perovskite-based tandem device development, I will discuss our recent effort on improving the optoelectronic properties of wide-bandgap as well as low-bandgap perovskite absorbers through solution chemistry engineering. Challenges and progress on perovskite-based tandem devices will also be discussed. These results demonstrate a promising path towards commercialization of the perovskite photovoltaic technology.

4:30 PM DISCUSSION PANEL: UNSOLVED PEROVSKITE PROBLEMS—OPPORTUNITIES AND CHALLENGES - DISCUSSION

LEADER: IVÁN MORA-SERÓ

SESSION ET04.06: Poster Session II
Tuesday Afternoon, November 27, 2018
8:00 PM - 10:00 PM
Hynes, Level 1, Hall B

ET04.06.01

Understanding the Doping Effect on NiO—Toward High-Performance Inverted Perovskite Solar Cells [Wei Chen](#)^{1,2}, Yinghui Wu¹, Aleksandra B. Djurišić² and Zhubing He¹; ¹Southern University of Science and Technology, Shenzhen, China; ²Physics, The University of Hong Kong, Hong Kong, Hong Kong.

Metal organic halide perovskite solar cells (PSCs) are emerging photovoltaic technology of significant interest due to their high power conversion efficiency (PCE), with record efficiency exceeding 22%. The use of inorganic hole transport layers (HTLs) in PSCs has been attracting increasing attention to improve the stability of the devices. Among various inorganic hole extraction/hole transport materials, NiO is of particular interest for PSC application. However, low intrinsic conductivity of NiO is a significant drawback, since it can result in hole accumulation near the perovskite interface, increasing the

chance of recombination and reducing the charge collection. Therefore, considerable efforts have been made to improve the charge collection by improving the quality of deposited NiO and/or doping the NiO to improve conductivity and charge collection.

In this abstract, we synthesized high-quality copper doped nickel oxide (Cu:NiO) nanoparticle as hole transport layers in inverted perovskite solar cells at room temperature without further processing. In agreement with theoretical calculations predicting that Cu doping results in acceptor energy levels closer to the valence band maximum compared to gap states of nickel vacancies in undoped NiO, an increase in the conductivity in Cu:NiO films compared to NiO is observed. Cu in Cu:NiO can be found in both Cu⁺ and Cu²⁺ states, and the substitution of Ni²⁺ with Cu⁺ contributes to both increased carrier concentration and carrier mobility. In addition, the films exhibit increased work function, which together with the conductivity increase, enables improved charge transfer and extraction. Furthermore, recombination losses due to lower monomolecular Shockley-Read-Hall recombination are reduced. These factors result in an improvement of all photovoltaic performance parameters and consequently an increased efficiency of the inverted planar perovskite solar cells. A power conversion efficiency (PCE) exceeding 20% could be achieved for small-area devices, while PCE values of 17.41 and 18.07% are obtained for flexible devices and large area (1 cm²) devices on rigid substrates, respectively.

ET04.06.02

High Performance of Hybrid Perovskite Solar Cells via Organic Fullerene Doping and Interfacial Modification He Jiang¹, Gelei Jiang¹, Jian Shao¹, Biao Wang^{1,2} and Yue Zheng¹; ¹State Key Laboratory of Optoelectronic Materials and Technologies, Sun Yat-Sen University, Guangzhou, China; ²Sino-French Institute of Nuclear Engineering and Technology, Sun Yat-sen University, Zhuhai, China.

Of particular interest in current organic-inorganic hybrid perovskite solar energy research field is how to improve the photovoltaic conversion efficiency with current great demand of renewable energy. Possessing well optical-electronic properties such as long carrier diffusion length, simple preparation technology and excellent light absorption, perovskite materials has been utilized in photovoltaic and electroluminescence field. Recently, a leap on the PCE of perovskite solar cells has been achieved with a rise from original 3.9 % up to more than 20 %.

Conventional organolead halide perovskite solar cell in form of n-i-p architecture is consisted of a FTO or ITO, mesoporous/compact TiO₂, perovskite absorb layer, Spiro-OMeTAD and electrode in sequence. With respect to conventional configuration, a phenomenon of non-overlapped current J-V curves under different scanning directions (i.e. hysteresis effect) appears in PCE measurement when the mesoporous scaffold is absent, mostly due to the capture of electrons from ineluctable oxygen vacancy in TiO₂ compact layer. Moreover, the solution-processed organolead halide perovskite, especially, the methylammonium (CH₃NH₃⁺) lead halides (Cl, Br and I), is usually adopted for the ease of manipulation during the fabrication process. However, it is inevitable to bring morphological and compositional defects when solution-processing technique is employed. Both defects mentioned above contribute to recombination and trapping of charge carriers, which present insufficient current density as well as hysteresis effect in device in practical application. Thus, the modifications of compact layer or interface improvement have been investigated extensively to eliminate the inherent defects. Furthermore, most of works focused on improvement of the transfer layers or adjusted the element composition in perovskite absorb layer, the optimizations of perovskite layer were seldom reported. Thus, it is still a paradox to suppress the grain boundary defects of perovskite by employing solution process even though one or two-step solution method is adopted.

In our work, we demonstrate a high current density and low hysteresis effect planar CH₃NH₃PbI₃ perovskite cell solar, which is achieved by employing the [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) as dopant to fill the CH₃NH₃PbI₃ surface grain boundaries, and TiO₂/PCBM bilayer is used as electron transport layer in the process of planar perovskite solar cells preparation. By investigating the PCBM doping concentration in CH₃NH₃PbI₃, the best concentration at 0.1 wt% is found and a current density as high as 22.6 mA/cm² (close to theoretical maximum, about 25 mA/cm²) with the best photoelectric conversion efficiency of 18.3 % in such PCBM-doped perovskite solar cell is also detected. This work provides a facile doping method to stuff the surface grain boundary defects and proposed further exploration in the field of solar cells.

ET04.06.03

Enhancing Power Conversion Efficiency and Charge Carrier Lifetime of Metal Halide Perovskite Solar Cells via Insulating Polymer Induced PbI₂ Passivation Yuchen Zhou¹, Likun Wang¹, Yifan Yin¹, Zhenhua Yang¹, Chang-Yong Nam² and Miriam Rafailovich¹; ¹Stony Brook University, Stony Brook, New York, United States; ²Center for Functional Nanomaterials, Brookhaven National Laboratory, Upton, New York, United States.

The metal halide perovskite solar cells (PSCs) with remarkable power conversion efficiency (PCE) have been unprecedentedly popular in the research community in past several years. The state-of-art PSCs require a smooth and pinhole-free perovskite layer. It has been proved that key characters of high-quality perovskites can be obtained through optimizing the kinetics of nucleation and growth of perovskite crystals. Despite of several successful practices of modifying the crystal formation process, the lack of precise controls over the structure makes these methods less repeatable. In this study, we utilized a simple but effective doping method by firstly introducing a small amount of insulating polymer of poly (lactic acid) (PLA) into the perovskite layer as a dopant. The benefits of doping PLA polymer came in 2-folds: 1) the PLA additive can serve as heterogenous nucleus for preferential formation and growth of perovskite crystals in 2D direction; and more importantly, 2) PLA can also introduce PbI₂ passivation via the bonding of electron donor -acceptor pairs between C=O and Pb²⁺. The bonds induced precipitation of PbI₂ would preferentially assemble at grain boundaries of perovskites during the process. It is believed that the passivation of controllable amount of PbI₂ at the boundaries can largely reduce the defects and trap states and benefit the overall cell efficiency. Characterizations based on x-rays diffraction and scattering (XRD and GIWAXS), microscopes (scanning electron microscopy and atomic force microscopy) and spectrometers (photoluminescence emission and lifetime decay spectrometer) were carried out to probe the morphology, structure and optical variation of the doped/passivated perovskites. Doing so, we were able to confirm the increase of crystal grain size, the presence of PbI₂ passivations and the extended charge carrier lifetime, etc, of our passivated perovskites. Finally, as compared with the original counterparts, the non-encapsulated devices of passivated perovskites were able to obtain 20% PCE enhancement when measured under the ambient condition, with the best PCE exceeding 18%. (This work was supported by the NSF, Inspire #1344267)

ET04.06.04

Improving Uniformity and Reproducibility of Hybrid Perovskite Solar Cells via a Low-Temperature, Vacuum Deposition Process for NiO_x Hole Transport Layers Seong Ryul Pae, Segi Byun, Jekyung Kim, Min Kyu Kim and Byungha Shin; Korea Advanced Institute of Science and Technology, Daejeon, Korea (the Republic of).

Recently, the trend in inverted hybrid perovskite solar cells (PVSCs) has been to utilize NiO_x as hole transport layers. However, the majority of reported solution-processed NiO_x films require a high-temperature thermal annealing process which is unfavorable for large-scale manufacturing and suffers from lack of uniformity. We report, for the first time, e-beam evaporation as a low-temperature, vacuum process for the deposition of NiO_x hole transport layers for PVSCs. Device characterization shows that efficiency is on par with solution-processed methods, the highest efficiency at 15.4% with no obvious hysteresis. Differences are found to be due to the presence of more Ni³⁺ in e-beam evaporated NiO_x which are responsible for a lower transmittance but higher conductivity. Most importantly, e-beam evaporated NiO_x-based PVSCs show greater uniformity and reproducibility compared to those of spin-coated NiO_x-based PVSCs. Finally, e-beam evaporated NiO_x has the additional advantage of being a low-temperature deposition process and being applicable over large areas. This work, therefore, represents a significant step towards large-area PVSCs where e-beam evaporation can be used for the low-temperature, uniform deposition of charge transport layers such as NiO_x.

ET04.06.05

Lead Free Methyl Ammonium Bismuth Iodide Based Perovskite Solar Cells—Optimization of Electron and Hole Transport Layers by Simulation and Analysis Towards Development of Tandem Configurations Jalen Harris¹, Leslie Maciel¹, Saquib Ahmed² and Sankha Banerjee¹; ¹California State University, Fresno, Fresno, California, United States; ²Mechanical Engineering, SUNY-Buffalo State College, Buffalo, New York, United States.

Perovskite solar cells are especially promising when considering the technology lifespan. The advantages of using perovskite for the active layer include but are not limited to broad a light absorption spectrum, tunable band gaps, long charge carrier diffusion, and low fabrication cost. The current project involves the design and simulation of different configurations of Methyl Ammonium Bismuth Iodide active layer based lead-free perovskite solar cell. The goal of the project is to develop a configuration that is non-toxic as well as stable in natural open air environments with a specific resistance to moisture. This design incorporates the use of organic and inorganic materials, as well as the efficient use of the perovskite crystalline structure that is produced by using the properties of Bismuth (III). The project also includes opto-electronic simulations of a variety of different configurations using two software packages. The configurations include perovskite layers using low toxicity alternatives of Pb: Bi and Mn. Different halide species has also been explored to evaluate the impacts on opto-electronics, and photon-to-current conversion efficiencies. The stacking structure is further modulated within the cell by progressively including a recombination-inhibiting thin TiO₂ of a ZnO layer with the FTO, followed by an electron-transport layer (various oxides). The aim of these studies is to delineate the sources and quantify the impacts of efficiency-limiting process such as recombination. This work is intended to build up to a broader project of selecting the most optimal low-toxicity perovskite cell to stack onto a Si or FTO bottom cell for tandem configurations.

ET04.06.06

In Situ Atmospheric Deposition of Ultra-Smooth Metal Oxides for Efficient Perovskite Optoelectronic Devices Baodan Zhao, Lana Lee, Richard H. Friend, Judith L. MacManus-Driscoll and Dawei Di; University of Cambridge, Cambridge, United Kingdom.

Owing to their remarkable photovoltaic performance, hybrid organic-inorganic perovskite solar cells have attracted tremendous research interest. The high efficiencies are enabled by the outstanding electronic properties of the hybrid perovskite materials. On the other hand, the design of the device structure, including the selection of electron- and hole- transport materials, determines how efficiently the photo-excited charge carriers can be selectively extracted from the perovskite absorber, ultimately influencing the energy conversion efficiency. The use of alternative metal oxide charge-transport layers is a strategy to improving device reliability for large-scale fabrication and long-term applications.

Here we demonstrate solution-processed perovskite solar cells employing nickel oxide hole-extraction layers produced in situ using an atmospheric pressure spatial atomic layer deposition (AP-SALD) system, which is compatible with high-throughput processing of electronic devices from solution. Our sub-nanometer-smooth (average roughness ≤ 0.6 nm) oxide films enable efficient collection of holes and the formation of perovskite absorbers with high electronic quality. Highly uniform, sub-nm smooth AP-SALD NiO_x films also improve the reproducibility of perovskite optoelectronic devices. Initial solar cell experiments show a power-conversion efficiency of 17%, near-unity ideality factor, and a fill factor of $> 80\%$ with negligible hysteresis. Transient measurements reveal that a key contributor to this performance is the reduced luminescence quenching trap density in the perovskite/nickel oxide structure. We also present perovskite green light-emitting diodes(LEDs) adopting AP-SALD NiO_x with an EQE $> 8\%$ and luminance over 10000 cd cm⁻². Further improvements are possible through the optimization of AP-SALD NiO_x growth.

ET04.06.07

Impact of Grain Size on Photovoltaic Performance in Halide Perovskite Solar Cells Ekyu Han², Dohyung Kim³, Jincheol Kim¹ and Jae Sung Yun¹; ¹School of Photovoltaic and Renewable Energy Engineering, University of New South Wales, Kensington, New South Wales, Australia; ²Korea Electronics Technology Institute, Seongnam, Korea (the Republic of); ³Materials Science and Engineering, University of New South Wales, Kensington, New South Wales, Australia.

The past two years have seen the uniquely rapid emergence of a new class of solar cell based on mixed organic-inorganic halide perovskite. Organic-inorganic hybrid materials have been demonstrated to be excellent photovoltaic materials having a large absorption coefficient, high carrier mobility, high carrier diffusion length, and direct band gap. Conversion efficiencies have increased from 3.8% in to 22.7%. Despite a rapid increase in the performance, there are still many unknown fundamental properties that requires further investigation. The perovskite film consists of large amount of grain boundaries due to its polycrystalline nature. There have been contradicting reports on the role of the grain boundaries in photovoltaic performance. Although it is originally known that the grain boundaries limit the effective diffusion length of the solar cells, recent studies performed by Kelvin Probe Force Microscopy showed that the grain boundaries have benign or even beneficial properties. In this work, we measure average grain size of halide perovskite films that has been reported in the literatures and plot with each photovoltaic parameter, i.e. Voc, Jsc, FF, and efficiency. We provide a mathematical model to examine the relevance between grain size and photovoltaic parameter and discuss its influence. Our findings suggest that the size of grain is not a key factor for improving the solar cell performance. Rather, specific chemical species exist at the grain boundaries tunes their properties which could enhance the macroscopic solar cell performance.

ET04.06.08

A Green Fabrication Route Avoiding the Usage of Toxic Solvents in Perovskite Solar Cells Liming Zhao^{1,2}, Xianyong Zhou¹, Deng Wang¹, Jian Wen¹ and Baomin Xu¹; ¹Southern University of Science and Technology, Shenzhen, China; ²University of California Irvine, Irvine, California, United States.

In recent years, organic-inorganic hybrid perovskite solar cells have attracted extensive attention, the photoelectric conversion efficiency (PCE) of which rose rapidly from 3.8% [1] to 22.7%, due to their impressive PCE, low cost and the ease of making flexible solar cells. However, most perovskite solar cells require the usage of toxic organic solvents during the manufacturing process, such as N,N-Dimethylformamide (DMF) [2], Dimethyl sulfoxide (DMSO) [3][4] and Chlorobenzene (CB) [2][4], which are prohibited in the commercialized production. Thus, how to avoid using these toxic solvents is a problem that needs to be solved urgently. Aimed at this problem, we developed a novel route to fabricate invert “p-i-n” perovskite solar cells without any toxic solvents. The structure of the perovskite solar cells is FTO/PEDOT:PSS/CH₃NH₃PbI₃/C₆₀/BCP/Ag. The perovskite layer was synthesized via two-step method by lead acetate trihydrate and methylamine iodine. We found a new eco-friendly solvent, glycerol [5] and 1-butanol component solvent, to dissolve lead acetate trihydrate, and methylamine iodine was dissolved in isopropanol. PEDOT:PSS and C₆₀ served as the hole transport layer and electron transport layer, respectively. C₆₀, BCP and Ag electrode were sequentially thermally deposited on the top of solar cells. The J-V test shows that the PCE of the solar cells with 0.1cm² reaches 4.84%. The XRD indicates that the CH₃NH₃PbI₃ synthesized by this route possesses a high purity. The FTIR shows that glycerol and 1-butanol can be removed just at low temperature, 110°C, which means that this method can be applied in flexible devices. The AFM images reveal that both lead acetate and perovskite layers obtained by this route have low roughness. It can be expected that this preparation technique offering a safe and non-toxic environment has a great potential to fabricate perovskite solar cells in the industrial assembly lines, such as roll-to-roll production.

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ET04.06.09

Light-Assisted Size- and Dimension-Control of Perovskite Nanocrystals and Their Optoelectronic Devices Qingfeng Dong; Jilin University, Changchun, China.

Perovskite Nanocrystal (NCs) offer simply solution synthesis and low-cost film forming process, which take advantages of quantum confinement effect and controlled size distribution, and show higher photoluminescence quantum yield (PL QY) and higher open circuit voltage in photovoltaic devices than perovskite thin film. Here, we developed lead halide perovskite NCs with controllable crystal structures and semiconductor properties by light soaking. The dimension and the size of perovskite NCs correlate with a soaking duration. Light soaking change the crystallization environment, inducing the formation of differently perovskites CsPbBr₃, Cs₄PbBr₆, or CsPbBr₃assembled in Cs₄PbBr₆. Bright perovskite mixture (CsPbBr₃@Cs₄PbBr₆) with the PL QY reaching 90% were employed for fabrication of light-emitting diodes (LEDs), with the peak external quantum yield of 8% and current efficiency of 20 cd A⁻¹. Since Cs₄PbBr₆ is insensitive to the atmosphere, the optical stability of the CsPbBr₃ within the Cs₄PbBr₆ was greatly improved, and thus the storage and operational stability, the enhanced stability also enable efficient photovoltaic devices with high environment stability.

ET04.06.10

Enhanced Performance and Mechanical Durability of a Flexible Perovskite Solar Cell from the Dry Transfer of PEDOT:PSS with Polymer Nanoparticles Jonghwa Lee¹, Jin Hyuck Heo², Sang Hyuk Im² and O Ok Park¹; ¹Korea Advanced Institute of Science and Technology, Daejeon, Korea (the Republic of); ²Department of Chemical and Biological Engineering, Korea University, Seoul, Korea (the Republic of).

Stamping transfer has been considered as an alternative process because of its various advantages such as a simple, flexible, and repeatable process, which is suitable for large area fabrication. In this research, Inverted-type CH₃NH₃PbI₃ flexible perovskite solar cells with enhanced cell performance and mechanical durability were fabricated by performing a simple dry transfer of a poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate) (PEDOT:PSS) hole transport layer (HTL) with polystyrene nanoparticles (PS NPs). In order to ensure the stable flexibility of these flexible solar cells, the cross-linked PS NPs synthesized with a size of 70nm were introduced to the PEDOT:PSS HTL. The transfer of the PEDOT:PSS layer with PS NPs onto the polymer electrode (PH1000) was performed completely via stamping transfer with polyurethane acrylate stamp. The power conversion efficiency of flexible perovskite solar cells prepared by the transfer of PEDOT:PSS with PS NPs was 16.8%, which was significantly higher than that of the spin-cast device. The charge transport from the active layer to the PEDOT:PSS HTL was improved by the tuned morphology of the PEDOT:PSS achieved through transfer and the increased surface area of the PEDOT:PSS resulting from the corrugated structure provided by the protruding PS NPs. This in turn resulted in an enhanced short-circuit current density. In addition, the introduced PS NPs significantly improved the mechanical stability of these flexible devices, allowing the devices prepared by the transfer of PEDOT:PSS with PS NPs to tolerate more cycles of strain in the bending test. The introduced PS NPs enhanced the mechanical strength of PEDOT:PSS by acting as not only binders within PEDOT:PSS, but also as interfacial modifiers which can improve the interfacial adhesion between the active layer and PEDOT:PSS HTL. Thus, the transfer of a PEDOT:PSS layer with PS NPs will contribute to the long-term operation of flexible solar devices with enhanced device performance and mechanical durability.

ET04.06.11

Metal Oxides Charge Transport Layers and Interface Tailoring for Highly Stable Perovskite Solar Cells Chao Zhao¹, Jia Zhang², Meng Li³, Adam Pockett¹ and Matt Carnie¹; ¹Swansea University, Swansea, United Kingdom; ²Harbin Institute of Technology, Harbin, China; ³Soochow University, Suzhou, China.

Solution processed hybrid organic-inorganic perovskite solar cells (PSCs) have recently attracted tremendous attention due to their ease of fabrication and excellent photovoltaic efficiency. However, challenges of long-term working stability under normal conditions of PSCs (i.e., perovskite material and/or the charge transport layers (CTLs)) are still existed. In this work, we achieved reasonable improved PSC stability with good performance by applying an interlayer (ionic-liquid and/or graphene based 2- dimension(2D) material) as either CTL modifying interlayer. Correlations between performance/characteristics of the PSCs and interlayers will be investigated. Performance of PSCs and their relation between carrier dynamics and material properties will be studied based on measurements of current density-voltage, quantum efficiency and transient. The initial study indicating interlayers/composite of the interlayer used in the devices will be a promising way to enhance stability and suppress carrier recombination in the whole PSCs, facilitate carrier injection into the carrier transport layers, and maintain a good carrier extraction at the electrodes, thus resulting a good PSC performance.

ET04.06.12

Ultrafast Room-Temperature Reactive Ion Etching Process for High-Efficiency Flexible Perovskite Solar Cells Byeong Jo Kim¹, Dong Geon Lee¹, Gill Sang Han¹, Sangwook Lee² and Hyun Suk Jung¹; ¹School of Advanced Materials Science & Engineering, Sungkyunkwan University, Suwon-Si, Korea (the Republic of); ²School of Materials Science and Engineering, Kyungpook National University, Deagu, Korea (the Republic of).

Perovskite solar cells (PSCs), which have surprisingly emerged in recent years, are now aiming at commercialisation. Rapid, low-temperature, and continuous fabrication processes that can produce high-efficiency PSCs with a reduced fabrication cost and shortened energy payback time are important challenges on the way to commercialisation. Herein, we report a reactive ion etching (RIE) method, which is an ultrafast room-temperature technique, to fabricate mesoporous TiO₂ (mp-TiO₂) as an electron transport layer for high-efficiency PSCs. Replacing the conventional high-temperature annealing process [A1] by RIE, reduces the total processing time for fabricating 20 PSCs by 40%. Additionally, the RIE-processed mp-TiO₂ exhibits enhanced electron extraction, whereupon the optimized RIE-mp-TiO₂-based PSC exhibits a power conversion efficiency (PCE) of 19.60% without *J-V* hysteresis. Finally, a flexible PSC employing the RIE-mp-TiO₂ is demonstrated with 17.29% PCE. Considering that the RIE process has been actively used in the semiconductor industry, including for the fabrication of silicon photovoltaic modules, the process developed in this work could be easily applied towards faster, simpler, and cheaper manufacturing of PSC modules.

ET04.06.13

Interface Engineering of Solution Processed Hybrid Organohalide Perovskite Solar Cells Shanshan Zhang; University of Queensland, Brisbane, New South Wales, Australia.

Rapid progress has been achieved in improving the power conversion efficiency (PCE) of organohalide perovskite solar cells (PVSCs), which have now reached 22.1%. Engineering the interlayers between the junction and electrodes has enabled enhancement of charge extraction efficiency and open-circuit voltage (V_{oc}), and reduction of device hysteresis. Herein, a simple oxygen plasma treatment is reported and used to change the surface energy and work function of “hydrophobic” organic semiconductor interlayers for perovskite solar cells. The UV-ozone treatment was also found to increase the semiconductor conductivity, which can lead to more efficient hole extraction. In this presentation, we report the effect of an oxygen plasma treatment on the surface energy, work function and device performance of four different *p*-type interlayers. After the plasma treatment, the “hydrophobic” surfaces of the different *p*-type polymers were found to have changed to “hydrophilic” and the ionisation potential (IP) increased to be closer to the IP of the perovskite active layer. Finally, the performance of inverted MAPbI₃ perovskite devices with treated interlayers will be discussed. The best perovskite solar cells were found to have a V_{oc} of 1.05 V, FF of 0.80, J_{sc} of 22.7 mA/cm² and PCE of 19%.

ET04.06.14

The Effects of Crystallization Rate on Metal-Halide Perovskite Film Formation by the Shear Coating Jihye Choe¹, Hansol Kim¹, Ji-Ho Song¹, Ji-Young Jeong¹, Choong-Heui Chung¹, Seung-Cheol Lee², Jaekyun Kim³ and Ki-Ha Hong¹; ¹Hanbat National University, Daejeon, Korea (the Republic of); ²Indo-Korea Science and Technology Center (IKST), Bangalore, India; ³Hanyang University, Ansan, Korea (the Republic of).

Metal-halide perovskite solar cells are considered as one of leading candidates for next-generation photovoltaics, exhibiting the excellent performance over 22% PCE (power conversion efficiency) in spite of its simple and low-cost solution process. Despite their excellence in PCE, the development of large-area coating technology is demanding to replace the spin coating for maximizing the benefits of solution-processed perovskite solar cells. Therefore, it is critical to find out other processes which replace spin coating and enable roll-to-roll (R2R) and continuous processes. Our prior studies presented that the shear coating process can be an efficient way to produce large-scale perovskite layers and the formation of smooth interface and surface is quite relevant to achieve higher device performance. Anti-solvent treatment is commonly adopted to make smooth perovskite films for the spin-coating process. However, anti-solvent cannot be adopted for R2R processes so that the solution engineering becomes essential to produce high-quality perovskite films. This study presents that the crystallization rate control of perovskite films is a crucial factor to realize the smooth surface film formation. We fabricate perovskite films by controlling the ratio of additives and substrate temperature, and then confirm the film roughness and existence of additive particles in the grain. The Solution engineering can control the perovskite crystallization kinetics. The effects of additives and the composition of precursor solution on crystallization kinetics during shear coating will be presented.

ET04.06.15

Study of Charge-Carrier Transport in Perovskite Solar Cells Utilizing Drift-Diffusion Equation Spandan K. Ranpariya and Dhirendra K. Sinha; Department of Sciences and Humanities, Indian Institute of Information Technology Vadodara, Gandhinagar, India.

Among the strategies for developing highly efficient solar cells, the organic-inorganic hybrid lead-halide perovskite solar cells (PSCs) have emerged as a potential scheme. The power conversion efficiency in such PSCs is reported to be drastically increased from 3.8% in 2009 to 22.7% in 2018. The use of organic-inorganic hybrid lead-halide perovskite as an active material in solar cells, for instance CH₃NH₃PbI₃, is mainly due to its high optical absorption coefficient with sharp absorption onset, long charge-carrier lifetime, tunable band-gap and low-cost fabrication. However, the underlying physics of charge-carrier transport in such material needs important attention in order to control and optimize the overall device performance. In this work, we evaluate numerical solutions of drift-diffusion equation over a wide range of operating conditions of practical interest to study steady- and transient-state current-voltage characteristics of a realistic planar PSC. The underlying interest is to propose a phenomenological model of the charge-carrier transport which shed light on whether the transport of charge-carriers in such class of material is electric field assisted or diffusion dominated.

ET04.06.16

The Effect of Oxygen Content on Nb₂O₅ Film Used as Hole Blocking Layer in Perovskite Solar Cell Silvia L. Fernandes¹, Carlos F. Graeff² and Elson Longo¹; ¹Federal University of Sao Carlos- UFSCAR, Sao Carlos, Brazil; ²University of São Paulo State-UNESP, Bauru, Brazil.

Organic-inorganic lead halide hybrid perovskite solar cells have become one of most promising up-and-coming photovoltaic technologies. Currently, the field is developing diversely across the whole world focusing on different technologies. In perovskite solar cells, CH₃NH₃PbI₃ play the role of the sensitizer injecting holes into a hole transport layer (HTL) and electrons into an oxide n-type layer, known as hole blocking layer (HBL). The n-type layer has the important role of protecting the recombination process, blocking the flow of electron from the transparent conductive substrate (FTO) to HTL or holes from the HTL to FTO. Most of the perovskite devices have been produced using HBL such as TiO₂, however oxides such as Nb₂O₅ have been less explored. Nb₂O₅ has attracted considerable attention due its comparable electron injection efficiency and a better chemical stability compared with TiO₂. These properties can potentially enhance the efficiency of solar cell devices, increasing the open circuit voltage and photoconversion efficiency. Here, we present the use of niobium pentoxide as HBL in mesoporous solar cell configuration: FTO/ Nb₂O₅ compact/ TiO₂ mesoporous/ CH₃NH₃PbI₃/ Spiro-OMeTAD/ Au. Nb₂O₅ compact layers were deposited by reactive sputtering. Parameters such as deposition time, oxygen flow and power as well as its influence on the performance of the cells were studied. Our results show that the oxygen flow have influence on the niobium pentoxide films growth and consequently on the performance of the solar cells. Cells fabricated with Nb₂O₅ deposited using considerable oxygen flow (10 sccm), resulted in a V_{oc} of 900 mV, J_{sc} of 13 mA/cm² and efficiency of ~12%. Moreover, films deposited using 8 sccm of oxygen flux given rise to cells with V_{oc} of 850 mV, J_{sc} of 11 mA/cm² and efficiency of ~10%. We attribute these results to the oxygen content present in the Nb₂O₅ films which could have influence on the charge transfer properties between the perovskite and the HBL.

ET04.06.17

Organolead Trihalide Perovskite Thin Films Converted from Sputtered Lead Iodide José Maria C. Silva Filho, Nelson F. Villegas, Rafael B. Merlo, Gustavo A. Viana and Francisco d. Marques; Department of Applied Physics, State University of Campinas, Campinas, Brazil.

Synthesis of high-quality organolead trihalide perovskite (CH₃NH₃PbI₃) has been subject of intense investigation due to their attractive optical and electronic properties, e.g., direct bandgap, high absorption coefficient and ambipolar charge transport. The main route used to synthesize CH₃NH₃PbI₃ thin films for high efficient solar cells is based on spin-coating deposition. This approach has been used to produce solar cells of surprising power conversion efficiencies higher than 20%. However, this technique is inadequate for large-scale and massive production. Therefore, we present here a new route for CH₃NH₃PbI₃ thin films synthesis, which is completely compatible with large-scale production. Lead Iodide (PbI) films were deposited through the well-known, reproducible, and precisely controlled technique of sputtering, which allows films evenly deposited on large areas and on different substrates. The as-deposited PbI₂ were converted into CH₃NH₃PbI₃ by vapor reaction in methylammonium iodide (CH₃NH₃I) atmosphere. By this method, we synthesized CH₃NH₃PbI₃ thin films with good optical and structural properties. Both the conversion process and the resulted CH₃NH₃PbI₃ were studied by x-ray

diffraction, UV-Vis transmission, scanning electron and atomic force microscopies. This new method is fully compatible with the large-scale manufacture. Besides, it has potential to open a way toward reproducible and high-efficiency $\text{CH}_3\text{NH}_3\text{PbI}_3$ solar cells.

ET04.06.18

Dielectric and Phonon Behaviors in Lead-Free Advance Ferroelectric $[\text{KNbO}_3]_{1-x}[(\text{BaNi}_{1/2}\text{Nb}_{1/2}\text{O}_3)_x]$ Compound Blanca Y. Rosas, Alvaro Instan, Karuna K. Mishra and Ram Katiyar; Department of Physics, University of Puerto Rico, San Juan, Puerto Rico, United States.

Potassium niobate (KNbO_3) is known to be an important eco-friendly lead-free ferroelectric material that possess excellent physical properties such as large electro-optical coefficients, electromechanical coupling constant, and nonlinear optical coefficients for several photonic device and electronic applications. The physical properties of KNbO_3 can be modified by substituting isovalent or heterovalent cations into K and/or Nb sites. Herein, we present systematic investigations carried out on structural, optical, dielectric, charge transport and ferroelectric properties of a solid solution $[\text{KNbO}_3]_{1-x}[(\text{BaNi}_{1/2}\text{Nb}_{1/2}\text{O}_3)_x]$ for $x = 0.1$ and $\delta = 0.25$ (KBNNO). The electro-ceramics were prepared by standard solid-state reaction method using K_2CO_3 (99.9%), BaCO_3 (99.95%), Ni_2O_3 (99.9%), and Nb_2O_5 (99.9%) as starting reagents. Formation of ferroelectric orthorhombic pure phase of the as synthesized sample was confirmed using x-ray diffractometry. Temperature dependent Raman spectra measured from liquid nitrogen temperature to 800 K and analyzed using damped harmonic oscillator model; provides evolution of phonon behaviors and suggests absence of any structural phase transition. A direct optical band gap E_g of 3.16 eV was estimated from Kubelka-Munk analyses of the diffuse reflectance spectra. Investigations on dielectric behaviors on a metal-KBNNO ferroelectric-metal capacitor in the T -range 80–500 K with the frequencies range 10^2 – 10^6 Hz suggests a broad peak with discernible dispersive features with frequencies indicating its relaxor-like behavior. A slim P - E loop measured up to 1800 V corroborates its relaxor behaviors. The frequency dependence of ac conductivity showed typical features of universal dynamic response and satisfy the known power law, $\sigma_{ac} = \sigma_{dc} + A\omega^n$. The I - V characteristic curves measured in between ± 600 V at several temperatures (100–500 K) suggest a typical Schottky-type (diode) behavior. The vibrating sample magnetometer results at room temperature show a linear magnetization curve with negative slope suggesting its diamagnetic behavior. Our experimental results establish the fundamental physics and materials science of the KBNNO compound and its potential for ferroelectric device applications.

ET04.06.19

Spatially-Resolved Ion Migration in Mixed Cation Lead Hybrid Perovskite Sergiu Draguta¹, Jeffrey A. Christians², Joseph Luther² and Masaru Kuno¹; ¹University of Notre Dame, Notre Dame, Indiana, United States; ²National Renewable Energy Laboratory, Denver, Colorado, United States.

In this study, by spatially-resolved emission measurements, we directly monitor cation migration in triple cation (FA, MA and Cs) lead hybrid perovskite. We show, that under applied voltage cations segregates and form single cation perovskite phases. This leads to degradation and decreasing of photovoltaic performance of solar cell devices. Next, by tuning the composition of cations we show improved stability against cation migration in perovskite solar cell devices.

ET04.06.20

Ultra-High Vacuum Investigations of Methylammonium Lead Tribromide Single Crystals Perovskites—Sample Stability and Photo-Carrier Recombination Pablo A. Fernandez Garrillo¹, Yann Almadori³, Benjamin Grévin³, David Moerman², Philippe Leclere² and Lukasz Borowik¹; ¹CEA LETI, Grenoble, France; ²University of Mons, Mons, Belgium; ³CNRS, CEA, INAC, Grenoble, France.

Methylammonium lead tribromide ($\text{CH}_3\text{NH}_3\text{PbBr}_3$) single crystals are studied under Ultra High Vacuum (UHV) by non-contact Atomic Force Microscopy (nc-AFM) and Kelvin Probe Force Microscopy (KPFM). [1, 2] We demonstrate that when exposed to ambient atmosphere, the sample exhibit important surface degradations. Even when sample is cleaved in air and exposed shortly (around few minutes) to ambient conditions, it reveals surface nanometric droplets (<100 nm). We demonstrate that such surface modifications can be avoided by UHV sample cleavage. The sample prepared and analyzed under UHV does not exhibit surface modifications even under illumination with laser power of few tens of mW per mm^2 . Furthermore, we perform time-resolved measurement by KPFM on this UHV-cleaved sample. While most of the experimental approaches developed so far consist in studying recombination by techniques such as: transient photovoltage or charge extraction, these techniques average sample properties over macroscopic scales, making them unsuitable for directly assessing the impact of local heterogeneity on the recombination process. Recently, we showed that it is possible to measure the photo carrier lifetime with nanometric spatial resolution by photo-modulated techniques based on KPFM over organic and inorganic solar cells. [3, 4, 5] We will present the principle of this original method based on the nanometrically resolved measurement of the surface potential by KPFM under a modulated illumination. Finally, we apply this protocol to measure nanometric resolved images of photo-carrier dynamics on $\text{CH}_3\text{NH}_3\text{PbBr}_3$. During this talk, we will show results of lifetime mapping as a function of laser power.

This work was supported by the French “Recherche Technologique de Base” Program.

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ET04.06.21

Investigating the Effects of Functionalized Benzylphosphonic Acid SAMs on Triple Cation Lead Halide Perovskite Based Solar Cells Jimmy Mangalam¹, Thomas Rath¹, Stefan Weber¹, Birgit Kunert², Theodoros Dimopoulos³, Alexander Fian⁴ and Gregor Trimmel¹; ¹Institute for Chemistry and Technology of Materials, Graz, Austria; ²Institute of Solid State Physics, Graz, Austria; ³Austrian Institute of Technology, Center for Energy, Photovoltaic Systems, Vienna, Austria; ⁴Institute for Surface Technologies and Photonics, Joanneum Research Forschungsgesellschaft mbH, Weiz, Austria.

The modification of interfaces with self-assembled monolayers (SAMs) are an interesting approach for enhancing the performance of perovskite solar cells.^{[1],[2],[3]} Recently, Wang *et al.* outlined the importance of the dipole moment by modifying nickel oxide (NiO_x) hole transport layers in perovskite solar cells with differently functionalized benzoic acid SAMs.^[3] In this work, we investigate the influence of para-functionalized benzylphosphonic acid (R-BPA) SAMs on Cs/FA/MA based triple cation perovskite solar cells prepared in inverted architecture using NiO_x as hole and PC_{60}BM as electron transport layer. The phosphonic acid groups act as an anchor to the NiO_x hole transport layer and besides the dipole moment of the molecules, the functional groups (we investigated: -Br, -F, - NH_2 , - NO_2 and - OCH_3) can also act like a seed layer influencing the perovskite crystallization. The presence of R-BPA SAMs on the NiO_x films was confirmed by contact angle measurements and X-ray photoelectron spectroscopy (XPS). Further, the influence of the SAM modifications on the perovskite layer morphology was studied by scanning electron microscopy (SEM) and X-ray diffraction (XRD) measurements. The SEM images reveal smaller grain sizes and narrower grain size distributions for (4-nitrobenzyl) and (4-methoxybenzyl) phosphonic acid SAM based solar

cells compared to the reference (without SAM modification) and other R-BPA SAM based solar cells. The introduction of (4-bromobenzyl) phosphonic acid led to solar cells with an improved power conversion efficiency of 16.5% (reference 12.3%). Similarly, (4-fluorobenzyl) phosphonic acid SAM based solar cells exhibited an improved open circuit voltage (V_{OC}) of 1.087 V (reference 0.977 V). On the contrary, a reduction of the V_{OC} was observed for solar cells modified with a (4-aminobenzyl) phosphonic acid SAM.

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SESSION ET04.07: Interfaces II
Session Chairs: Henk Bolink and Laura Herz
Wednesday Morning, November 28, 2018
Hynes, Level 3, Room Ballroom C

8:00 AM *ET04.07.01

Radiative and Non-Radiative Excited State Decay in Lead Halide Perovskites Richard H. Friend; University of Cambridge, Cambridge, United Kingdom.

Lead halide perovskite materials can show very high internal luminescence efficiencies, and this has enabled the fabrication of LEDs with high external quantum efficiencies, approaching 20%. High luminescence yield is also critical for efficient solar cell operation. I will discuss recent approaches to eliminate non-radiative decay channels within the bulk at also at charge injection/extraction interfaces. I will also discuss how recycling of internally-generated photons, both within LEDs and also in solar cells, affects device performance and design.

8:30 AM *ET04.07.02

Long-Range Hot Carrier Transport in Hybrid Perovskites Visualized by Ultrafast Microscopy Libai Huang; Purdue University, West Lafayette, Indiana, United States.

The Shockley-Queisser limit for solar cell efficiency of ~33% can be overcome if hot carriers can be harvested before they thermalize. Recently, carrier cooling time up to 100 picoseconds was observed in hybrid organic-inorganic lead halide perovskites, but it is unclear whether these long-lived hot carriers can migrate long distance for efficient collection. Here we report direct visualization of hot carrier migration in $\text{CH}_3\text{NH}_3\text{PbI}_3$ thin films by ultrafast transient absorption microscopy, demonstrating three distinct transport regimes. Quasi-ballistic transport was observed to correlate with excess kinetic energy; resulting in up to 230 nanometers transport distance in 300 fs that could overcome grain boundaries. The nonequilibrium transport persisted over tens of picoseconds and ~600 nanometers before reaching the diffusive transport limit. These results suggest potential applications of hot carrier devices based on hybrid perovskites.

9:00 AM ET04.07.03

Perovskite—A Wonder Material for High Efficiency Solar Cells and Optoelectronic Applications Shengzhong Liu^{1,2}; ¹Dalian Institute of Chemical Physics, Dalian, China; ²Shaanxi Normal University, Xi'an, China.

The organic lead halide perovskites have been demonstrated as a group of wonder materials for their excellent optical absorption, long range charge-carrier diffusion and apparent tolerance to defects. In just a few years, the efficiency of these perovskite solar cells has been improved from 3.8% to 23%. We have developed a few dry deposition processes without using any solvent to fabricate high efficiency perovskite solar cells with high stability. The new deposition processes allow us to relax the strict deposition monitoring and control measures, while realizing superior uniformity in film morphology, surface coverage and smoothness, together with crystalline phase purity, leading to high efficiency solar cells. Our current status for the rigid thin film cell efficiency is over 21.5% (Newport certified) and that for the flexible device over 18.3%, both are the highest for their respective categories. Meanwhile, the devices show very good stability over long term exposure in ambient with very low degradation. After a representative cell was exposed in ambient lab condition for more than two years, its final cell efficiency is as high as ~90% of its initial efficiency with its degradation accounts for only ~10%. Further analysis on the stability of the perovskite solar cells will be discussed. We have also developed a series of single-crystalline perovskites with superior stability and optoelectronic performance.

9:15 AM ET04.07.04

One Step High-Throughput Deposition for Flexible Perovskite Solar Cells Tae-Youl Yang¹, Young Yun Kim¹, Rikka Suhonen² and Jangwon Seo¹; ¹Korea Research Institute of Chemical Technology, Daejeon, Korea (the Republic of); ²VTT, Oulu, Finland.

Despite a high efficiency in the perovskite solar cells (PSCs) of over 22%, the large-area fabrication of PSCs is another issue that is receiving growing attention. The large-area PSCs requires more reliability than lab-scale devices for precisely controlling the crystallization behavior of perovskites. In order to transfer these technologies from laboratory scale to industrial-scale, large-area PSC manufacturing using scalable coating and printing processes have been evolved. The key advantage of printing in comparison to coating is the possibility of direct patterning on substrates. Printing provides a large degree of freedom for module design in arbitrary shapes and sizes.

In this presentation, we demonstrate one step fabrication of perovskite film via gravure printing. SnO_2 nanoparticles layer as an electron transport layer, $\text{CH}_3\text{NH}_3\text{PbI}_3$ as a photoactive layer, and Spiro-OMeTAD as a hole transport layer were sequentially printed on ITO-PET substrate. We optimized properties of each solution and drying process conditions to deposit uniform films. The resulting devices showed the power conversion efficiency of up to 15%. This study illuminates the possibility of the fabrication of high-performed printed PSCs using gravure printing which is a high throughput production technologies that enables more cost-effective industrial production.

9:30 AM ET04.07.05

Effective Passivation of Perovskite Film for Highly Efficient and Stable Solar Cell Using Adamantanes [Mohammad Mahdi Tavakoli](#)^{1,2}; ¹Materials Science and Engineering, Sharif University of Technology, Tehran, Iran (the Islamic Republic of); ²Electrical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

Passivation of electronic defects is an effective strategy to boost the performance and operational stability of perovskite solar cells (PSCs). Identifying molecular materials that achieve this purpose is a key target of current research efforts. Here, adamantane (AD) and adamantylamine (ADA) are introduced as molecular modulators to abate electronic defects present within the bulk and at the perovskite–hole conductor interface. To this effect, the modulator is added either into the antisolvent (AS) to precipitate it together with the perovskite (AS method) or they are spin coated (SC) onto its surface (SC method). Time resolved photoluminescence measurements show substantially longer lifetimes for perovskite films treated with AD and ADA compared to the reference sample. In line with this observation, it is found that the presence of AD and ADA molecules at the interface between the perovskite film and the hole conductor increases all photovoltaic metrics, in particular the open circuit photovoltage (V_{oc}) as well as the operational stability of the PSC.

9:45 AM BREAK

10:15 AM *ET04.07.06

Synthesis and Ionic Conductivity Measurements of Highly Efficient Perovskites from Blade Coated and Non-Toxic Solvents [Antonio Guerrero](#); Institute of Advanced Materials (INAM), Castellón de la Plana, Spain.

Understanding crystallization of lead halide perovskites by industrially relevant techniques is a topic that needs development as large area crystallization processes lead to inhomogeneous films, extremely large perovskite thickness or presence of pinholes. In this work, we show that efficient one-step perovskite solar cells can be obtained by doctor blade by controlling the coordination chemistry with non-toxic solvents *via* Spherulitic growth mechanism. This method results in highly crystalline perovskite films with preferential crystal orientation and spherulitic growth.¹ Optical and electrical measurements indicates that generated chemical defects are confined at the boundary of spherulites and these do not have a negative effect on the extracted photocurrent. Strikingly, spherulitic formation leads to better photovoltaic performance in hybrid perovskite films with record efficiencies of 18.0% for MAPbI₃ for doctor bladed processing using one-step and non-toxic solvents. Alternatively, ionic conductivity plays a key role in perovskites during photovoltaic device operation and degradation.^{2,3} In this presentation it is also described how to characterize the ionic properties of lead halide perovskites by electrical (impedance spectroscopy) and optical techniques (PL confocal microscopy).^{4,5} Approaches to minimize the electronic contribution to the measured current are used so the ionic current can be probed.

References

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2. Guerrero *et al.* Ionic reactivity at contacts and aging of methylammonium lead triiodide perovskite solar cell *Adv. Energy Mater.* **2016**, *6*, 1502246.
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4. Peng *et al.* Quantification of Ionic Diffusion in Lead Halide Perovskite Single Crystals. *ACS Energy Lett.* **2018**, 1477-1481.
5. Li *et al.* Real-Time Observation of Iodide Ion Migration in Methylammonium Lead Halide Perovskites. *Small* **2017**, *13*, 1701711.

10:45 AM ET04.07.07

Interfacial Modification for Highly Stable and Efficient SnO₂ Based Planar Perovskite Solar Cells [Kyoungwon Choi](#), Hong Il Kim, Minjun Kim, Hyuntae Choi and Taiho Park; POSTECH, Pohang, Korea (the Republic of).

We report a facile and effective interface modification for highly stable and efficient planar perovskite solar cells (P-PSCs) by employing a zwitterion-modified SnO₂ electron transport layer (ETL). A 3-(1-pyridinio)-1-propanesulfonate is used to modify the SnO₂/perovskite interface. The zwitterion plays a few important roles in P-PSCs: (1) Shifting the work function of the SnO₂ to a more suitable energy level for charge extraction. (2) Pulling electrons from perovskite toward the ETL/perovskite interface. (3) Suppressing backward transport of electrons from SnO₂ to the perovskite layers. (4) Passivating halide-induced deep traps and improving thermal stability of devices. With these desirable properties, the efficiency of devices and thermal stability increase remarkably. Therefore, P-PSCs with the modified SnO₂ ETL show reduced hysteresis owing to effective electron extraction and reduced recombination. The best device achieved a power conversion efficiency (PCE) of 21.43% in reverse scans. Accordingly, newly developed interface engineering is a promising method for fabricating efficient and hysteresis-less P-PSCs with high thermal stability.

11:00 AM ET04.07.08

Crystalline Metal Oxide Contact Layers in Organic and Hybrid Photovoltaics Mehrad Ahmadpour¹, André Cauduro², Mina Mirsafaei¹, John Lundsgaard Hansen³, Brian Julsgaard³, Horst-Günter Rubahn¹, Peter Balling³, Nadine Witkowski⁴, Andreas K. Schmidt² and Morten Madsen¹; ¹Mads Clausen Institute, SDU NanoSYD, University of Southern Denmark, Sønderborg, Denmark; ²The Molecular Foundry, LBNL Berkeley, National Center for Electron Microscopy, Berkeley, California, United States; ³Department of Physics and Astronomy and iNano, Aarhus University, Aarhus, Denmark; ⁴Institut des Nanosciences de Paris (INSP), Sorbonne Universités, UPMC Univ Paris 06, Paris, France.

Thin metal oxide films have attracted a lot of attention in the past years due to their unique ability to act as electrode contact layers in novel electronic and optoelectronic devices. Prominent examples are molybdenum oxide (MoO_x) and titanium oxide (TiO_x) thin films used as hole and electron contact layers, respectively, in organic and hybrid photovoltaics. Amongst many different methods used for fabrication of these films, reactive sputtering remains as a promising technique, due to the unique composition tuning and industrial scale processing possibilities¹. In the work presented here, crystalline MoO_x and TiO_x layers are developed from reactive sputtering and vacuum annealing, and implemented as contact layers in organic and hybrid solar cells.

The film composition is characterized using X-Ray Photoelectron Spectroscopy (XPS), work function using Low Energy Electron Microscopy (LEEM) and Ultraviolet Photoelectron Spectroscopy (UPS), structure using Transmission Electron Microscopy (TEM) and X-Ray Diffraction (XRD), morphology using Atomic Force Microscopy (AFM) and optical properties using UV-VIS spectroscopy. Importantly, we find that both the structure and work function of the developed thin films can be tuned by the annealing process, spanning an almost 2eV tuning range in the case of MoO_x.² Furthermore, due to the formation of the crystalline films with a low defect density, made possible via the reactive sputtering method, more efficient and stable contact layers for photovoltaic devices are developed. Non-encapsulated DBP/C₇₀ solar cell devices based on the sputtered MoO_x are demonstrated to remain with impressive 80% of the initial performance after 240 hours of light soaking under 1 sun (1000W/m²) at ~60°C, which is superior to similar devices based on conventional thermally evaporated MoO_x layers³. Fabricated PTB7/PCBM solar cells devices based on the sputtered TiO_x are demonstrated to lead to shape-free high performing devices, otherwise typically appearing when employing TiO_x as contact layers. Integration of the crystalline metal-oxide interlayers in perovskite solar cells is furthermore investigated and discussed. The underlying film properties leading to these appealing device properties are evaluated based on the extensive surface and film characterization performed.

The work thus demonstrates a viable method for tuning the electronic and optoelectronic properties of metal oxide thin films, which can be applied in combination with a wide range of materials in e.g. organic and hybrid photovoltaics.

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11:15 AM ET04.07.09

Light- and Bias-Induced Structural Variations in Metal Halide Perovskites [Dohyung Kim](#)¹, Jae Sung Yun², Pankaj K. Sharma¹, Da Seul Lee², Jincheol Kim², Arman M Soufiani², Shujuan Huang², Martin Green², Anita Ho-Baillie² and Jan Seidel¹; ¹School of Materials Science and Engineering, University of New South Wales, Sydney, New South Wales, Australia; ²Australian Centre for Advanced Photovoltaics (ACAP), School of Photovoltaic and Renewable and Engineering, University of New South Wales, Sydney, New South Wales, Australia.

Organic-inorganic metal halide perovskites have gained considerable attention for next-generation photovoltaic cells due to rapid improvement in power conversion efficiencies. Even though there have been immense efforts towards fabricating high performance solar cell devices, fundamental understanding of underlying mechanisms related to light and bias induced effects at the nanoscale is still required. In this study, structural variations of the perovskites induced by light and bias are systematically investigated using scanning probe microscopy techniques. We show that periodically striped ferroelastic domains, spacing between 40 nm to 350 nm, exist within grains and can be modulated significantly under illumination as well as by electric bias. Williamson-Hall analysis of X-ray diffraction results shows that strain disorder is induced by these applied external stimuli. We show evidence that the structural emergence of domains can provide transfer pathways for holes to a hole transport layer (HTM) with positive bias, whereas negative bias attracts organic cations to the surface, which can induce structural damage to the perovskite-HTM interface. Our findings point to potential origins of I-V hysteresis in halide perovskite solar cells and provide fresh microscopic insight into external stimuli-induced structural disorder governing the superior performance of the metal halide perovskites solar cells.

11:30 AM ET04.07.10

Hydrophobic Self-Assembling Monolayers for Stable Perovskite Solar Cells [Laura Canil](#) and Antonio Abate; Helmholtz Zentrum Berlin, Berlin, Germany.

With a power conversion efficiency over 22%, perovskite solar cells (PSCs) are considered a rising star in the solar energy field. Nevertheless, the device long-term stability under working condition remains a big challenge. In particular, most of the halide perovskite compositions are highly sensible to moisture. Indeed, the initial device performances degrades abruptly in only a few days of air exposure. Our strategy to enhance the moisture stability of PSCs is to functionalize the interface between the perovskite and the charge selective contacts within the device. We make use of specific molecule-to-substrate interaction to self-assembly perfluorinated small molecules on the perovskite surface. The formation of a nanometer thick perfluorinated layer results in hydrophobicity and potentially in super-hydrophobicity of the perovskite surface, which prevents the ingress of water from the atmosphere. Notably, such a functionalization can be done through scalable solution processing methods, which are compatible with fast output production including roll-to-roll and inject printing. We investigate the impact of the functionalization on material and device stability, providing data from lab-scale devices aged in real working conditions – under light and voltage load. Our results show that the interface functionalization with perfluorinated molecules is an effective new approach to enhance PSCs lifetime.

11:45 AM ET04.07.11

Hole Transport Bilayer for Improved Photocurrent and Stability in Perovskite Solar Cells for 2-Terminal Tandems [James A. Raiford](#)¹, Rebecca A. Belisle², Kevin A. Bush², Axel F. Palmstrom^{1,3}, Rohit Prasanna², Michael D. McGehee^{2,4} and Stacey F. Bent¹; ¹Chemical Engineering, Stanford University, Stanford, California, United States; ²Materials Science & Engineering, Stanford University, Stanford, California, United States; ³National Renewable Energy Laboratory, Golden, Colorado, United States; ⁴Chemical and Biological Engineering, University of Colorado Boulder, Boulder, Colorado, United States.

Perovskite solar cells used in tandem with existing silicon cell technology is a promising pathway towards achieving next-generation, high efficiency devices at a lower cost. To date, the highest efficiency monolithic perovskite/silicon tandems are fabricated in the inverted p-i-n architecture, despite the fact that the best single-junction devices have been reported in the standard n-i-p orientation. The primary source of performance loss in the standard architecture, 2-terminal tandem is optical losses associated with replacing an opaque contact with a transparent one. Common hole transport and window layers like doped spiro-OMeTAD and molybdenum oxide, respectively, parasitically absorb significant amounts of light before it can reach the perovskite and be converted to useful photocurrent. Additionally, these hole contact layers have been shown to be sources of chemical instability, leading to long-term degradation of device performance. In this work, we present an alternative hole contact bilayer, consisting of a thin, undoped organic small molecule and an air-stable vanadium oxide (VO_x) buffer layer deposited via atomic layer deposition (ALD). This novel bilayer allows for the subsequent sputtering of a transparent indium tin oxide top electrode. Its minimal absorption in the ultra-violet and visible regions of the solar spectrum result in the fabrication of a semi-transparent perovskite cell with 2.3 mA/cm² more photocurrent than its spiro-OMeTAD counterpart without a loss in cell voltage. Our design also leverages the conformal, compact nature of the ALD buffer layer to help slow the thermal degradation of mixed cation, mixed halide perovskite films. Unlike molybdenum oxide, we show that our VO_x ALD buffer layer is inert to the perovskite material by demonstrating stable device performance after 1000 hours of thermal aging at 85°C in an inert N₂ atmosphere. Lastly, we will discuss the implications of this work as they relate to the fabrication of more efficient 2-terminal perovskite/silicon tandems.

SESSION ET04.08: Stability and Testing
Session Chair: Michael McGehee
Wednesday Afternoon, November 28, 2018
Hynes, Level 3, Room Ballroom C

1:45 PM ET04.08.01

Firing up Perovskite Solar Modules [Bert Conings](#), Aslihan Babayigit and Hans-Gerd Boyen; Materials Research Institute, Hasselt University, Diepenbeek, Belgium.

All metal halide perovskite solar cells with decent efficiencies so far contain lead (Pb). Since the rapidly evolving perovskite photovoltaic technology is on the cusp of commercialization, the existence and gravity of hazardous components as a consequence of its Pb content is a growing point of debate.

Probably the most likely scenario for an uncontrolled exposure to the enclosed Pb-containing chemicals and related reaction products—that can fuel this debate—is that where perovskite PV installations are involved in structure fires, the latter statistically representing a significant risk. To shed light on the potential impact of such an event, a careful assessment of the fire safety of perovskite-containing PV mini-modules is presented. A balanced discussion is provided comparing the hazard originating from an encapsulation failure of a perovskite-based rooftop installation (worst case scenario) and that associated with the burning of common materials found in buildings. In addition, a rough atmospheric dispersion model is used to estimate the heavy metal concentrations downwind of a typical structure fire.

2:00 PM ET04.08.02

Barrier Layer Design Using Transparent Conducting Oxides for 1,000 Hour Thermally Stable MAPbI₃ Solar Cells Caleb C. Boyd¹, Rongrong Cheacharoen¹, Kevin A. Bush¹, Rohit Prasanna¹, Tomas Leijtens¹ and Michael McGehee²; ¹Stanford University, Stanford, California, United States; ²Chemical and Biological Engineering, University of Colorado Boulder, Boulder, Colorado, United States.

Hybrid organic-inorganic lead halide perovskite solar cells have surpassed other commercialized thin-film solar cell technologies in record efficiency,¹ but they have yet to demonstrate excellent stability that precludes commercialization. While moisture exposure can be mitigated through careful encapsulation, the thermal stability of the cell is intrinsic to operation and must be improved.²

We show that thermal stability of semitransparent perovskite solar cells in the inverted (p-i-n) architecture (ITO/NiO_x/FA_{0.83}Cs_{0.17}Pb(I_{0.83}Br_{0.17})₃/evaporated C60/SnO₂/ITO/metal) at 85°C in a nitrogen environment is limited by reaction with metal contacts, regardless of whether Ag, Cu, or Au is used. We found similar results with MAPbI₃ and FA_{0.75}Cs_{0.25}Sn_{0.5}Pb_{0.5}I₃ devices. We used x-ray photoelectron spectroscopy (XPS) and secondary ion mass spectroscopy (SIMS) depth profiling to show that Ag not only creates a driving force for iodine migration from the perovskite, but also surprisingly has the potential to diffuse through a sputtered tin-doped indium oxide (ITO) window layer, an atomic layer deposited (ALD) tin oxide layer, and an evaporated fullerene electron transport layer into the perovskite, harming the performance of the perovskite solar cell.

We found using scanning electron microscopy (SEM) that the poor barrier quality of the transparent conducting oxide (TCO) is due largely to diffusion channels created by a proliferation of the existing rough perovskite morphology. This also occurs when the crystalline ITO is replaced with amorphous indium zinc oxide (IZO).

We found that the key to creating a good barrier layer to prevent metal degradation and escape of volatile halide species is by (1) adding a planarizing layer to disrupt the perovskite morphology and (2) extending the TCO barrier layer to completely cover the edges of the perovskite layer. We do so here by using spin-cast PCBM instead of evaporated PCBM, and we show that a similar design principle applies in the regular (n-i-p) architecture with the commonly-used spiro-OMeTAD. Finally, we demonstrate 1000-hour stability at 85°C in a N₂ environment using volatile MAPbI₃ solar cells, showing that the improved TCO barrier layer can provide excellent thermal stability to a wide range of perovskite compositions and architectures.

1. Best Research-Cell Efficiencies (NREL, 2018); <https://www.nrel.gov/pv/assets/images/efficiency-chart.png>.

2. K. A. Bush, A. F. Palmstrom, et al., Nat. Energy 2, 17009 (2017).

2:15 PM ET04.08.03

A Chain is as Strong as its Weakest Link—Stability Study of MAPbI₃ Under Light and Temperature Philippe J. Holzhey^{1,2}, Pankaj Yadav², Silver-Hamill Turren-Cruz^{1,2}, Michael Graetzel², Anders Hagfeldt² and Michael Saliba¹; ¹Adolphe-Merkel Institute, Fribourg, Switzerland; ²Chemistry, École Polytechnique Fédérale de Lausanne, Lausanne, Switzerland.

The stability of perovskite solar cells is considered poor compared to other solar cells. One reason for this is thought to be the volatile organic methylammonium (MA) cation. At the same time, small amounts of MA are used for practically all highest performing solar cells with efficiencies beyond 21%. These compositions have also shown some of the best reported stabilities indicating that MA might not be as unstable as previously assumed. This raises the question of whether excluding MA for the sake of stability has been concluded prematurely. Interestingly, MA instability was mainly concluded from thin film studies that differ strongly from full devices. Therefore, the degradation behaviour on complete MA containing devices is crucial to quantify the long-term stability of MA. Only then, it is possible to determine at which timescales MA is unstable and if it must be categorically excluded from future compositions. Without such assessment, valuable time may be lost due to false prioritisation that is not justified by actual data. Here, we use weakest link devices, i.e. MAPbI₃, to study the stability under light and different temperatures.

2:30 PM BREAK

3:30 PM ET04.08.04

Organic Gelators as Growth Control Agents for Stable and Reproducible Hybrid Perovskite-Based Solar Cells Natalie Stingelin; Georgia Institute of Technology, Atlanta, Georgia, United States.

Low-molecular-weight organic gelators are widely used to influence the solidification of polymers, with applications ranging from packaging items, food containers to organic electronic devices, including organic photovoltaics. Here, I discuss how this concept can be extended to hybrid halide perovskite-based materials. In situ time-resolved grazing incidence wide-angle X-ray scattering measurements performed during spin coating reveal that organic gelators beneficially influence the nucleation and growth of the perovskite precursor phase. This can be exploited for the fabrication of planar n-i-p heterojunction devices with MAPbI₃ (MA = CH₃NH₃⁺) that display a performance that not only is enhanced by ≈25% compared to solar cells where the active layer is produced without the use of a gelator but that also features a higher stability to moisture and a reduced hysteresis. Most importantly, the presented approach is straightforward and simple, and it provides a general method to render the film formation of hybrid perovskites more reliable and robust, analogous to the control that is afforded by these additives in the processing of commodity “plastics.”

4:00 PM ET04.08.05

Efficient and Stable of Inorganic Perovskite Solar Cells Jingbi You; Chinese Academy of Sciences, Beijing, China.

Inorganic halide perovskites such as cesium lead halide have attracted great attentions due to their excellent thermal stability. Cesium lead iodide (CsPbI₃) has a bandgap of 1.73 eV and is very suitable for making efficient tandem solar cells, either with low bandgap perovskite or silicon. However, the phase instability is hindering the further optimization of the device performance. Here, we show that high quality and stable black-phase CsPbI₃ film is obtained *via* solvent-controlled growth of the precursor film in dry environment. A 15.7% power conversion efficiency of CsPbI₃ solar cells is achieved, which is the highest efficiency reported so far for inorganic perovskite solar cells. And more importantly, the devices can tolerate continuous light soaking for more than 500 hours without efficiency drop. Recently, we have pushed the efficiency of inorganic perovskite solar cells to 17%.

References

4:15 PM ET04.08.06

Enhanced Photovoltaic Performance and Stability of Tin-Based Perovskites by Forming 3D Hollow Structure with Diammonium Dications Weijun Ke, Constantinos Stoumpos, Ioannis Spanopoulos, Lingling Mao, Oleg Kontsevoi, Michelle Chen, Michael R. Wasielewski and Mercouri G. Kanatzidis; Northwestern University, Evanston, Illinois, United States.

The power conversion efficiency of perovskite solar cells has increased from 3.8 to above 22% within a few years.^[1] Currently, the highest-efficiency perovskite solar cells are made on lead-based light absorbers; however, the toxicity of lead constitutes a serious issue which hinders the commercialization attempts of the perovskite solar cells technology. It is therefore imperative to reduce or altogether eliminate Pb from these devices and replace them with other less toxic elements. Sn is an especially attractive candidate because its perovskite analogs have similar or even superior optical and electronic characteristics compared to those of Pb. However, the efficiency of the Sn-based perovskite solar cells is low and the stability of Sn-based perovskite solar cells is usually very poor in air. Here, we demonstrate a new type of tin-based perovskite absorber that incorporates both ethylenediammonium (*en*) and formamidinium (FA)/methylammonium (MA) forming new materials of the type $\{en\}FASnI_3/\{en\}MASnI_3$.^[2-4] We show that *en* can serve as a new A dication capable of achieving dramatic increases in bandgap without the need of solid solutions. The *en* introduces a new bandgap tuning mechanism that arises from massive Schottky style defects. Our best-performing $\{en\}FASnI_3$ and $\{en\}MASnI_3$ solar cells have the highest efficiency of 7.23% and 6.63%, respectively. Most importantly, the stability of tin-based perovskite solar cells is significantly enhanced by the incorporation of *en* dication in the structure. Recently, we also found two other new diammonium cations of propylenediammonium (PN) and trimethylenediammonium (TN) which have slightly larger size but can still be incorporated into 3D $FASnI_3$ structure. A similar efficiency enhancement was also observed for the $\{PN\}FASnI_3$ and $\{TN\}FASnI_3$ solar cells. Our results suggest that developing tin-based perovskites with suitable diammonium cations such as *en*, TN, and PN in their structure is a new promising approach for fabricating high-performance tin-based perovskite solar cells.

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4:30 PM ET04.08.07

Outdoor Analysis of the Active Layer Temperature in Perovskite Photovoltaic Modules Robert Gehlhaar, Tamara Merckx and Weiming Qiu; imec, Leuven, Belgium.

Perovskite solar cells have seen an enormous improvement in the relevant photovoltaic parameters of power conversion efficiency and device lifetime. Within less than a decade of development, efficiencies exceeded 22% and lifetimes increased from a couple of seconds to more than 10000 hours. A various number of device configurations is showing the potential to improve the performance to industrial relevant levels. Leaving the level of research from lab environment, the temperature of a perovskite solar cell can have a serious effect on the performance. The power conversion efficiency as well as the stability can be drastically influenced and reduced by increasing the device temperature.

We report on the temperature of perovskite modules under outdoor conditions and the modeling of the temperature fluctuations in dependence in the influential parameters. The report provides insights into the exact temperature evolution of the photoactive layer over a wide range of solar irradiance and various ambient temperatures. The provided model allows for an accurate prediction of the module temperature beyond the measured range of the parameters.

The evolution of the device temperature of a perovskite module of 225 cm² area has been recorded during a period of 25 days under central European conditions. The temperature of the glass-glass packaged perovskite solar module was directly measured at the back contact by a thermocouple. The device was exposed to ambient temperatures from 3 °C to 34 °C up to solar irradiation levels of 1300 W m⁻² resulting in a maximum module temperature of 61 °C. Under strong fluctuations of the global solar irradiance, temperature gradients of more than 3 K min⁻¹ with total changes of more than 20 K are measured. Based on the experimental data, a dynamic iterative model is presented for the module temperature evolution in dependence on ambient temperature and solar irradiation. Furthermore, specific thermal device properties that enable an extrapolation of the module response beyond the measured parameter space can be determined.

The presented set of data and analysis gives an insight in the expected device temperature in real world applications. This knowledge is essential to design future experiments to bring the perovskite PV technology to the next level. The analysis of temperature coefficients for power conversion efficiency, stability and hysteresis are going to benefit from the provided measurements and model of the exact layer temperature.

4:45 PM ET04.08.08

Stability Studies of Perovskite PV Devices Using Natural and Concentrated Sunlight Iris Visoly-Fisher¹, Eugene A. Katz¹, Mark V. Khenkin¹, K.M. Anoop¹, Yulia Galagan², Francesco Di Giacomo², Morten Madsen³, Bhushan R. Patil³, Golnaz Sherafatipour³ and Vida Turkovic³; ¹Department of Solar Energy and Environmental Physics, Swiss Institute for Dryland Environmental and Energy Research, Jacob Blaustein Institutes for Desert Research, Ben-Gurion University of the Negev, Midreshet Ben-Gurion, Israel; ²Holst Centre – Solliance, Eindhoven, Netherlands; ³SDU NanoSYD, Mads Clausen Institute, University of Southern Denmark, Sønderborg, Denmark.

Standard, outdoor operation under natural sunlight includes diurnal light/ dark cycling. Both reversible improvement and reversible degradation of perovskite solar cell efficiency were observed under illumination-darkness cycling.^[1] Quantifying the performance and stability of cells exhibiting significant diurnal performance variation is challenging, and we suggest that its figures of merit should be reconsidered.^[2]

Concentrated sunlight allows accelerated stability studies and separating the effect of light on material and cell stability from other factors. We recently demonstrated an experimental methodology with independent control of sunlight intensity, the sample temperature, bias and environment during the exposure. Studies of perovskite devices as a function of sunlight concentration were aimed at determining which degradation factors are more dominant: light and spectrum, bias or their combination? Preliminary results of studies of ITO/SnO₂/Cs_{0.15}(CH₃NH₂)₂_{0.85}PbI_{2.75}Br_{0.25}/Spiro-OMeTAD/Au cells show a monotonic dependence of the PCE degradation kinetics on sunlight concentration, as expected. This dependence on intensity was significantly stronger than the degradation dependence on the illumination dose (in sun*hours).^[3] Significant effect of UV- and IR- filtering on the cell's degradation rate was also noted. Possible underlying degradation mechanisms will be discussed.

[1] *ACS Applied Energy Materials* 1 (2018), 799-806

[2] *Energy and Environmental Science*, **11** (2018), 739 - 743

[3] In preparation.

SESSION ET04.09: Poster Session III
Wednesday Afternoon, November 28, 2018
8:00 PM - 10:00 PM
Hynes, Level 1, Hall B

ET04.09.01

The Role of Bismuth Doping in the Stability of Lead-Halide Perovskite Natalia d. Coutinho and Francisco d. Marques; UNICAMP, Campinas, Brazil.

In the last few years a new type of solar cell, the lead-halide perovskite solar cell, $\text{CH}_3\text{NH}_3\text{PbI}_3$, has gained interest in photovoltaic community due to its high efficiency and low cost compared with the well-known silicon solar cells. In spite of incredible efficiencies as high as 22.1% that it have presented, it faces a problem concerning the commercial use due to its lead content and poor stability. In this way, new lead-free materials have been studied in the last few years. One of it is the lead-free perovskite-like material $(\text{CH}_3\text{NH}_3)_3\text{Bi}_2\text{I}_9$ that can act as the absorption material in solar cells and has a better stability than $\text{CH}_3\text{NH}_3\text{PbI}_3$ [1]. In spite of the good stability, the efficiencies this type of solar cell has achieved are still very low. In this work we combined this two semiconductors, $\text{CH}_3\text{NH}_3\text{PbI}_3$ and $(\text{CH}_3\text{NH}_3)_3\text{Bi}_2\text{I}_9$, by the addition of small amounts (1% to 25%) of Bi in the lead-perovskite in order to observe if this would affect the stability of the final perovskite, inspired in a similar study where one has inserted tin in $\text{CH}_3\text{NH}_3\text{PbI}_3$ [2]. The films were made by one-step, mixing suitable amounts of PbI_2 , MAI (methylammonium iodide) and BiI_3 in dimethylformamide. The films were obtained by spin coating this solution in glass substrates. After deposition we monitored the degradation of the films exposed to light and humidity for 16 days through X-ray Diffraction and Ultraviolet-Visible Spectroscopy measurements as well as photographs of the films. The last ones indicate that the lead-perovskite (dark gray) degrades to PbI_2 (yellow) faster than the ones where small amounts of Bi were inserted, indicating that the material stability was increased through the bismuth-doping. X-ray diffraction measurements of as-deposited films indicate that the crystal structure of all films, including the Bi-doped ones, have the crystal structure of lead-perovskite. The results indicate that with the implantation of small amounts of Bi (<25%) does not affect the crystal structure of the lead-perovskite and increases the stability of the material.

Acknowledgements: CNPq, Capes, Fapesp, Lamult Unicamp.

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ET04.09.02

Chemical Doping Effect on the Electron Transport Layer of Perovskite Solar Cells Kazunori Ito, Hiroya Kiuchi, Yuki Fukazawa, Takamasa Takeuchi, Toshiya Kobayashi, Masato Gocho and Hironori Ogata; Hosei University, Tokyo, Japan.

Organic-inorganic perovskite solar cells are one of the promising candidates for highly efficient next-generation solar cells. For mass production of perovskite solar cells, an electron transport layer including a low temperature process is desirable. In general perovskite solar cells, TiO_2 is widely used as the electron transport layers (both compact layer and mesoporous layer). However, high temperature treatment is necessary for the fabrication of TiO_2 layer. On the other hand, ZnO can be fabricated at a lower temperature than TiO_2 . Furthermore, ZnO has high electric mobility and is considered to be a promising electron transport layer. Perovskite solar cells using ZnO as an electron transporting layer have been reported so far, but their conversion efficiencies are lower than in the case of using TiO_2 . Also, low thermal stability of the perovskite film deposited on the ZnO layer has been reported. In this study, a perovskite solar cell using doped ZnO nanoparticles as the electron transport layer was fabricated and systematically investigated their charge transport properties and thermal stabilities of the perovskite layers and photovoltaic properties by doping. We will present detailed results on the meeting.

ET04.09.03

Fabrication and Characterization of Inverted Perovskite Solar Cells Using Fullerene Derivatives for Electron Transporting Layer Toshiya Kobayashi, Hiroya Kiuchi, Takamasa Takeuchi, Kazunori Ito, Masato Gocho, Yuki Fukazawa and Hironori Ogata; Applied Chemistry, Hosei University, Tokyo, Japan.

Perovskite solar cells are currently reporting high energy conversion efficiencies exceeding 22%.

In a normal type perovskite solar cells having mesoporous structure, a metal oxide layer such as titanium oxide is used. However, it is not suitable for the application to flexible solar cells because it requires high temperature treatment for film formation. Therefore, studies on reverse structure type perovskite solar cells which can form a thin film at low temperature have attracted attention.

Fullerene derivatives [6,6]-Phenyl-C₆₁-Butyric Acid Methyl Ester (PCBM) is widely used for the electron transport layer of the inverted-structured perovskite solar cell, but the annealing process causes aggregation in the PCBM layer, which is considered to have a negative influence on photovoltaic characteristics. Therefore, development of fullerene derivatives that form thin film having high morphological stability up to about 100 °C is one of the important challenges.

In addition, PEDOT: PSS widely used for the hole transport layer, is considered to have a negative influence on the solar cell characteristics due to strong acidity, hygroscopicity, etc. Therefore, the development of chemically inert hole transport layers is another important challenges.

In this study, inverted perovskite solar cell using several kinds of fullerene derivatives were prepared, and their local structures, morphological changes of the electron transport layers by annealing, charge transport properties and photovoltaic properties were systematically investigated.

Detailed experiment results will be presented.

ET04.09.04

Durability Evaluation of Organic-Inorganic Perovskite Films Yuki Fukazawa, Hiroya Kiuchi, Takamasa Takeuchi, Kazunori Ito, Masato Gocho, Toshiya Kobayashi and Hironori Ogata; Hosei University, Tokyo, Japan.

Degradation of metal-organic halide perovskites when exposed to ambient conditions is a crucial issue that needs to be addressed for commercial viability of perovskite solar cells. It has been reported that stability is improved by mixing inorganic cations such as Cs and Rb with organic cations such as CH_3NH_3^+ (MA^+) and $\text{HC}(\text{NH}_2)_2^+$ (FA^+). In addition, recently, it has been reported that energy conversion efficiency and stability are improved by mixing

CH_6N_3^+ as an organic cation, but these deterioration suppressing mechanisms have not been sufficiently elucidated yet. We have investigated the durability of the perovskite compound of layer. In this study, we focused on Cs-Rb-FA-MA-PbI_{3-y}Br_y type mixed compounds, the effect of the proportion of inorganic and organic cations on the structure, thin film morphologies, optical absorptions and electronic properties under several ambient conditions. Detailed results will be reported on the day.

ET04.09.05

Effect of Ion Irradiation on the Properties of Perovskite Solar Cells Hironori Ogata, Tomoaki Nishimura, Hiroya Kiuchi, Kazunori Ito, Toshiya Kobayashi and Yuki Fukazawa; Hosei University, Tokyo, Japan.

Perovskite solar cells are an important photovoltaic technology with high efficiencies exceeding 20% due to their optimal band gap, large absorption coefficient, and high charge mobilities. One of these challenges is the understanding and control of their defect structures because perovskite compounds are relatively soft ionic crystals and ions are migrating in the crystals relatively low activation energy.

In this study, we have investigated the effect of low energy ion irradiations to both all inorganic and organic-inorganic lead halide perovskite films on the structure, morphology optical and electronic properties systematically. Several kinds of halogen ion beam irradiations on the perovskite thin film was performed by using a tandem type ion accelerator with changing acceleration voltages and irradiation time. Incorporation of ions in perovskite crystals by irradiations were confirmed under several conditions.

Detailed experimental results on the structure, optical properties, electronic properties and photovoltaic properties by ion irradiations will be reported on the conference.

ET04.09.06

Solvent-Engineering Method to Deposit Compact Bismuth-Based Thin Films—Mechanism and Application to Solar Cells Seong Sik Shin^{1,2} and Tonio Buonassisi²; ¹Korea Research Institute of Chemical Technology, Cambridge, Massachusetts, United States; ²Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

Bismuth-based materials have been investigated as an alternative to lead-based perovskite materials for photovoltaic applications. However, inferior film quality has limited device performance. Here, we propose a one-step solvent engineering method for deposition of various bismuth-based films. Through this one-step method, we obtain compact films of methylammonium bismuth iodide (MBI), cesium bismuth iodide (CSI), and formamidinium bismuth iodide (FBI). On the basis of film growth theory and experimental analyses, we propose a possible mechanism of film formation. Additionally, we demonstrate that the resultant compact MBI film is more suitable to fabricate efficient and stable photovoltaic devices, compared to baseline MBI films with pinholes. We further employ a new hole-transporting material to reduce the valence-band offset with the MBI. The best-performing photovoltaic device exhibits an open-circuit voltage of 0.85 V and fill factor of 73%, and a power conversion efficiency of 0.71 %.

ET04.09.07

Tuneable Silver Bismuth Sulphoiodide Solar Cells Narendra Pai¹, Jianfeng Lu², Phillip C. Andrews¹, Yi-Bing Cheng³, Udo Bach² and Alexandr N. Simonov⁴; ¹Chemistry, Monash University, Clayton, Victoria, Australia; ²Chemical Engineering, ARC Centre of Excellence in Exciton Science, Monash University, Clayton, Victoria, Australia; ³Materials Science and Engineering, ARC Centre of Excellence in Exciton Science, Melbourne, Victoria, Australia; ⁴Chemistry, ARC Centre of Excellence for Electromaterials Science, Monash University, Melbourne, Victoria, Australia.

Organolead halide perovskite solar cells have recently emerged as a solar energy technology with immense potential for large-scale generation of renewable electricity. However, the hazardous nature of lead and intrinsic instability of perovskites has driven the search for simpler and more robust light-absorbing materials. From this perspective, cheap, abundant and non-toxic bismuth-based systems with favourable optoelectronic properties are attracting an increasing attention. Unfortunately, bismuth-based perovskites provide incomparably lower photovoltaic performance than the lead counterparts due to poor interfacial charge extraction and wide indirect band gap. Viable alternatives are silver(I) and copper(I) iodobismuthates that have been recently found to exhibit promising photovoltaic performance. However, their relatively wide band gaps (E_g) of 1.8-1.9 eV and downshifted valence band edges (E_{VB}) limit the charge transfer through conventional charge transport materials and the photocurrent density. Interestingly, silver bismuth sulphides, which are also currently explored as photovoltaic materials, have an excessively positive E_{VB} and too narrow E_g of 1.2-1.4 eV. Herein, silver bismuth sulphoiodides are introduced, for the first time, as a new class of light harvesting materials that balance out the unfavourable optoelectronic properties of iodides and sulphides.

We demonstrate a facile and efficient strategy to tune the optoelectronic properties of silver bismuth iodobismuthates by varying the sulphide: iodide ratio. A consistent narrowing of the bandgap by 0.1 eV and an upshift of the valence band edge by 0.1–0.3 eV upon modification with small amounts of sulphide is demonstrated for thermodynamically stable $\text{Ag}_d\text{Bi}_b\text{I}_{a+3b}\text{S}_x$ compositions. Photovoltaic devices based on new silver bismuth sulphoiodide light absorbers embedded into a mesoporous TiO_2 electron transporting scaffold and covered with PTAA hole transporting layer outperform control solar cells based on sulphide-free materials, in full agreement with changes in the optoelectronic properties. An enhanced power conversion efficiency of 5.44 ± 0.07 % under 1 sun AM 1.5G irradiation and over a month stability under ambient conditions for photovoltaic devices based on $\text{Ag}_d\text{Bi}_b\text{I}_{a+3b-2x}\text{S}_x$ is demonstrated.

ET04.09.08

Low-Temperature SnO₂-Based Planar Perovskite Solar Cells—Interface Engineering, Large-Scale Manufacturing and High Performance Achievement Junjie Ma, Guojia Fang, Zhiliang Chen and Xiaolu Zheng; Wuhan University, Wuhan, China.

Perovskite solar cells (PSCs) have attracted considerable research interest because of their excellent photovoltaic performance and simple fabrication process. Tin oxide (SnO₂) has emerged as a promising candidate for electron transfer layer (ETL), which shows much higher electron mobility, good antireflection, low-temperature process. Herein, we report a simple and effective interfacial engineering method for achieving highly efficient Low-temperature SnO₂-based PSCs. An ultrathin wide bandgap dielectric MgO nanolayer is incorporated between electrode and SnO₂ ETL, realizing enhanced electron transporting and hole blocking properties. A power conversion efficiency (PCE) of 18.82% is demonstrated.

On the other hand, Systematic exploration of commercialized application in SnO₂-based PSCs is conducted. We prepared SnO₂ ETL through the electron beam evaporation (e-beam) technology, realizing large-scale, low-cost and uniform manufacture which would be available for industrial deployment. A Cs-containing blended perovskite absorber layer was introduced into the PSCs to effectively enhance the ambient stability. As a result, PSCs exhibit a high efficiency of 18.2% without any interface modification, and remarkable long-term stability, which remained 97% of its initial PCE after being stored over 34 days. Our result demonstrated the great potential of the PSCs based on SnO₂ ETL towards commercially viable.

ET04.09.09

Single-Step CVD Approaches for Producing Thin-Film Perovskites Andrew J. Clayton, Arthur Connell, Rosie V. Anthony, Leo W. Furnell, Eurig W.

Jones, Stuart J. Irvine and Peter J. Holliman; Swansea University, St. Asaph, United Kingdom.

Chemical vapor deposition (CVD) is a proven method [1-4] for depositing organic-inorganic metal halides, such as methylammonium lead iodide (MAPbI₃) [1, 2] and cesium lead iodide (CsPbI₃) [3], including Pb-free perovskite materials [4] for thin film photovoltaics (PV). The CVD process can be used in conjunction with other processes (hybrid) [1] or as a single step process [2-4]. The latter offers a simpler approach with reduced processing time. CVD is a controllable process with consistent results, also negating the requirement for solvents and limiting moisture incorporation. In this present study, different single step CVD approaches have been investigated for effective deposition of thin film MAPbI₃ and CsPbI₃. A CVD growth chamber with simple quartz tube design and two separately controlled temperature zones has been employed. The first zone was operated at high temperature (HT) to evaporate the precursor materials and sublime the chemical vapor in a low temperature (LT) zone on to a substrate. This was positioned on an angled graphite susceptor to counteract gas phase depletion and improve thickness uniformity. Temperature control was achieved using K-type thermocouples inserted into the chamber from each end to measure and control the HT and LT zones. A small quartz tube was attached to the growth chamber, in which a thermocouple was inserted to at different sections along the tube to profile the temperature across the two zones. Both reactor tube and attached thermocouple tube were enclosed in a furnace encompassing both ceramic heaters for each temperature zone. A nitrogen (N₂) gas carrier was used to carry the chemical vapor downstream to the substrate in the growth zone. The N₂ carrier was dried by molecular sieves as it entered the CVD gas delivery system and a hygrometer was used to measure the dew point of the gas. Two approaches were used to deliver the precursor chemical vapor to the substrate; firstly, a graphite crucible with two precursor positions was used, transporting the precursors in the same carrier flow [2, 3]; secondly, an additional inner tube was inserted into the main reactor tube to independently transport the lead iodide (PbI₂) to the substrate. The methylammonium iodide (MAI) or cesium iodide (CsI) were sublimed from a graphite crucible further upstream with vapor transported outside of the inserted tube carrying the PbI₂. Both approaches were to ensure sufficient reaction on the substrate in the LT growth zone. The different approaches were assessed to identify the best method for producing the perovskite films. Thin film solar cells will be prepared utilising the preferred CVD approach for the perovskite films and PV performances presented.

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ET04.09.10

Interaction of Oxygen with Halide Perovskites [Alessandro Senocrate](#)^{1,2}, Tolga Acartuerk¹, Gee Yeong Kim¹, Rotraut Merkle¹, Ulrich Starke¹, Michael Graetzel^{1,2} and Joachim Maier¹; ¹Max Planck Institute for Solid State Research, Stuttgart, Germany; ²École Polytechnique Fédérale de Lausanne, Lausanne, Switzerland.

The significance of degradation processes involving halide perovskite materials and devices is widely recognized, as it jeopardizes their practical application. Among the various degrading agents, oxygen has been shown to be extremely problematic,^[1-3] and to even pose a severe threat to the technology as it is ubiquitous. On the other hand, oxygen exposure can also be beneficial for the materials, since it greatly improves their photoluminescence response.^[4,5] For these reasons, it is highly important to understand the interaction of oxygen with halide perovskites from a mechanistic point of view. Here, we investigate the consequences of oxygen exposure on the stability and transport properties of halide perovskites, focusing on methylammonium lead iodide. Thermodynamic considerations show that the material is unstable against O₂, and this decomposition reaction is indeed observed, but only under illumination. In contrast, in the dark a sluggish surface reaction kinetics maintains the material metastable. Light accelerates the interaction kinetics, resulting in a quick and significant O₂ dissolution in the material lattice (directly observed through ¹⁸O incorporation experiments), that can ultimately lead to degradation. Remarkably, this accelerated incorporation (in conditions that precede degradation) can significantly vary the electronic and ionic transport properties of the material in a way that conforms to acceptor doping.^[7] We discuss these issues quantitatively on the basis of point defect chemistry, and extend these considerations to mixed-cation and mixed-anion compositions, as these are applied in state-of-the-art devices. While some compositions show a higher kinetic stability, the degradation tendency is still observed.^[6]

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ET04.09.11

Applications of Fused-Ring Electron Acceptor ITIC-Th in Perovskite Solar Cells [Minchao Qin](#) and Xinhui Lu; The Chinese University of Hong Kong, Hong Kong, Hong Kong.

Solution-processed perovskite solar cells offer a great potential of low-cost roll-to-roll fabrication. However, the degradation of aged precursor solutions will become a critical obstacle to mass production. In this report, we employ a small molecule (ITIC-Th) to stabilize the perovskite precursor solution containing mixed cations and halides. We find that ITIC-Th can effectively suppress the formation of yellow δ -phase in the films made from aged precursor solutions. Consequently, the devices fabricated from the aged precursor solution with ITIC-Th experience much less efficiency drop with the increase of the precursor aging time - from 19.20% (fresh) to 16.55% (39 days), compared with the devices made from conventional precursor solutions dropping from 18.07% (fresh) to 1.76% (39 days). The characterizations suggest that ITIC-Th is beneficial for MA cations to be incorporated into the crystal structure, facilitating the formation of perovskite phase. Furthermore, the presence of ITIC-Th in the perovskite thin film gives rise to additional photocurrent as well as improved fill factor due to the well-matched energy levels, the passivation of defects and the complementary absorption spectra, suggesting a new route towards future high-efficiency solar cells - incorporating organic non-fullerene acceptors and halide perovskite materials into the same active layer.

ET04.09.12

In Situ X-Ray Observation of Lead Iodide Perovskite Films Prepared by a Gas Blowing Method Yoshihiko Nishihara^{1,2}, Tetsuhiko Miyadera², Masayuki Chikamatsu² and Yuji Yoshida^{1,2}; ¹University of Tsukuba, Tsukuba, Japan; ²National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Japan.

The lead iodide perovskite solar cells have an energy conversion efficiency about 22%, and the bottleneck for practical use is the stability, and the large

area fabrication process. The conventional antisolvent method has poor yield and is not suitable for large area. Thus, a combination of a coating method and a gas blowing method has attracted attention. However, its control technique has not been established and it is necessary to elucidate the formation mechanism.

In this study, we introduced an *in situ* observation system including synchrotron based grazing incident X-ray diffraction for the film formation process by coating and gas blowing methods, and compared with a nitrogen drying process. A simple bar coater was used as a coating method, and nitrogen gas was blowing from a nozzle set onto the coating film.

After drying process, perovskite crystals were overgrowth and the film surface was roughened, preparing it unsuitable for solar cells. As shown in the X-ray diffraction images of the precursor films before formation of perovskite, many bright spots showing random growth of large crystals were observed. However, in the case of gas blowing, the ring patterns indicates uniform film formation, and 020+002 diffractions oriented normal to the film surface. It is considered that the orientation of the precursor crystal contributes to the formation of a flat thin film having a large crystalline domain and hence improvement of the photovoltaic performance.

ET04.09.13

Understanding the Effects of Oxygen on Light-Induced Degradation of Perovskite Solar Cells to Achieve Long-Term Operational Stability Tae-Youl Yang¹, Nam Joong Jeon¹, Hee-Won Shin², Seong Sik Shin¹, Young Yun Kim¹ and Jangwon Seo¹; ¹Korea Research Institute of Chemical Technology (KRICT), Daejeon, Korea (the Republic of); ²Sungkyunkwan University, Suwon, Korea (the Republic of).

Perovskite solar cells (PSCs) in which organometal halides act as photoactive materials have achieved power conversion efficiency (PCE) of approximately 23 % by improving perovskite materials and fabrication process. Nowadays the substantial progress in long-term stability have been also achieved to commercialize PSCs based on such as high PCE with developing durable perovskite composition, interlayers, and encapsulation.

It has been known that the degradation of PSCs is induced by stress conditions such as light (UV), heat, moisture, and oxygen. Even though the degradation mechanisms for heat and moisture was clearly explained, that for light soaking has not been clarified yet. In practice, because the protocols to test long-term operational stability of PSCs is not standardized, the results of light soaking tests have been reported in a number of combinations of stress conditions. We reason that the operational stability under light soaking correlates with the stress factors from the atmosphere because the stability of PSCs depends on encapsulations or the testing atmosphere.

In this work, we systemically investigate the effects of oxygen on the degradation of PSCs under illumination. When PSCs were exposed to oxygen and light simultaneously, the devices were degraded quickly within an hour despite the perovskite material, (FAPbI₃)_{0.95}(MAPbBr₃)_{0.05}, was stable in the same condition. While most of discussions focus on the degradation at the interface between electron transport layers such as TiO₂ and perovskite, here we present the degradation of the interface between perovskite and hole-transporting layer (HTL). We found that oxygen and light induce iodine diffusion from perovskite to HTLs, and reveal that charge transport from the perovskite to the HTM becomes ineffective before the degradation of bulk perovskite. Based on this understanding we demonstrated the long-term operational stability over 1000h of high-efficient *mp*-TiO₂ used PSCs even under light including UV by preventing the iodine migration and oxygen ingress.

ET04.09.14

Morphology Mapping of Hybrid Perovskite Coated with Solution Shearing Min Kyu Kim¹, Hyeon Seok Lee¹, Seong Ryul Pae¹, Issam Gereige², Steve Park¹ and Byungha Shin¹; ¹KAIST, Daejeon, Korea (the Republic of); ²Saudi Aramco Research & Development Center, Dhahran, Saudi Arabia.

Large area scaling of hybrid perovskite is essential to bring the technology into commercialization. Various large-scale printing techniques have been successfully employed to fabricate high performance perovskite solar cell. In particular, solution shearing is a versatile technique in which many processing parameters can be tuned in order to produce films with desired structure and morphology. In this study, we have examined the impacts of substrate temperature and coating speed (i.e., how fast the blade is moving), two of the most influential process parameters, on morphology of the resultant perovskite films. Four distinct phases are identified and a morphology-phase map is constructed with the aforementioned parameters. Through optical analysis, an optimal phase window is chosen and the device performance with the chosen condition exhibits power conversion efficiency over 15%, which is comparable to a reference device prepared by the conventional spin-coating process. A uniform perovskite film of an area > 55 cm² is prepared with solution shearing. Several small-area devices from different locations of the large-area films shows uniform efficiencies within 5% deviation, illustrating the good uniformity achievable with our solution shearing techniques.

ET04.09.15

High-Efficient Perovskite Solar Cells Using Selectively Grown TiO₂ Nanorod-Patterned Substrates Daihong Huh¹, Minjin Kim^{1,2}, Wonjoong Kim¹, Kwan Kim¹, Minseop Byun¹, Dong Suk Kim² and Heon Lee¹; ¹Korea University, Seoul, Korea (the Republic of); ²Advanced Center for Energy, Korea Institute of Energy Research, Ulsan, Korea (the Republic of).

Organic-inorganic hybrid perovskite solar cells (PSCs) are attracting tremendous attention for new-generation photovoltaic devices because of their excellent power conversion efficiency and simple fabrication process. One of the various approaches to increase the efficiency of PSCs is to change the material or structure of the carrier transport layer. Here, optically long and electrically short structural concept is proposed to enhance the characteristics of a PSC by employing selectively grown single crystalline TiO₂ nanorods. The approach has the merit of increasing the electron-hole separation effectively and enables a thicker active layer to be coated without electrical loss by using TiO₂ nanorod as an electron pathway. Moreover, selectively grown TiO₂ nanorods increase the optical path of the incident light via scattering effects and enable a smooth coating of the active layer. Nanoimprint lithography and hydrothermal growth were employed to fabricate selectively grown TiO₂ nanorod substrates. The efficiency of fabricated PSCs have about 20 % higher than that of planar-type devices. The fabricated PSCs exhibits an efficiency of 19.86% with a current density, open-circuit voltage, and fill factor of 23.13 mA cm⁻², 1.120 V, and 76.69%, respectively. Time-resolved photoluminescence, UV-Vis spectroscopy, and the incident photon to current efficiency (IPCE) analysis were conducted to understand the factors responsible for the improvement in characteristics of the fabricated PSCs.

ET04.09.16

Degradation Pathways of CH₃NH₃PbI₃ Perovskite Films Depending on the Polarity of Localized Charges Min-cheol Kim^{1,2}, Namyoun Ahn^{1,2}, Byeong Jo Kim³, Young Un Jin³, Hyun Suk Jung³ and Mansoo Choi^{1,2}; ¹Seoul National University, Seoul, Korea (the Republic of); ²Global Frontier Center for Multiscale Energy Systems, Seoul, Korea (the Republic of); ³School of Advanced Materials science and engineering, Sungkyunkwan University, Suwon, Korea (the Republic of).

Localized charge states which are stagnated in perovskite crystal has been spotted as the main culprit for the degradation of metal halide perovskite materials. Experimental and simulational results on the trapped-charge driven degradation of perovskite materials have testified to the detrimental effect of localized charge inside the perovskite crystals. Nevertheless, the polarity of such localized charge states dependency on degradation has not been investigated yet. Here, it was found out for the first time that the charge polarity (hole-rich and electron-rich) inside the perovskite films, which is induced by a selectively charge transporting half devices, play a critical role on degradation depending on the combination of surrounding gaseous molecules. The perovskite films with the localized hole were degraded rapidly in only-moisture condition, while the ones with localized electron were degraded faster in

only-oxygen condition. Interestingly, with the existence of both oxygen and moisture which represents real solar-cell operation condition, perovskite films with localized hole degraded much faster than any other circumstances. We discovered the mechanism of different degradation rates via *ab initio* molecular dynamics simulations based on density functional theory calculation. Strong Pb-O interactions and formation of hydroxide species led to fast destroy of perovskite crystal, which was confirmed by X-ray assisted spectroscopic measurements. This study highlights that while either localized positive or negative charges are the fundamental cause for the degradation of perovskite materials, the degradation pathways are totally different depending on the polarity of localized charges and de-bonding of perovskite crystals via localized holes under the actual atmospheric condition is found to be more active than that by localized electrons.

ET04.09.17

Influence of Perovskite Film Formation and Morphology on Textured Perovskite/Silicon Tandem Solar Cells Md Wayesh Qarony¹, Mohammad I. Hossain¹, Vladislav Jovanov², Dietmar Knipp³ and Yuen H. Tsang¹; ¹Department of Applied Physics and Materials Research Center, The Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong; ²Department of Physics and Earth Sciences, Jacobs University Bremen, Bremen, Germany; ³Geballe Laboratory for Advanced Materials, Department of Materials Science and Engineering, Stanford University, Stanford, California, United States.

The influence of the film formation and morphology of perovskite top solar cells prepared on textured silicon bottom solar cells was investigated by modeling the deposition process and the optics of the perovskite/silicon tandem solar cells. An efficient photon management is required to realize perovskite/silicon tandem device with energy conversion efficiency exceeding the efficiency of crystalline silicon single junction solar cells. The perovskite solar cell has to be deposited on a textured crystalline silicon solar cell to allow for an efficient incoupling of light in the low refractive index top and the high refractive index bottom solar cell [1]. A recently developed fully textured perovskite/silicon tandem solar cell exhibits the record efficiency of 25.2% [2]. The formation of films on textured surfaces varies from the non-conformal deposition, which is typically observed for physical deposition techniques (e.g. PVD), to conformally prepared films obtained for some chemical deposition techniques (e.g. CVD, ALD). A 3D morphological algorithm was used to model the film formation [3]. The investigation is carried out for a wide range of pyramidal textured surfaces with a constant period to height ratio. A hybrid approach is used to investigate the optics by combining a three-dimensional (3D) finite-difference time-domain simulations with experimental measurements. Short-circuit current densities exceeding 20 mA/cm² were obtained for non-conformally and conformally grown perovskite films. A comparison of non-conformally and conformally deposition shows that short circuit current densities of 20 mA/cm² can be reached for distinctly thinner conformally deposited films. On the other hand, the roughness of the underlying silicon bottom solar cells has to be larger in the case of the conformally deposited films. Guidelines will be provided on how to achieve high short circuit currents for non-conformal and conformally prepared perovskite films.

Acknowledgement: This work is financially supported by the The Hong Kong PhD Fellowship Scheme supported by the Hong Kong RGC.

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ET04.09.18

Spin Coated Copper (I) Thiocyanate as a Hole Transport Layer for Perovskite Solar Cells Utku Er^{1,2}, Kerem Cagatay Icli^{1,2} and Ahmet Macit Ozenbas^{1,2}; ¹Orta Dogu Teknik University, Ankara, Turkey; ²GUNAM, Ankara, Turkey.

Application of a low cost and efficient p-type inorganic hole-transporting material, copper thiocyanate (CuSCN), on mesoporous n-i-p configured perovskite based devices was conducted in this study. Diethylsulfide was chosen for the preparation of precursor solution in order to deposit CuSCN layer on perovskite without degrading it. Topographical, elemental and electrical characterizations of spin coated CuSCN layers were performed using XRD, AFM, SEM, XPS, UPS, and UV-Vis studies. A power conversion efficiency exceeding 11.02 % with an open circuit voltage of 0.83 V was succeeded in the perovskite solar cells under full sun illumination. Low-temperature solution process used for the deposition of CuSCN and a fast solvent removal method allowed the creation of compact, highly conformal CuSCN layers that facilitate rapid carrier extraction and collection. The differences in series and recombination resistances for CuSCN free and CuSCN containing cells were also determined using impedance spectroscopy (IS) analysis. Moreover, the effect of TiO₂ layer thickness on the cell performance was studied where these TiO₂ layers were used not only for electron extraction and transportation but also as hole blocking layer in perovskite solar cells. The impedance spectroscopy results were also consistent with the differently configured cell performances. This work shows a well defined n-i-p configured perovskite cell with optimized layers which utilizes low cost and abundant material for photovoltaic applications.

ET04.09.19

Area Loss Analysis in Perovskite Modules Using Dark Lock-In Thermography and Luminescence Imaging Lucija Rakocevic^{1,2}, Laura Mundt³, Robert Gehlhaar¹, Tamara Merckx¹, Tom Aernouts¹, Martin Schubert³, Stefan Glunz³ and Jef Poortmans^{1,2,4}; ¹TFPV, imec, Leuven, Belgium; ²ESAT, Katholieke Universiteit Leuven (KUL), Leuven, Belgium; ³Photovoltaics, Fraunhofer Institute for Solar Energy Systems, Freiburg, Germany; ⁴University of Hasselt, Hasselt, Belgium.

Organometallic halide perovskites are effective low-cost photoactive materials that require low energy fabrication processes. Perovskite thin film PV technology has reached a cell power conversion efficiency of 23 % within less than a decade of focused research activity. The major breakthroughs arose from innovation in materials used for the photoactive layer and their combination with appropriate transport layers. Transferring these research efforts into commercially viable PV technology requires achieving long term stability and upscaling with minimal performance losses.

Upscaling from sub-square centimeter cell area to module with monolithic serially interconnected cells introduces several losses. In our devices, layer inhomogeneities are the main loss mechanism that scales up with module size and represent up to 40 % of the total loss in aperture area efficiency going from a 0.1 cm² cell to a 4 cm² module.

In this study, we use dark lock-in thermography, electroluminescence and photoluminescence to analyze losses in solution processed perovskite modules, focusing on layer inhomogeneities. In contrast to small area perovskite devices which are processed using a radial coating method, upscaled devices are processed using linear coating techniques. We compare layer inhomogeneities in 4 cm² n-i-p modules processed using either spin coating or blade coating. By comparing results from dark lock-in thermography, electroluminescence and photoluminescence (PL) we can identify differences in layer formation and specific particle inhomogeneities stemming from different layers. Moreover, we can identify and localize inhomogeneities with high spatial resolution of several 10 μm with micro PL and a micro light beam induced current (LBIC) method. As a result, we pinpoint the failures in the film formation that cause performance losses and thus show the potential of the device imaging by thermography and different luminescence techniques in post-process analysis of perovskite modules. Current processing techniques result in 12-15 % power conversion efficiency for 16 cm² aperture area modules, depending on the

coating technique. We will apply lessons learned to further optimize module performance.

SESSION ET04.10: Upscaling and Industrial Considerations

Session Chair: Yabing Qi

Thursday Morning, November 29, 2018

Hynes, Level 3, Room Ballroom C

8:00 AM *ET04.10.01

Industrial Case of Perovskite Solar Cells Konrad Wojciechowski; Saule Technologies, Wroclaw, Poland.

Metal halide perovskites constitute a very attractive class of materials for optoelectronic applications, such as solar cells, light emitting diodes, lasers and photodetectors. Most notably, solid-state photovoltaic devices based on these materials have reached power conversion efficiencies (PCEs) of 22% after just five years of academic research.

Perovskite solar cells have a great commercial potential, but there still remain few challenges, which need to be resolved to prove the viability of the technology. Some of the well-known issues include material stability. Furthermore, cost-effective, reliable fabrication process capable of delivering highly efficient, large-area perovskite modules is yet to be demonstrated.

This talk will outline the industrial challenges of perovskite solar cells including legislative hurdles as well as the potential impact on the solar industry. Moreover, we will present fully scalable ink-jet printing process of the perovskite PV stack and fabrication of perovskite printable mini-modules of areas up to A4 size, complemented with a robust encapsulation methodology.

8:30 AM ET04.10.02

Up-Scaling of Organic-Inorganic Hybrid Perovskite Solar Cells and Modules Luis K. Ono¹, Matthew Leyden^{1,2}, Yan Jiang¹, Longbin Qiu¹, Sonia R. Raga^{1,3}, Mikas Remeika^{1,4}, Emilio J. Juarez-Perez¹, Shenghao Wang^{1,4} and Yabing Qi¹; ¹Okinawa Institute of Science and Technology, Okinawa, Japan; ²Center for Organic Photonics and Electronics Research (OPERA), Kyushu University, Fukuoka, Japan; ³Melbourne Centre of Nanofabrication, Monash University, Melbourne, Victoria, Australia; ⁴Department of Applied Physics, University of Tsukuba, Tsukuba, Japan.

Owing to the intensive research efforts across the world since 2009, lab scale (<0.1 cm²) organic-inorganic hybrid perovskite solar cells were demonstrated to achieve power conversion efficiencies (PCEs) comparable to several other photovoltaic technologies. However, development of up-scaling processes (>10 cm²) with high PCE and stability is important for moving forward this technology towards commercialization [1,2]. At OIST, a team of researchers in the Energy Materials and Surface Sciences Unit has been making concerted efforts to develop processes aiming at high PCE, high-throughput, and minimum batch-to-batch variation, and compatible with large-area perovskite solar cells and modules. In this talk, we will present our current progress to use chemical vapor deposition CVD [3-6] to fabricate perovskite solar cells and modules. Also, we will introduce a novel methylamine (CH₃NH₂) gas induced crystallization process [7,8], which provides valuable insight into the formation of perovskite films.

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8:45 AM ET04.10.03

Reliability Improvement of Perovskite Solar Cells Through a Roll-to-Roll (R2R) Continuous Process Mei Gao¹, Chuantian Zuo¹, Dechan Angmo¹, Youn-Jung Heo², Doojin Vak¹ and Fiona Scholes¹; ¹CSIRO Manufacturing, Melbourne, Victoria, Australia; ²Gwangju Institute of Science and Technology (GIST), Gwangju, Korea (the Republic of).

A groundbreaking breakthrough with a power conversion efficiency over 22% has been achieved for perovskite solar cells on a laboratory scale (1). To successfully translate this technology to commercial scaling, the engagement with industrial compatible processing methods must be used. Through this, more information is gathered during the development stage in catalysing the commercialization.

Among the reported scalable coating methods such as screen printing, spray-coating and doctor-blade, slot-die coating in conjunction with R2R processes present several advantages, including low material waste, fast processing, good film thickness control and one-dimensional patterning suitable for the processing of serially interconnected cells without the need for substantial patterning process (2). However, to achieve reliable, large grain size, pin-hole free, smooth films over a continuous process in commercially acceptable scale remains a great challenge. In this talk, we will present an innovative approach to enable the production of much smoother film with substantially improved devices reproducibility, and this approach is readily to be adopted by the existing printers in large scale coating. The correlation between the precursor composition and the complex coordination embodies a range of parameters including concentration, web speed, solution feeding rate as well as substrate temperature for the fabrication of high quality films, which will be discussed. The paralleled performance comparison of the same device structures made using slot-die batch-to-batch on glass substrates will also be presented.

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9:00 AM DISCUSSION TIME

9:15 AM ET04.10.05

Upscaled Roll-to-Roll Manufacturing of Perovskite Based Solar Cells [Pim Groen](#)^{1,2}; ¹Holst Centre, Eindhoven, Netherlands; ²Aerospace Engineering, Delft University of Technology, Delft, Netherlands.

Metal-halide based perovskites are promising novel materials for thin-film photovoltaics, exhibiting high power conversion efficiencies. A number of challenges still need to be addressed before PSCs can enter the PV market. One of these challenges is the development of industry-relevant technologies for scaling up the perovskite module manufacturing. The feasibility of upscaling the perovskite solar cells technologies to high volume production using Roll-to-Roll (R2R) slot die coating is demonstrated in this talk. Perovskite solar cells were produced by R2R slot die coating on flexible PET/ITO substrates with the width of 30 cm. Roll-to-Roll deposition of electron transport layer (ETL) and perovskite is performed at ambient atmosphere from non-toxic solvents compatible with industrial manufacturing. The average stabilized power conversion efficiency of the devices made from the foils randomly cut from different places was 12%, with the best value of 13.5%. The demonstrated achievement is an important milestone and a big solid step towards future commercialization of perovskite-based solar cells technologies.

9:30 AM ET04.10.06

R2R Compatible High-Speed Coating of Perovskite Solar Cell [Benjia Dou](#), David T. Moore, Kai Zhu and Maikel van Hest; National Renewable Energy Laboratory, Lakewood, Colorado, United States.

High efficiency combined with transformative roll-to-roll (R2R) printability makes metal halide perovskite (MHP)-based solar cells the most promising solar technology to address the terawatt challenge of the future energy demand. However, translation from lab-scale deposition techniques to large-scale R2R methods has typically led to reduced photovoltaic performance. Here, we demonstrate an MHP ink that allows R2R compatible high-speed (>2.5 m min⁻¹) one-step blade coating. MHP solar cells from the developed ink can produce power conversion efficiency over 19% in the ambient environment, without any addition of antisolvent, gas blow, vacuum treatment or high-temperature stage temperature. This report on one-step antisolvent (or similar processing) treatment-free blade coating technique paves the way for the R2R production of high-efficiency MHP solar cells.

9:45 AM BREAK

10:00 AM *ET04.10.08

Vacuum Deposited Single and Double Junction Perovskite Solar Cells [Henk J. Bolink](#), Ana Igual Munoz, Benedikt Daenekamp, Jorge Ávila, Daniel Pérez del Rey, Michele Sessolo and Pablo P. Boix; University of Valencia, Paterna, Spain.

We will report on the progress on vapor phase deposited perovskites, including low bandgap Pb-Sn and wider bandgap multiple cation versions. The performance of these materials in both single and double junction solar cells will be reported. The influence of the use of thin organic charge extraction layers, using strong dopants, ionic compounds and conjugated polymers will be described.

10:30 AM ET04.10.09

Coevaporated p-i-n Perovskite Solar Cells Deposited at Elevated Substrate Temperature—Process Optimization and Photo Stability [Ranjith Kottokkaran](#), Harshavardhan A Gaonkar, Hisham A. Abbas, Max Noack and Vikram L. Dalal; Microelectronics Research Center, Iowa State University of Science and Technology, Ames, Iowa, United States.

Thin-film photovoltaics represents the next generation of promising photovoltaics technology. Exhibiting a verified efficiency of over 22%, perovskite solar cells are the fastest growing solar material to date. Lead tri-halide perovskites (MAPbX₃) are a new and exciting technology among perovskite solar cells. Solution process-based fabrication of perovskite solar cells have known problems of reproducibility, whereas vacuum deposition, which involves sequential or co-evaporation of lead halide and methyl ammonium iodide (MAI), is a much more reproducible technique. Devoid of any organic solvents, vapor deposited perovskites show superior photo stability.

In this work, we report on co-evaporated MAPbI₃ perovskite deposited at various substrate temperatures using a multi-source thermal evaporator. The central challenge involved with the co-evaporation process is precise control of the MAI pressure during the deposition process. A p-i-n device architecture of FTO/PTAA/MAPbI₃/PCBM/Al with power conversion efficiency of >17.5% was achieved by maintaining the MAI pressure between 5.5-6 x10⁻⁵ Torr for a room temperature deposition. Further, we also carried out co-evaporation of MAPbI₃ perovskite at higher substrate temperatures of 50 °C and 75 °C. Here, elevating the MAI pressures (9-9.5x10⁻⁵ Torr and 1.2-1.3x10⁻⁴ Torr respectively) is essential to achieve efficiencies of >16%. SEM micrographs show grain enhancement for films deposited at higher temperatures. Photo degradation studies show that perovskite devices deposited at 75 °C show superior photo-stability, with less than 1% degradation in the short circuit current for over 100 hours of light exposure.

10:45 AM ET04.10.10

A Novel Cryo-Controlled Growth Technique for High Efficiency Organometal Halide Perovskite Solar Cells [Annie Ng](#)¹, Zhiwei Ren², Qian Shen², Sin Hang Cheung³, Aleksandra B. Djurišić⁴, Shu Kong Su³, Gang Li² and Charles Surya¹; ¹Nazarbayev University, Astana, Kazakhstan; ²Hong Kong Polytechnic University, Hong Kong, China; ³Hong Kong Baptist University, Hong Kong, China; ⁴The University of Hong Kong, Hong Kong, China.

Perovskites with multi-components have demonstrated significant potential for the development of high performance photovoltaic cells with better device efficiency and stability. Optimization of perovskite growth techniques are crucial for acquiring mixed halide perovskite films with precise stoichiometry, desirable morphology and low defect density. Reports on growth processes involving the formation of Lewis acid-base adduct in precursor films and the application of anti-solvent dripping process have become the mainstream for preparing solution based mixed halide perovskites. However, a number of limitations are found for using anti-solvent techniques to prepare large-scale samples. The resultant morphology of the perovskite films is significantly affected by many factors such as the anti-solvent dripping time, volume and location on the samples. Furthermore, the anti-solvent technique commonly works together with the spin-coating process and it would be difficult to apply on other large-scale solution processing techniques.

We report a novel cryo-controlled growth technique for the growth of mixed halide perovskites. The abrupt decrease in the ambient temperature results in a supersaturation condition in the as-casted precursor films, leading to the formation of uniform nucleation sites for subsequent crystal growth. A blow dry process is introduced subsequently to facilitate the removal of residual solvents from the films before thermal annealing. Our proposed strategy can effectively retard the pre-mature crystallization of the perovskites and, thereby, decoupling the nucleation and crystallization phases. This material growth

approach can be applied to different types of mixed halide perovskites, ensuring excellent uniformity of the nucleation layers and, subsequently, higher quality perovskite films. A power conversion efficiency (PCE) of 21.4 % with a fill factor of 80 % for the champion PSC is achieved using the proposed perovskite growth technique without utilizing any anti-solvents.

11:00 AM ET04.10.11

Chemical Vapor Deposition for 10 cm × 10 cm Large-Area Perovskite Solar Modules Longbin Qiu, Yan Jiang, Zonghao Liu, Luis K. Ono, Dae-Yong Son and Yabing Qi; Energy Materials and Surface Sciences Unit (EMSSU), Okinawa Institute of Science and Technology Graduate University (OIST), Okinawa, Japan.

Perovskite solar cells have shown efficiency approaching silicon photovoltaic counterparts, but mostly achieved on a small area. To commercialize this low cost technology, scalable fabrication is one of the main challenges to be addressed [1]. For large-area, uniform and high quality film deposition, we have employed industry compatible chemical vapor deposition to deposit MAPbI₃, FAPbI₃, and Cs_xFA_{1-x}PbI₃ films with high quality for solar cells/modules [2-5]. In this work, fully scalable perovskite solar modules with high-geometric fill factor have been fabricated by a further optimized chemical vapor deposition process. Upon increasing of device area, device performance decreases only gently. 10 cm × 10 cm solar modules showed an aperture efficiency approaching 10% with a geometric fill factor greater than 90%. We show that chemical vapor deposition is compatible for large-area, uniform and high quality perovskite films and solar modules.

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[2] M.R. Leyden, L.K. Ono, S.R. Raga, Y. Kato, S. Wang, Y.B. Qi*, *J. Mater. Chem. A* **2** (2014) 18742.

[3] M.R. Leyden, M.V. Lee, S.R. Raga, Y.B. Qi*, *J. Mater. Chem. A* **3** (2015) 16097.

[4] M.R. Leyden, Y. Jiang, Y.B. Qi*, *J. Mater. Chem. A* **4** (2016) 13125.

[5] Y. Jiang, M.R. Leyden, L. Qiu, S. Wang, L.K. Ono, Z. Wu, E.J. Juarez-Perez, Y.B. Qi*, *Adv. Funct. Mater.* **28** (2018) 1703835.

11:15 AM ET04.10.12

Towards Completely Inkjet-Printed Perovskite Solar Cells Aron J. Huckaba, Yonghui Lee, Andreas Lesch, Hubert Girault and Mohammad K. Nazeeruddin; Ecole Polytechnique Federale de Lausanne, Sion, Switzerland.

In the past ten years, the efficiencies of perovskite solar cells have risen from 3.8 to > 22% power conversion efficiency (PCE). The highest performing devices typically have small areas (<1 cm²) and are fabricated by spin-coating deposition of most of the active layers. While spin-coating works well for small area substrates, it is not industrially applicable due to the high percentage of material loss and substrate size limitation. Reports of perovskite absorber layer deposition by industrially relevant techniques such as slot-die coating, evaporation, and inkjet printing are becoming more frequent. Inkjet printing is a digital, mask-less and contact-less fabrication technique that allows the direct deposition of miniscule ink volumes onto substrates with full pattern control, where the pattern resolution is limited by the droplet volume (generally below 100 pL) and the spreading diameter of the droplet on the substrate. Complete Organic Light Emitting Diodes (OLEDs), Field Effect Transistors (FETs), and Organic Photovoltaic (OPV) devices have been fabricated using inkjet printing, but this has not yet been achieved with perovskite solar cells. Herein, efforts towards the fabrication of completely inkjet-printed perovskite solar cells by bottom-up layer construction are described. Optimization studies of each active layer will be discussed, as well as the inclusion of inkjet-printed active layers in high-efficiency perovskite solar cells.

11:30 AM ET04.10.13

A Vacuum-Free Plasma Enhanced Ultrasonic Spray Deposition Process for Highly Efficiency Large-Area Perovskite Solar Cells Dmitry Lopatin², Oleg Baranov², Elizaveta Korzhova³, Bogdan Bragin² and Vinay Gupta¹; ¹Advanced Materials and Devices Division, National Physical Laboratory, New Delhi, India; ²Kuban State University, Krasnodar, Russian Federation; ³University of Franche-Comté, Besançon, France.

The photovoltaic performance of Metal halide perovskite solar cells (PSCs) has reached beyond 20% on a small device area (≤0.1cm²) and shown potential to overtake silicon solar cell. However, the researchers are still grappling with maintaining high efficiency over large device area due to the current technological barrier. Here we have achieved a single cell efficiency of ~ 14% over an area of 10 x 10 cm² by inventing a disruptive vacuum-free plasma enhanced ultrasonic spray deposition (PEUSD) technology and obtained uniform and high-quality perovskite film over large area. The PEUSD is a vacuum free technology that can print all the layers of a PSC i.e. Ni/NiO_x/CH₃NH₃PbI₃/C₆₀/TiO₂/Cu-NWs/ITO including metal contacts. This technology would enable low-cost architecture for the commercialization of PSCs and can potentially replace current vacuum-based coating technologies for thin film deposition.

11:45 AM ET04.10.14

Pulsed Flash Infrared Annealing for Efficient and Stable Perovskite Inorganic Solar Cell Sandy Sanchez¹, Michael Saliba¹ and Antonio Abate²; ¹Adolphe Merkle Institute, Fribourg, Switzerland; ²Helmholtz-Zentrum Berlin, Berlin, Germany.

Organic-inorganic perovskite solar cells have achieved impressive power conversion efficiency over the past years, yet operational stability remains the key concern. One strategy to improve long-term stability is to replace the thermally unstable organic with inorganic cations comprising the perovskite lattice. Here, for the first time, we make use of pulsed infrared light to drive the crystallisation of inorganic mixed halide CsPb_{1-x}Br_(3-x) perovskite films in solar cells with a power conversion efficiency exceeding 10%. By varying the iodide-bromine ratio systematically, we found that to keep the inorganic perovskite black phase stable at the room temperature we need to limit the iodine content to lower than 60% - bromine content higher than 40%. Our finding revises previous reports claiming stable compositions with higher iodine content, which was systematically exploited to reduce the perovskite bandgap with the aim to enlarge the light absorption spectra and thus to boost the device efficiency. We demonstrate that the newly defined stable compositional range enables devices that retain 90% of the initial efficiency after stressing the perovskite at 200°C for one hour. This result is a key finding for the application of perovskite in concentrated photovoltaic.

SESSION ET04.11: Beyond Solar Cells and New Materials
Session Chairs: Richard Friend and Prashant Kamat
Thursday Afternoon, November 29, 2018
Hynes, Level 3, Room Ballroom C

1:30 PM *ET04.11.01

Near Infrared-Emissive Colloidal Multinary Lead Halide Perovskite Nanocrystals for Optoelectronic Applications Ioannis Lignos¹, Yevhen Shynkarenko^{1,2}, Maryna Bodnarchuk², Andrew deMello¹ and Maksym V. Kovalenko^{1,2}; ¹Chemistry and Applied Biosciences, ETH Zurich, Zurich, Switzerland; ²Empa, Swiss Federal Laboratories for Materials Science and Technology, Dübendorf, Switzerland.

Hybrid organic-inorganic and fully inorganic lead halide perovskite nanocrystals (NCs) have recently emerged as versatile solution-processable light-emitting and light-harvesting optoelectronic materials [1]. The photoluminescence of these NCs is characterized by narrow emission line-widths of 12–42 nm, wide color gamut covering up to 140% of the NTSC color standard, high quantum yields of up to 100%. Cs_{1-x}FA_xPbI₃ and FAPbI₃ reach the near-infrared wavelengths of 800 nm [2]. A particularly difficult challenge lies in warranting the practical utility of such semiconductor NCs in the red and infrared spectral regions. In this context, all three archetypal A-site monocationic perovskites—CH₃NH₃PbI₃, CH(NH₂)₂PbI₃, and CsPbI₃—suffer from either chemical or thermodynamic instabilities in their bulk form. A promising approach towards the mitigation of these challenges lies in the formation of multinary compositions (mixed cation and mixed anion). In the case of multinary colloidal NCs, such as quinary Cs_xFA_{1-x}Pb(Br_{1-y}I_y)₃ NCs, the outcome of the synthesis is defined by a complex interplay between the bulk thermodynamics of the solid solutions, crystal surface energies, energetics, dynamics of capping ligands and the multiple effects of the reagents in solution. Accordingly, the rational synthesis of such NCs is a formidable challenge. We show that droplet-based microfluidics can successfully tackle this problem and synthesize Cs_xFA_{1-x}PbI₃ and Cs_xFA_{1-x}Pb(Br_{1-y}I_y)₃ NCs in both a time- and cost-efficient manner. In this showcase study, we fine-tune the photoluminescence maxima of such multinary NCs between 700 and 800 nm, minimize their emission linewidths (to below 40nm), and maximize their photoluminescence quantum efficiencies (up to 89%) and phase/chemical stabilities [3]. Detailed structural analysis revealed that the Cs_xFA_{1-x}Pb(Br_{1-y}I_y)₃ NCs adopt a cubic perovskite structure of FAPbI₃, with iodide anions partially substituted by bromide ions. Most importantly, we demonstrate the excellent transference of reaction parameters from microfluidics to a conventional flask-based environment, thereby enabling up-scaling and further implementation in optoelectronic devices. As an example, Cs_xFA_{1-x}Pb(Br_{1-y}I_y)₃ NCs with an emission maximum at 735 nm were integrated into light-emitting diodes, exhibiting high external quantum efficiency of 5.9% and very narrow electroluminescence spectral bandwidth of 27 nm [3].

1. M. V. Kovalenko *et al.* *Science* **2017**, *358*, 745-750
2. L. Protesescu *et al.* *ACS Nano* **2017**, *11*, 3119–3134
3. I. Lignos *et al.* *ACS Nano* **2018**, DOI: 10.1021/acsnano.8b01122

2:00 PM *ET04.11.02

Monolithically Integrated On-Chip Lasers Based on Perovskite Optoelectronics Anna Lena Giesecke¹, Piotr Cegielski¹, Stefanie Neutzner², Caroline Porschatis¹, Daniel Schall¹, Marina Gandini², Jens Bolten¹, Carlo Andrea Riccardo Perini², Stephan Suckow¹, Bartos Chmielak¹, Satender Kataria³, Annamaria Petrozza² and Max Lemme^{3,1}; ¹AMO GmbH, Aachen, Germany; ²CNST @Polimi, Istituto Italiano di Tecnologia, Milan, Italy; ³Electronic Devices, RWTH Aachen University, Aachen, Germany.

We demonstrate latest achievements of integrated perovskite devices on a silicon nitride photonic platform. Perovskite as a class of solution processed semiconductors with a direct bandgap offering a variety of interesting emission wavelengths for on-chip photonics. Spin-coating enables a possibility of direct integration of the lasing material as a counterpart to epitaxial growth with is not applicable on amorphous substrates such as silicon nitride.

We report on methylammonium lead iodide (MAPbI₃) perovskite micro-disc and microring lasers which are monolithically integrated into silicon nitride photonic integrated circuits showing low lasing thresholds at room temperature. The perovskite micro-discs are placed in the vicinity of a single mode silicon nitride waveguides so that the generated laser light can be directly used by a photonic circuitry.

A top-down lithographic structuring approach has been developed to pattern perovskite micro-discs without degenerating the active material. This method paves the way to more complicated circuits and structures enabling electrically pumped perovskite laser in the near future. High-throughput fabrication techniques can be applied enabling the usage of the material in commercial systems; i.e. optoelectronic circuits with monolithically integrated lasers. We report on fabrication technologies for reproducible on-chip devices with low device-to-device variations and low sample-to-sample variation with almost 100 measured devices. The lasing thresholds are in the order of 5 μJ/cm² which outperforms most unpatterned single crystal perovskite lasing demonstrations. The laser emission lies at ~785 nm and is narrow in linewidth (~1 nm). The micro-discs were optically pumped at room temperature in ambient conditions with 120 fs laser pulses with 250 kHz repetition rate at 630 nm wavelength. X-ray diffraction crystallography has been performed prior to processing the perovskite and on the final device showing only small changes in the material after the patterning process. Device performance is confirmed by simulations (Finite Difference Time Domain, FDTD).

Our fabrication approach is fully reproducible and is a technological base for mass-fabrication of active optoelectronic circuits with hybrid perovskite-dielectric waveguide materials.

2:30 PM ET04.11.03

A Strategy for Architecture Design of Crystalline Perovskite Light-Emitting Diodes with High Performance and Stability Zhaoxin Wu, Yifei Shi, Hua Dong, Chenxin Ran, Jinfei Dai, Fang Yuan, Bo Jiao and Xun Hou; School of Electronic and Information Engineering, Xi'an Jiaotong University, Xi'an, China.

Hybrid halide perovskites have recently emerged as new promising semiconductors for both photovoltaic and optoelectronic applications. Given the rapid rise in performance of perovskite solar cells, the demonstration of high photoluminescence quantum efficiency and optical gain in these hybrid perovskites suggests that these materials should also be potential light emitters for light emitting diodes and lasers.

Here, we introduce a new design strategy and conception, “Insulator-Perovskite-Insulator” (IPI) architecture tailored to perovskite light-emitting diodes (PeLEDs). We experimentally show that the IPI structure effectively induces charge carriers into perovskite crystals, blocks leakage currents via pinholes in the perovskite film, avoids exciton quenching simultaneously. Consequently, as for FAPbBr₃, a 30-fold enhancement in the current efficiency of IPI-structured PeLEDs compared to a control device was achieved - from 0.64 cd/A to 20.3 cd/A. As the example of CsPbBr₃, compared with the control device, both current efficiency and lifetime of IPI-structured PeLEDs were obviously improved [1]. In addition, we also demonstrate tin (Sn)-based PeLEDs with all-inorganic heterostructure fabricated by the vapor-deposition process. The all-inorganic hetero-structured PeLEDs exhibited a maximum EQE of ~0.34%, and withstood current density up to 915 A/cm² with small emission zone of 0.01 mm². Besides, low threshold (7 μJ/cm²) amplified spontaneous emission was presented from the extremely smooth and uniform cesium tin halide perovskite films. These characteristics demonstrate the great potential of using them as gain media for electrically pumped lasers [2,3].

References

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- [2] Yuan F, Xi J, Wu ZX*, *et al.* *Phys Status Solidi RRL* (2018), DOI: 10.1002/pssr.201800090.
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2:45 PM ET04.11.04

Space Based Perovskite Photovoltaics Samuel Loke, Nina Vaidya, Pilar Espinet Gonzalez, Michael Kelzenberg, Qin Yang, Emily C. Warmann and

Harry A. Atwater; California Institute of Technology, Pasadena, California, United States.

Organo-lead halide perovskite solar cells are an exciting candidate for future space based photovoltaics. Perovskites have potential for significantly higher specific power (power generated per unit mass) compared to other photovoltaic technologies, since intrinsic radiation hardness may potentially enable radiation shielding to be omitted as a cell component. This creates an opportunity for perovskites to be a leading photovoltaics technology for space power, where the Cost per kg is a demanding metric owing to high payload launch costs, provided radiation robustness and environmental stability can be validated. It is thus imperative to study how perovskites respond to thermal and radiative loads in space. We have demonstrated methylammonium lead iodide (MAPbI₃)-based solar cells to be resistant to 30, 50 and 350 keV proton irradiation at 10¹² p⁺/cm² fluence, and 1 MeV electron irradiation at 10¹⁵ e⁻/cm² fluence. In order to deepen our understanding of the space performance of perovskite solar cell devices, we fabricate several perovskite device structures, with various hole transport layer (HTL) materials and electron transport layer (ETL) materials, and characterize their performance in simulated space environments with respect to radiation stability, under air mass 0 (AM0) illumination in vacuum and under thermal cycling. Finally, we examine the feasibility of fabricating perovskites on various flexible substrates that will allow for even lower areal mass density as well as easier payload storage. For this study, we examine the perovskite materials MAPbI₃, formamidinium lead iodide (FAPbI₃), as well as efficient mixed cation perovskites. For our carrier selective contacts, we examine NiO and CuSCN for the HTL; and TiO₂ and C60-PCBM for the ETL. For evaluating the effects of radiation, we conduct photoluminescent lifetime measurements on the perovskites; 4-point probe and Hall effect measurements on the HTLs and ETLs; and I-V curve measurements on the solar cell devices; all performed before and after radiation exposure. To evaluate the response to extended illumination, we load cells of similar architecture before and after irradiation into a vacuum chamber and expose them to AM0 sunlight via a solar simulator, measuring their I-V performance at regular time intervals. Finally, we endeavor to heat the cells to a range of operating temperatures and measure their stability while operating at maximum power point, open circuit, and closed circuit conditions.

3:00 PM BREAK

3:30 PM *ET04.11.05

Toward Closed-Loop Automated Materials Discovery for Lead-Free Perovskite-Inspired Materials Enabled by Machine Learning Shijing Sun¹, Zekun Ren², Felipe Oviedo¹, Rachel C. Kurchin¹, Noor Titan Putri Hartono¹, Juan-Pablo Correa-Baena¹ and Tonio Buonassisi^{1,2}; ¹Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; ²Singapore-MIT Alliance for Research & Technology (SMART), Singapore, Singapore.

Despite significant advances in simulation and theory, progress toward identifying lead-free perovskite materials has been limited by low experimental throughput and reproducibility. For early-stage materials, characterization tools are often slow or imprecise in pinpointing the bulk or interface property that limits efficiency and/or reliability. Lack of proper diagnosis makes the process-optimization feedback loop more open ended, and driven by intuition rather than the scientific method.

In this talk, we present progress toward a closed-loop, automated experimental system for novel photovoltaic materials discovery. We present advances in rapid diagnosis, enabled by a combination of machine learning and non-destructive electrical testing. The closed-loop feedback loop enables more rapid process optimization to occur. We discuss prospects of using this improved experimental loop for new materials discovery, and realization in thin-film form of materials that previously had only been synthesized in bulk (e.g., certain double perovskites).

4:00 PM ET04.11.06

Machine Learning Bandgaps of Inorganic Mixed Halide Perovskites Alessio Gagliardi, Jared Stanley and Waldemar Kaiser; Technische Universitat Munchen, Munich, Germany.

The identification of suitable lead-free perovskites is crucial for their envisioned applications in photovoltaics. Homovalent substitution of lead with Sn and Ge-based compounds are under intense investigation as potential alternatives, but suffer from stability issues, for example, due to the susceptibility of these ions toward the 4+ oxidation state. Mixed compositions, with two or more possible ions for each lattice position, have been proposed for overcoming these issues and enhancing performance [1, 2]. However, as it is computationally and experimentally prohibitive to measure the vast configuration space available to the mixed perovskites, statistical learning techniques are needed to find a more efficient mapping of mixing parameters to the properties of interest.

Efficient and accurate vetting of perovskites for a range of properties has recently been accomplished in high-throughput Density Functional Theory (DFT) studies of compounds by use of Kernel Ridge Regression (KRR) [3, 4]. Crucial to their success is the determination of adequate material fingerprints which uniquely define the materials and capture the property of interest. Here we demonstrate how one such important screening parameter, the fundamental bandgap, can be predicted for a family of inorganic mixed halide perovskites using novel globally valid material fingerprints based solely on the atomic configurations of arbitrary unit cells. The Partial Radial Distribution Function method [5] is expanded upon to include densities for a variety of elemental properties, enabling us to define a more robust material fingerprint while illuminating the underlying drivers of target properties in a chemically intuitive manner. The results are supplemented with thermodynamic and geometric data to identify the best compositions and the features responsible for them.

References

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4:15 PM ET04.11.07

Halide Perovskites—A Platform for ‘Defect-Tolerance’ and ‘Self-Healing’ Yevgeny Rakita, Davide R. Ceratti, Gary Hodes and David Cahen; Weizmann Institute of Science, Rehovot, Israel.

In recent years, halide perovskites (HaPs) have taken what seems to be a unique place among functional semiconductors, surpassing expectations, and surprising many materials researchers. An often-asked question is: *what may be the reason(s) that HaPs performance gets close to that of high-quality optoelectronic semiconductors, although their fabrication can be similar to that of the organic electronic materials which, though, are of considerably lower semiconductor quality?*

As ‘high quality’ refers (here) to ‘low density of defects/traps that are optical or electronically active’ (the defect density of HaPs is ~10¹⁰ cm⁻³ in single crystals and <~10¹⁶ cm⁻³ in polycrystalline films),¹ ‘defect-tolerance’ and ‘self-healing’ have been proposed as possible explanations. Although these two properties may seem to be related, ‘defect tolerance’ is a property that *does not exclude* the presence of structural defects, but only their impact on the charge carrier dynamics and optical absorption and emission. This will give rise to an effectively reduced optoelectronically relevant defect density. ‘Self-

healing', however, is the property of elimination of structural defects over time by a driving force within the structure (likely to reduce the system's free energy).

To support the 'defect tolerance' and 'self-healing' hypothesis, I will present experimental evidence that strongly supports the idea that HaPs (not limited to the commonly used APb(I,Br)₃) are a platform for both 'defect tolerance' and 'self-healing', physically as well as chemically. The 'physical' part includes experimental analysis of the 'deformation potential', which makes 'defect tolerance' very probable, both due to its absolute value and algebraic sign. The 'chemical' part includes assembly of evidence that support recyclability of degradation products back to the starting material, which means a path for 'self-healing' back to a perovskite structure.² A chemical path for 'defect tolerance', where degradation products complex to form off/ sub-bandgap states, is still theoretical.³ New experimental evidence, via comparison of novel chemically synthesized AX₃ compounds with the perovskite APbX₃ compounds, support this.

1. Brenner, T. M., Egger, D. A., et al. Hybrid organic-inorganic perovskites: low-cost semiconductors with intriguing charge-transport properties. *Nat. Rev. Mater.* 16011 (2016).

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4:30 PM ET04.11.08

Solar Cells with LaYS₃ Perovskite-Like Absorber Discovered by Computational Screening [Andrea Crovetto](#), Rasmus Nielsen, Brian J. Seger, Ole Hansen, Peter Vesborg and Ib Chorkendorff; Technical University of Denmark, Kgs. Lyngby, Denmark.

Fully inorganic chalcogenide perovskite photoabsorbers are a relatively unexplored class of materials that could potentially overcome the stability issues of hybrid perovskites. However, only few chalcogenide perovskites have been synthesized to date, and no reports of solar cell devices based on chalcogenide perovskite absorbers exist to the best of our knowledge. Chalcogenide perovskites have recently been the subject of a few computational screening studies, including the one carried out by our group and focusing on sulfide (ABS₃) perovskites [1]. Among the 705 ABS₃ compounds that were screened, 15 of them were identified as promising. One of the new compounds that passed all the screening rounds (LaYS₃) was successfully synthesized in thin film form in our group, confirming the theoretically predicted crystal structure and band gap [1]. The main challenge in fabricating LaYS₃ solar cells is the relatively high temperature needed to crystallize the material. As a consequence, we were only able to fabricate prototype LaYS₃ solar cells using back contact materials with high temperature resistance. At the present stage, those devices exhibit diode-like rectification but no photocurrent. Nevertheless, we believe this is the first solar cell fabrication attempt using a sulfide perovskite photoabsorber, and one of the first examples of a solar cell fully inspired by computational screening. In this contribution, we will present the updated status of LaYS₃ solar cell performance, as well as the main challenges encountered in this project and possible future directions.

[1] Kuhar, Crovetto et al., *Energy Environ. Sci.* **10**, 2579 (2017).

4:45 PM ET04.11.09

High Bandgap, High Open-Circuit Voltage Perovskite Solar Cells Achieved via Guanidinium Alloying and Interface Engineering [Ryan Stoddard](#), Ian Braly and Hugh W. Hillhouse; University of Washington, Seattle, Washington, United States.

The open-circuit voltages (V_{OC}) of hybrid perovskite (HP) solar cells do not increase sufficiently with increasing bandgap (for Eg > 1.70eV). We study the impact of A⁺ size mismatch induced lattice distortions (in ABX₃ structure) on the optoelectronic quality of high-bandgap HPs and find that the highest quality films have high A-site size-mismatch, where large guanidinium (GA) compensates for small Cs to keep the tolerance factor in the range for the perovskite structure. Specifically, we find that 1.84eV bandgap (FA_{0.33}GA_{0.19}Cs_{0.47})Pb(I_{0.66}Br_{0.34})₃ and 1.75eV bandgap (FA_{0.58}GA_{0.10}Cs_{0.32})Pb(I_{0.73}Br_{0.27})₃ attain quasi-Fermi level splitting of 1.43eV and 1.35eV, respectively, which is >91% of the Shockley-Queisser limit for both cases¹. To study the optoelectronic quality of perovskite films and understand device losses, we employ absolute intensity photoluminescence and compare device V_{OC} with absorber quasi-Fermi level splitting for perovskite films with bandgaps spanning from 1.35 to 1.85eV². Further, we employ wide-field photoluminescence imaging to identify interface recombination in our device stack and explore various interlayer alternatives to ultimately achieve high V_{OC} . Films of 1.75eV bandgap (FA,GA,Cs)Pb(I,Br)₃ are then used to fabricate p-i-n photovoltaic devices that have a V_{OC} of 1.24 V¹. This V_{OC} is among the highest V_{OC} reported for any HPs with similar bandgap (1.7 to 1.8 eV) and a substantial improvement for the p-i-n architecture, which is desirable for two-terminal tandems with Si, CIGS, or a low-bandgap HP. Methods to improve high-bandgap device V_{OC} further using passivation and controlled crystallization are also explored and discussed. Collectively, our results show that non-radiative recombination rates are reduced in (FA,GA,Cs)Pb(I,Br)₃ films and prove that FA-GA-Cs alloying is a viable route to attain high V_{OC} in high-bandgap HP solar cells.

References

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SESSION ET04.12: Poster Session IV
Thursday Afternoon, November 29, 2018
8:00 PM - 10:00 PM
Hynes, Level 1, Hall B

ET04.12.01

Micro Lasers by Scalable Lithography of Metal-Halide Perovskites Ofer Bar-On¹, Philipp Brenner², Uli Lemmer² and [Jacob Scheuer](#)¹; ¹Tel Aviv University, Tel Aviv, Israel; ²Karlsruhe Institute of Technology, Karlsruhe, Germany.

Metal-halide perovskites have emerged in recent years as a powerful material system in the field of photonics. Due to their promising electronic and optical

properties, tremendous progress has been made in the performance of perovskites solar cells. Rapid progress was also demonstrated in the field of light emitting diodes and lasers. As the field advances, new approaches for patterning perovskite films are becoming essential. More specifically, a lithographic approach that can define desired perovskite patterns is highly needed in order to utilize these materials for the realization of integrated perovskite photonic devices.

During the past few years, several attempts have been made in order to address this challenge. Nevertheless, many of the attempts were only partially successful, being unable to remove completely the perovskite from the undesired area, or necessitating slow and serial fabrication techniques which are not compatible with mass production. Hence, a complete, efficient and scalable lithographic approach for the patterning of metal halide perovskite films is still highly needed and sought for. Here, we demonstrate a complete lithographic scheme for thin metal halide perovskite films, and utilize it for the realization of perovskite micro lasers. The process consists of nano imprint lithography followed by ion beam milling. The approach is simple, fast, scalable, and exhibits sub-micron resolution. Lines with critical dimensions of <250nm are realized, followed by complete removal of the perovskites in the non-protected areas. The optical properties of the perovskite films are obtained by employing analytical tools as well as by characterizing distributed feedback laser fabricated from these films. It is shown that the material properties are not impaired by the lithographic process. Using this approach, on chip, micro lasers are fabricated. The experimental characterization of these lasers shows that they exhibit low threshold levels and single-mode lasing. To the best of our knowledge this is the first demonstration of complete, high-resolution lithography of perovskites films exhibiting the smallest perovskite features realized using a top-down lithography technique. This process offers a scalable approach for patterning large areas of perovskites devices with tens of nanometers resolution. This is an important tool towards integrated perovskite photonics and is highly applicable also for the fields of photovoltaics, meta-surfaces, electronics and other promising applications.

ET04.12.02

Temperature-Dependent Chemical-Structural Correlation in $\text{CH}_3\text{NH}_3\text{PbI}_3$ [Yongtao Liu](#)¹, Anton V. Ievlev², Liam Collins², Miaosheng Wang¹, Jong K. Keum², Alex Belianinov², Stephen Jesse², Scott Retterer², Kai Xiao², Mahshid Ahmadi¹, Bobby G. Sumpter², Sergei V. Kalinin², Bin Hu¹ and Olga Ovchinnikova²; ¹Department of Materials Science and Engineering, The University of Tennessee, Knoxville, Tennessee, United States; ²Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States.

Hybrid organic-inorganic perovskites (HOIPs) have been demonstrated as a promising candidate for photovoltaic applications. For efficient and stable photovoltaic devices, it is critical to understand the effects of environment on the material. In this work, we investigate the evolution of chemical distribution as a function of temperature and its correlation to lattice distortion. Using time-of-flight secondary ion mass spectrometry (ToF-SIMS), we reveal the chemical gradient of CH_3NH_3^+ and Pb into the bulk at room temperature. As temperature increases, the CH_3NH_3^+ distributes uniformly and Pb^{2+} gradient does not change. These results prompted a further crystal structure study as our earlier investigations revealed a strong interaction between ion segregation and lattice strain. We performed grazing incidence X-ray diffraction (GIXRD) to explore the lattice change in the direction normal to the sample surface by adjusting grazing incidence angle. As expected, the GIXRD results indicate lattice expansion in (110) and compression in (002) directions with the grazing incidence angle increase corresponding to depth increases. Moreover, both chemical and lattice strain gradients decrease as temperature increases. DFT simulations corroborate these results, suggesting a coupling between temperature, lattice distortion, and chemical distribution. Finally, we demonstrate that temperature, lattice distortion, and chemical distribution simultaneously alter photovoltaic performance. These measurements and results offer an in-depth understanding of the extrinsic and intrinsic chemical effects on device performance.

ET04.12.03

ALD of Tin Oxide on Metal Halide Perovskite Photovoltaics [Axel F. Palmstrom](#)¹, James A. Raiford², Rohit Prasanna³, Kevin A. Bush³, Jinhui Tong¹, Kai Zhu¹, Joseph J. Berry¹, Michael D. McGehee³ and Stacey F. Bent²; ¹National Renewable Energy Laboratory, Lakewood, Colorado, United States; ²Chemical Engineering, Stanford University, Stanford, California, United States; ³Materials Science and Engineering, Stanford University, Stanford, California, United States.

Metal halide perovskites offer a wide and tunable bandgap, making them promising candidates for top-cell absorbers in tandem photovoltaics. Atomic layer deposition (ALD) is becoming an increasingly prevalent technique for the conformal deposition of metal oxides in perovskite devices, including on top of perovskite materials for improved moisture stability and inorganic carrier selective contacts. We recently reported tin oxide by ALD on top of metal halide perovskites as a dual-purpose layer to achieve electron selectivity and sputter protection with high optical transmission; this layer was critical to achieving a 23.6 % record-efficient monolithic perovskite-silicon tandem devices. Engineering of an ALD charge extraction layer on top of perovskite materials is non-trivial due to interfacial degradation and energy band alignment.

In this work, we aim to understand the ALD precursor-perovskite interactions of the tin oxide ALD system and the role of organic fullerenes at the perovskite-tin oxide interface while establishing a framework for developing alternative perovskite-compatible ALD processes in the future. We show, in the case of tin oxide ALD growth with tetrakis(dimethylamino)tin(IV) and water on $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{0.83}\text{Br}_{0.17})_3$ perovskite, that perovskite stability is most sensitive to metal organic exposure at elevated temperatures with an onset near 110 °C, resulting in removal of the formamidinium (FA) cation. Transitioning from ALD to pulsed-chemical vapor deposition (pulsed-CVD) tin oxide growth can minimize the degradation effects. Investigation of fullerenes at the perovskite interface shows that thin fullerene layers offer minor improvements to perovskite stability under ALD conditions, but significant enhancement in carrier extraction. We report high efficiency semi-transparent perovskite devices utilizing fullerene materials, however, fullerenes are undesirable due to fabrication cost and poor mechanical stability. Compositional tuning of the perovskite material can improve the fullerene-free device performance. We demonstrate this method with a bromine-rich perovskite phase to enable an 8.2 % efficient perovskite device with all-inorganic charge extraction layers.

ET04.12.04

Role of Domain Walls in Halide Perovskite Solar Cells [Jae Sung Yun](#)¹, Dohyung Kim², Da Seul Lee¹, Pankaj K. Sharma², Jincheol Kim¹, Anita Ho-Baillie¹, Martin Green¹ and Jan Seidel²; ¹School of Photovoltaic and Renewable Energy Engineering, University of New South Wales, Kensington, New South Wales, Australia; ²Materials Science and Engineering, University of New South Wales, Kensington, New South Wales, Australia.

Organometal halide perovskite solar cells have shown a tremendous improvement in the photoconversion efficiency from 3.8% to 22.7% in recent years. Self-assembling organic-inorganic hybrid materials have been demonstrated to be excellent photovoltaic materials with several superior properties such as high optical coefficient, tuneable bandgap, long carrier diffusion length, and high ambipolar charge carrier mobility. Despite the enormous interest in these materials, many fundamental material properties still remains elusive. Here, we report role of domain walls in halide perovskite film which is systematically investigated using Scanning Probe Microscopy (SPM) techniques. Ion migration is found to be playing a significant role at the domain walls. We examined effect of domains in terms of photovoltaic properties using Kelvin Probe Force Microscopy (KPFM) and conductive AFM (C-AFM). Our findings suggest that these domains walls play a critical role in PV performance. These findings of domain properties can provide a new possibility to understand effect of domains and domain walls in solar cell device.

ET04.12.05

Manipulation of Metal Oxide-Based Electrodes for Semi-Transparent Perovskite Solar Cells Helen H. Park, Geun Jin Kim, Chan Su Moon, Seon Joo Lee, Seong Sik Shin, Nam Joong Jeon, Tae-Youl Yang and Jangwon Seo; Advanced Materials Division, Korea Research Institute of Chemical Technology, Daejeon, Korea (the Republic of).

Due to their high transparency and large bandgaps, transition metal oxides have been widely used in optoelectronic devices, such as light-emitting diodes and solar cells, including semi-transparent devices, tandem solar cells, and building-integrated photovoltaics (BIPV). Thermally evaporated molybdenum oxide (MoO₃) has been commonly used as the sputtering buffer material to protect the organic hole transporting layer from damage due to sputtering of the transparent conducting oxide. However, MoO₃ has strong extinction coefficient in the infrared and has detrimental impact on the fill factor, along with uncertain long-term stability. In this talk, we address a bilayer architecture approach for tunable metal oxide-based transparent electrodes through capping the transition metal oxide with a more stable material and possibly altering the electronic properties through a doping effect. Incorporation of this transparent electrode technique to the protective buffer layer significantly enhanced the fill factor from 70.4% to 79.6%, resulting in power conversion efficiencies over 18% for semi-transparent perovskite solar cells. Effects on the morphology, optical and electrical properties, and performance of working devices will be addressed, and the mechanisms involved in the enhanced performance will also be discussed in this presentation.

ET04.12.06

Integration of Electrospun Fibers into Perovskite Solar Cells Cavit Eyvogge; Mesoscale Chemical Systems, MESA+ Institute for Nanotechnology, University of Twente, Enschede, Netherlands.

Extensive studies performed in the past 5 years showed that power conversion efficiency values over 20% can be reached with perovskite solar cells. This achievement also led researchers to look for different cell architectures, not only for increasing the efficiency but also for extending application area. Electrospinning in that sense can be regarded as a promising method for flexible perovskite solar cell production. It is highly possible to use stacked fibers to form cell layers if one can control the fiber characteristics and deposition pattern. In this study, a modified electrospinning system was used to fabricate electron transport layer for perovskite solar cells, namely ZnO and TiO₂. Linearly aligned fibers of semiconducting oxides were electrospun with 1 kV/cm field strength in between the nozzle and parallel plate structure serving as a collector. Annealing was performed at 500 °C under ambient atmosphere for conversion into oxide. Physicochemical structure and morphology of the fibers were investigated with SEM and XRD. Applicability of the method for all-electrospun perovskite solar cells was also discussed.

ET04.12.07

In Situ Investigation of the Effect of the Lead Film Precursor States and Their Influence on the Conversion to MAPbI₃ Hybrid Perovskite Layers for Solar Cell Applications Dounya Barri¹, Peirui Cheng², Ming-Chun Tang¹, Hoang X. Dang¹, Kai Wang¹, Detlef-M. Smilgies³, Kui Zhao², Thomas Anthopoulos¹ and Aram Amassian¹; ¹King Abdullah University of Science and Technology, Thuwal, Saudi Arabia; ²Key Laboratory of Applied Surface and Colloid Chemistry, National Ministry of Education, Shaanxi Key Laboratory for Advanced Energy Devices, Shaanxi Engineering Lab for Advanced Energy Technology, School of Materials Science and Engineering, Shaanxi Normal University, Xi'an, China; ³Cornell High Energy Synchrotron Source (CHESS), Cornell University, Ithaca, New York, United States.

Due to their low-cost fabrication, the use of abundant materials and their high power conversion efficiency of 22.1%, metal halide perovskite solar cells are currently attracting tremendous attention as a prime alternative to incumbent photovoltaic technologies. In this work, we use the two-step conversion process to produce high quality layers of the prototypical hybrid organic-inorganic perovskite MAPbI₃. The processes is simple and involves the reaction of a solution deposited PbI₂ solid layer with MAI to produce the targeted MAPbI₃ film. Particular emphasis is placed on investigating the ink-to-solid conversion during the two-step solution process of PbI₂ from DMF solution by performing *in situ* grazing incidence wide angle X-ray scattering (GIWAXS) measurements. Obtained results reveal an elaborate sol-gel process involving three PbI₂-DMF solvate complexes—including disordered and ordered ones—prior to PbI₂ formation. The ordered solvates appear to be metastable as they transform into the PbI₂ phase in air within minutes without annealing. Complementary measurements including optical reflectance and absorbance and quartz crystal microbalance with dissipation monitoring (QCM-D) were further used to monitor the solution thinning behavior, changes in optical absorbance, and structural, viscoelastic properties during the PbI₂ film formation and its conversion to perovskite film. Results indicate that the conversion of PbI₂ to perovskite is largely dictated by the state of the PbI₂ precursor film in terms of its solvated state which have implications on solar cell manufacturing and overall performance.

ET04.12.08

Analysis for Efficiency Potential of Perovskite Solar Cells Masafumi Yamaguchi, Kan-Hua Lee, Kenji Aeaki and Nobuaki Kojima; Toyota Technological Inst, Nagoya, Japan.

Remarkable recent advances in perovskite solar cells with efficiencies of over 22% have drawn world-wide as high-efficiency and low-cost solar cells. However, there are some problems to be solved in perovskite solar cells. In addition to improvements in stability, developments in high-efficiency large-area solar cell modules are very important. Therefore, understanding and reducing non-radiative recombination losses in those materials and solar cells and resistance losses in order to realize higher efficiency perovskite solar cells and modules. In this paper, efficiency potential of perovskite solar cells is discussed based on external radiative efficiency (ERE), open-circuit voltage loss and fill factor loss and non-radiative recombination losses.

One of problems to attain the higher efficiency perovskite solar cells is to reduce non-radiative recombination loss. The open-circuit voltage drop compared to bandgap energy ($E_g/q - Voc$) is dependent upon non-radiative voltage loss ($Voc, nrad$) that is expressed by external radiative efficiency (ERE). Open-circuit voltage is expressed by

$$Voc = Voc,rad + (kT/q)\ln(ERE), \quad (1)$$

where the second term shows non-radiative voltage loss, and is radiative open-circuit voltage and 0.28V was used as the $\Delta Voc, rad = E_g/q - Voc,rad$ value for perovskite solar cells in this study. Correlation between Voc values for perovskite solar cells in the references estimated by eqs. (1) suggests that perovskite solar cells have still non-radiative loss and further improvements in efficiency are thought to be possible by improving minority-carrier lifetime. In addition, reduction in resistance loss is suggested to be decreased. The perovskite solar cells have efficiency potential of 25% by improving ERE from around 0.3-1% to 20%. Progress steps for efficiency of perovskite solar cells are analyzed. As a result of high quality thin film growth with large grain size and annealing, ERE have been improved from 8×10^{-10} % to 0.3-1%. By decrease in series resistance and increase in shunt resistance, resistance losses have been reduced from 0.65 to 0.12 with low normalized resistance $r_s + 1/r_{sh}$. As a result of increases in open-circuit voltage Voc and fill factor FF, conversion efficiency for perovskite solar cells has been improved from 3.81% to 22.7%. However, because perovskite solar cells have still higher non-radiative recombination losses and resistance losses compared to GaAs and crystalline Si solar cells, further improvements in efficiency are thought to be possible by improving minority-carrier lifetime due to reduction in recombination losses and by decreasing resistance losses. Importance of non-radiative recombination loss and resistance loss is also discussed.

ET04.12.09

Doping TiO₂ Electron Transport Layers in Halide Perovskite PV Cells by Combinatorial Material Science Anat Itzhak¹, Adi Kama¹, Shalom Avadyayev¹, Adam Ginsburg¹, Hannah Noa Barad¹, David A. Keller¹, Simcha Meir¹, Arie Zaban¹ and David Cahen^{1,2}; ¹Chemistry, Bar Ilan University, Ramat-Gan, Israel; ²Materials and Interfaces, Weizmann Institute of Science, Rehovot, Israel.

The optical properties, stability, wide band gap, and a conduction band just a bit deeper than the conduction band of Pb-based halide perovskites (HaP), makes TiO₂ a very good electron transport layer (ETL) in PV solar cells, based on these HaPs. As a result, TiO₂ is the most commonly used ETL in perovskite (n-i-p structure) solar cells. Here we report on results obtained, from combinatorial materials science, CMS, experiments to optimize the TiO₂ ETL layer by doping with other metals, to explore that route for more efficient and stable HaP solar cells.

To dope TiO₂ with other cations we use CMS, together with high-throughput characterization techniques to examine the effects of different metal cations on the TiO₂ ETL layer and, subsequently, on the HaP PV performance. Each measurement is conducted on a ~ 50 cm² FTO-coated glass, divided into a matrix of 13 x 13 measurement areas (a *library*), thus measuring 169 different compositions and or thicknesses, to look for trends in the properties. Different ETL mixtures were deposited on a substrate, using a custom-made spray pyrolysis deposition system¹, combining TiO₂ with cations, such as Zr⁴⁺ or Sn⁴⁺. This method of preparation assures a gradient of concentrations across the library. We used scanning EDX to verify the cation concentration at each examined point, and follow the changes in the library. As high-throughput characterization tools we used scanning optical spectroscopy, Kelvin probe, and XRD, to understand the influence of the different cations and their varying concentrations on the doped TiO₂ layer. To see how the changes in the ETL affect HaP PV performance, we fabricated complete MA-Pb-trihalide solar cells and used an additional high-throughput method, scanning I-V measurements, to monitor the changes as a function of the type and density of the doping cation.

We will in the presentation report on, and discuss how and with which trends the different cations affect the properties of the TiO₂ ETL layers and the PV performance of cells made with them.

Reference

1. Ginsburg, A. *et al.* Solid state ITO|Au-NPs|TiO₂ plasmonic based solar cells. *Sol. Energy Mater. Sol. Cells* **179**, 254–259 (2018).

ET04.12.10

All Vacuum Processed Large Area Perovskite Solar Cells Using Sputtered NiO_x as Hole Transport Layer Wiriya Soltanpoor^{1,2}, Gence Bektas^{1,2}, Mehmet C. Sahiner^{1,3}, Hava Z. Kaya¹, Esra Bag^{1,4}, Gorkem Gunbas^{1,4,5} and Selcuk Yerci^{1,2,3}; ¹The Center for Solar Energy Research and Applications (GÜNAM), Middle East Technical University, Ankara, Turkey; ²Micro and Nanotechnology, Middle East Technical University, Ankara, Turkey; ³Electrical and Electronics Engineering, Middle East Technical University, Ankara, Turkey; ⁴Polymer Science and Technology, Middle East Technical University, Ankara, Turkey; ⁵Chemistry, Middle East Technical University, Ankara, Turkey.

Metal halide perovskite solar cells have proven to be an inexpensive yet easy to manufacture photovoltaic technology in the last few years. This is due to numerous reasons including tunable optoelectronic properties along with high power conversion efficiencies beyond 22%. The planar configuration of perovskite solar cells has been especially popular due to its versatile use in tandem devices and over flexible substrates. However, in order to grant large scale fabrication of such devices, they need to be uniform, hysteresis free, viable with large areas, and have acceptable stability. Recently, NiO_x has been a favored hole transport layer providing more stable perovskite solar cells. Furthermore, NiO_x can be deposited via sputtering to form uniform, compact layer without high temperature treatments. In this study, sputtering power and Ar-pressure were shown to play the key role in suppressing the hysteresis and in achieving high power conversion efficiencies. As Ar-pressure increased, the transparency of NiO_x improved while reducing its conductivity. According to our experiments, 16 mTorr of Ar-pressure at an RF-power of 150 W resulted in the best performing devices. A uniform CH₃NH₃Pb_{1-x}Cl_x layer was deposited via co-evaporation on top of NiO_x-coated ITO substrates. The electron transport layer (C₆₀) and BCP/Ag were also evaporated on perovskite providing a fully-vacuum-processed planar perovskite solar cell. The fabricated devices worked without hysteresis with a maximum efficiency of 14.8%. In this presentation, we will demonstrate that sputtered NiO_x is a suitable material that can potentially provide an industrial solution towards achieving large area, stable and high efficiency perovskite solar cells.

ET04.12.11

Perovskite/Perovskite Lamination of Complex Compositions to Obtain Alternate Phase Spaces Amani Alfaifi^{1,3,4}, Sean Dunfield^{2,3}, Joseph J. Berry³, Matthew O. Reese³, Maikel van Hest³ and Davor Balzar¹; ¹University of Denver, Denver, Colorado, United States; ²University of Colorado Boulder, Boulder, Colorado, United States; ³National Renewable Energy Laboratory, Golden, Colorado, United States; ⁴Taif University, Taif, Saudi Arabia.

Hybrid perovskites' low temperature solution processing, extreme tolerance to defects, high absorption coefficients, and long carrier diffusion lengths have drawn much attention from the photovoltaic community, leading to a rapid advance in efficiency from just 3.8% in 2009 to 22.6% today. Despite having many benefits, the standard layer-by-layer solution process commonly utilized in fabrication creates several limitations in solvent compatibility and thermal budgeting that have prevented the implementation of various device material layer combinations. In order to overcome the aforementioned limitations while maintaining the advantages of the cost-effective solution processing, we recently developed a procedure to create perovskite devices by first fabricating two transparent conductive oxide/transport material/perovskite half stacks and then laminating them together at the perovskite/perovskite interface. Using various techniques, we show that the developed process marginally improves the electronic structure, reduces the number of defects, increases the crystallinity, and enhances the photophysical properties of MAPI (CH₃NH₃PbI₃). Moreover, we show that the procedure results in a self-encapsulated device format which permits processing above the temperatures allowed in standard fabrication due to its decoupling of the positive effects of annealing with the negative effects of normally-seen thermal degradation. E.g., MAPI films laminated together at 150 °C for 5 days kept black interiors rather than turning yellow, indicating no significant decomposition to PbI₂. While shown to work on a standard ABX₃ perovskite composition containing methylammonium, the original work forgoes applying the method to more complicated compositions containing multiple chemical constituents at any given site. This work builds off said study, improving the uniformity of pressure and temperature obtained in the lamination process and implementing the process on a more advanced perovskite, [Cs_{0.05}(MA_{0.17}FA_{0.83})_{0.95}Pb(I_{0.83}Br_{0.17})₃], at various temperatures to explore the newly afforded phase space for processing. Through ultraviolet-visible absorption spectroscopy, X-ray diffraction, and time-resolved photoluminescence spectroscopy, the effect of lamination at various temperatures is probed. The application of this technique to a mixed-cation and -anion perovskite composition shows the viability of the process on perovskites prone to phase segregation. Future work will focus on utilizing the procedure to explore compositions and defect passivating elements not obtainable by traditional solution processing routes.

ET04.12.12

Enhanced Photovoltaic Performance of Perovskite Solar Cells via Defect Passivation by Incorporating the Physisorbed Small Organic Molecule Shivam Singh¹, Sudip Chakaborty⁴, K. L. Narasimhan², Parag Bhargava³ and Dinesh Kabra¹; ¹Department of Physics, Indian Institute of Technology Bombay, Mumbai, India; ²Department of Electrical Engineering, Indian Institute of Technology Bombay, Mumbai, India; ³Department of Metallurgical Engineering and Material Science, Indian Institute of Technology Bombay, Mumbai, India; ⁴Materials Theory Division, Department of Physics and Astronomy, Uppsala University, Uppsala, Sweden.

Perovskite semiconductors are known to have dynamic disorder^[1] which is known to affect its recombination dynamics.^[2] These defects seem to be controlled via various processing conditions in literature. Here, we studied the role of small organic molecule, bathocuproine (BCP), as an additive in the

CH₃NH₃PbI₃ (MAPI) thin film based photovoltaic devices using optoelectronic measurements and first principle calculation. A solar cell with power conversion efficiency of 16% and fill-factor of 82% with no significant hysteresis is achieved, where BCP not only passivates the bulk and interfacial defects but also shows highly improved electroluminescence efficiency.^[3] Addition of BCP into perovskite precursor does not cause any structural change in the 3D structure of perovskite, which is confirmed using time-delayed emission spectroscopy and first principle electronic structure calculations. Furthermore, calculations suggest that a physisorption type of interaction has been found in between MAPI and BCP with an average distance of 2.9 Angstrom. Hence, hydrophobic organic molecule plays an important role in defect passivation to achieve very high fill factor and improving the film quality for efficient perovskite solar cells. This study has also shown to work for LED application, hence can be utilized for wider bandgap semiconductors LED application and/or triple cation based 3D perovskite solar cells.

Keywords: MAPI, Solar cells, Defect Passivation, Physisorption, Electroluminescence, Moisture Stability.

Reference:

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ET04.12.13

Double Perovskite Cs₂AgBiBr₆ Film for Optoelectronic Devices Cuncun Wu; Peking University, Beijing, China.

Recently, lead-free double perovskites have emerged as a promising environment-friendly photovoltaic material for their intrinsic thermodynamic stability, appropriate band gaps, small carrier effective masses, as well as low exciton binding energies. Herein, we report a first lead-free double perovskite planar heterojunction solar cell with high quality Cs₂AgBiBr₆ film, fabricated by low-pressure assisted (LPA) solution processing under ambient conditions. The device presents a best power conversion efficiency (PCE) of 1.44%. The preliminary efficiency, the high stability under ambient condition without encapsulation, together with the high film quality with simple processing, show a glimmer of hope for the lead free perovskite solar cell. Hole transport layer free planar heterojunction device based on this film was fabricated for photodetector application. The device is self-powered with two responsivity peaks at 350 nm and 435 nm, which is suitable for ultraviolet-A (320–400 nm) and deep-blue light detecting. A high responsivity of 0.11 A/W at 350 nm and a quick response time of less than 3 ms were obtained, which is significantly higher than other semiconductor oxide heterojunction based UV-detectors.

ET04.12.14

Controllable and Reproducible Doping of Spiro-OMeTAD in the Absence of LiTFSI and Air—Spiro-OMeTAD(TFSI)₂ in Perovskite Solar Cells with PCEs Exceeding 19% Boer Tan^{1,2} and Udo Bach^{1,2,3}; ¹Chemical Engineering, Monash University, Melbourne, Victoria, Australia; ²Manufacturing, Commonwealth Scientific and Industrial Research Organisation, Melbourne, Victoria, Australia; ³Melbourne Center for Nano Fabrication, Melbourne, Victoria, Australia.

2,2',7,7'-Tetrakis[N,N-di(4-methoxyphenyl)amino]-9,9'-spirobifluorene (spiro-OMeTAD) is the dominant hole transporting material (HTM) in high efficiency perovskite solar cells (PSCs). To achieve better photovoltaic performances, the conductivity of pristine spiro-OMeTAD needs to be improved through the addition of dopants. Conventional doping methods use redox inactive ionic compounds, in particular lithium bis(trifluoromethylsulfonyl)-imide (LiTFSI) and chemical p-dopants, such as tris(2-(1H-pyrazol-1-yl)-4-tert-butylpyridine) cobalt(III) (FK209). However, the power conversion efficiency (PCE) and the reproducibility of device performance are contingent on a combination of factors, such as light exposure, ambient air conditions and the concentration of LiTFSI/ FK209. Therefore, the reproducibility of these devices is typically problematic.

In this study, spiro-OMeTAD(TFSI)₂ is implemented as a p-dopant in spiro-OMeTAD to reproducibly control the doping level without the need for air exposure and LiTFSI addition. Device performances comparable with conventional LiTFSI doping have been obtained by simply mixing the dopant with spiro-OMeTAD during precursor solution preparation. Unlike the conventional doping method, device performance is less influenced by the environment (oxygen and light). Furthermore, good device performances can be obtained without hygroscopic LiTFSI, which potentially introduces a source of instability in the perovskite structure. Remarkably, the reproducibility is strongly enhanced with minimal variation in PCE at the optimized doping concentration. A maximum PCE of 19.3% is achieved in reverse scan with minor hysteresis observed in forward scan with a PCE of 18.1%, performing a stabilized power output of 18.5%. Our comprehensive study of the hole transfer process and device performance enables us to determine the optimum doping concentration and also confirm the influence of the spiro-OMeTAD doping level on device performance. These are critical to highly efficient and reproducible perovskite solar cells.

ET04.12.15

A Machine Learning Algorithm for Analyzing the Crystal Morphology of Perovskite Solar Cells Thomas Chen¹, Yifan Yin² and Yuchen Zhou²; ¹Mission San Jose High School, Fremont, California, United States; ²Department of Materials Science and Chemical Engineering, Stony Brook University, Stony Brook, New York, United States.

Perovskite solar cells (PSCs) are a rapidly evolving photovoltaic technology where performance and crystal grain size are highly correlated. Therefore, there is a constant need to analyze crystal size distributions in SEM images of the perovskite layer of PSCs. This research attempts to automate this process using both machine learning (ML) and non-ML approaches to edge detection. Once the edges of the crystal grains are located, a flood-fill algorithm can be used to find the area distribution. The ML based edge detection uses GNU Octave Programming Software[1] to run a regularized logistic regression algorithm that classifies each pixel of an input image as part of an edge or not part of an edge. The features used for the algorithm are each pixel's grayscale intensity, its Sobel derivative[2], and second order combinations. Training data is obtained by using non-ML Canny Edge Detection[2] to annotate the edges on a 100X100 pixel SEM image of a PSC modified with 16,000 amu Poly(lactic acid) at 0.3 mg/mL. The classifier exhibits an 85.2% accuracy, though it has difficulty with edge pixels with a low Sobel derivative. A macro for ImageJ Fiji Software was created to automate a non-ML approach using Sobel edge detection. A Gaussian blur with radius 2 pixels is applied to the 16K 0.3mg/mL image and Sobel edge detection is run. The resultant image is then thresholded to differentiate the brightest 50% of pixels and darkest 50%. Area distributions are found with ImageJ's particle analyzer. Edge detection was highly accurate, and the macro exhibited high automation. Both approaches offer a quick and automated way to analyze the crystal distributions of perovskite SEM images. The non-ML method exhibits better edge detection and immediate usefulness, but the ML based method requires far fewer operations than its counterpart, making it more efficient in the long run despite the initial time required for training. [1] GNU Octave. (n.d.). Retrieved from <https://www.gnu.org/software/octave/> [2] Savant, Shubhashree. (2014). A Review on Edge Detection Techniques for Image Segmentation. International Journal of Computer Science and Information Technologies. 4.

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SESSION ET04.13: Reducing Lead and Perovskite-Inspired Materials
Session Chairs: Aditya Mohite and Natalie Stingelin
Friday Morning, November 30, 2018
Hynes, Level 3, Room Ballroom C

8:00 AM *ET04.13.01

Towards Efficient and Stable Mixed Sn-Pb Perovskite Solar Cells Yanfa Yan; University of Toledo, Toledo, Ohio, United States.

Mixed Sn-Pb perovskite absorber materials have attracted extensive attentions because they offer opportunities to reduce the usage of toxic Pb, tune the bandgap to be more suitable for efficient single-junction solar cell applications, and enable the realization of all-perovskite tandem solar cells. Though significant progress has been made in the past several years, the record powder conversion efficiency (PCE) of mixed Sn-Pb perovskite solar cells is still significantly lower than the theoretical maximum PCE. Furthermore, the study of stability of mixed Sn-Pb perovskite solar cells is rarely reported. In this talk, we will present detailed analysis of the possible factors that limit the PCEs of mixed Sn-Pb perovskite solar cells and discuss possible solutions for overcoming the limitations. Furthermore, we will discuss the stability issues that mixed Sn-Pb perovskite solar cells may encounter.

8:30 AM *ET04.13.02

New Materials, Systems and Applications with Halide Perovskites Ivan Mora-Sero; Institute of Advanced Materials (INAM), Universitat Jaume I, Castello de la Plana, Spain.

Halide perovskite have demonstrated an outstanding performance for the development of photovoltaic devices. This excellent behavior is based, among others, in a benign defect physics producing low non-radiative recombination, making halide perovskite also enormously appealing for the development of other optoelectronic devices as LEDs or lasers. While first studies focused just in conventional hybrid halide perovskite materials with general formula ABX_3 , (where A=methylammonium, formamidinium, Cs, X=Pb, Sn, X=I, Br, Cl) and just in photovoltaic devices, the current interest has been extended. A broader range of material compositions are now been investigated and not just with 3D structure but as layered perovskites or as nanoparticles. These systems also are awaking a great interest as very high photoluminescence quantum yield can be obtained with relative easy synthesis processes. In addition, multiple materials are also analyzed as selecting contact layers. In this talk, I present non-conventional perovskite materials and contacts for photovoltaics and optoelectronic applications. The structural, chemical, electric and optical properties of materials and devices have been systematically characterized, highlighting the interest of these new systems for further development of perovskite technology. A new hole selective contact based on a fullerene derivative a new family of 2D/3D perovskites using conjugated anilinium as long organic cation will be introduced. The development of optical amplifiers based on halide perovskites and the use of perovskite nanoparticles for the development of optoelectronic devices will be also discussed.

9:00 AM ET04.13.03

Estimating Oxidised Sn⁴⁺Species at the Precursor Stage—On the Effect of Reducing Agents in Sn-Based Perovskites Aslihan Babayigit^{1,2}, Melissa Van Landeghem³, Bert Conings^{1,2}, Derese Desta¹, Nobuya Sakai², Etienne Govaerts³, Hans-Gerd Boyen¹ and Henry Snaith²; ¹Hasselt University, Diepenbeek, Belgium; ²Department of Physics, University of Oxford, Oxford, United Kingdom; ³Department of Physics, University Antwerp, Antwerpen, Belgium.

The poor opto-electronic properties often associated with tin (Sn) halide perovskites are usually ascribed to the oxidation of Sn²⁺ to Sn⁴⁺.^{1,2} Due to the generation of Sn²⁺ vacancies upon oxidation that limit the electron and hole diffusion lengths to 30 nm by acting as scattering centres, it remains challenging to obtain highly efficient Sn-based perovskite solar cells in planar as well as mesoporous device architectures. Theoretical calculations corroborate that reducing the background hole concentration by suppressing oxidation could allow favourable opto-electronic properties for these materials with diffusion lengths approaching 1 micron.¹ Nevertheless, innovative approaches based on reducing agents remain rather limited as only inadequate fractions of these compounds are tolerated in the formation of the desired efficient absorbers.³ Hence, it remains particularly challenging to maintain a stoichiometric solution for the development of highly efficient Sn-based perovskite solar cells.

Having demonstrated vast potential as a narrow bandgap rear-cell in perovskite-perovskite tandems, the optimisation of Sn (and thereby Pb-Sn mixed) perovskites is of particular relevance as currently all-perovskite multi-junction solar cells are being envisioned—with reports of theoretical performances surpassing 45%.^{4,5} To that end, this work focuses on the extent of oxidation present in supposedly pristine precursor solutions—an aspect currently not profoundly reported on in literature. Based on observed changes in morphology, crystallinity and optoelectronic properties of films obtained from corresponding solutions, an efficient method is discussed to estimate the early-on degradation induced at the precursor stage. The quantification can be used as an effective tool to characterise and extend the effect of reducing agents, and thereby assist in enhancing the performance of Sn-based solar cells.

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9:15 AM ET04.13.04

GeBr₂ as a Dopant for Fabricating Air Stable Tin-Based Perovskite Solar Cells Muhammad Akmal Kamarudin¹, Kohei Nishimura¹, Daisuke Hirotsu¹, Qing Shen², Taro Toyoda², Satoshi Iikubo¹, Takashi Minemoto³, Kenji Yoshino⁴ and Shuzi Hayase¹; ¹Kyushu Institute of Technology, Kitakyushu, Japan; ²The University of Electro-Communications, Chofu, Japan; ³Ritsumeikan University, Kusatsu, Japan; ⁴University of Miyazaki, Miyazaki, Japan.

The low performance of tin-based perovskite solar cells is attributed to the tendency of Sn²⁺ to oxidize to Sn⁴⁺ resulting in higher charge carrier concentration. This oxidation process also leads to the degradation of the perovskite solar cell over time even in N₂ atmosphere and much so in ambient atmosphere. To this effect, we have successfully employed GeBr₂ as passivation layer which could extend the lifetime of PSCs in air, in addition to

reducing the charge carrier concentration. The performance of GeBr₂-doped perovskite solar cell achieved a high efficiency of 4.2 % compared to 2.9 % for FA_{0.75}MA_{0.25}SnI₃ when measured in air. The increased in efficiency comes from the significant increase of short circuit current due to the reduction of charge carrier concentration. The reduction of trap states upon addition of GeBr₂ has also been confirmed by thermally stimulated current measurement. The formation of monolayer GeO₂ reduced the surface oxidation of the perovskite and helped to improve the air stability of the perovskite solar cell even without encapsulation. This work provides a platform of fabricating air stable tin perovskite solar cells with high efficiency.

9:30 AM ET04.13.05

Effect of GeI₂ Addition to Inorganic Perovskite CsPbI₂Br Perovskite for Enhancing Efficiency and Stabilization of α Phase at Room Temperature Fu Yang¹, Daisuke Hirotani¹, Gaurav Kapil¹, Yaohong Zhang², Qing Shen² and Shuzi Hayase¹; ¹Graduate School of Life Science and Systems Engineering, Kyushu Institute of Technology, Kitakyushu, Japan; ²Faculty of Informatics and Engineering, The University of Electro-Communications, Tokyo, Japan.

One of the disadvantages for conventional MAPbI₃ are thermal instability since they are composed of organic ammonium cations. All inorganic perovskite such as CsPbI₃ are expected to have durability for high temperature conditions, however, these cell efficiencies are not satisfactory. One of the reasons for the low efficiency is that they are apt to take δ phases which are yellow and are not suitable for the light harvesting layer at room temperature. One of the inorganic halogenated perovskite "CsPbI₂Br" (Pb-1) also have the problem. We found that the addition of GeI₂ to perovskite (Pb-1) stabilized the α phase of the Pb-1 at room temperature. The highest power conversion efficiency of 10.8% with high open-circuit voltage (V_{OC}) of 1.27 V in planar solar cell based on CsPb_{0.8}Ge_{0.2}I₂Br (Pb-Ge(0.2)) perovskite was achieved. The highest V_{OC} of up to 1.34 V was obtained by CsPb_{0.7}Ge_{0.3}I₂Br (Pb-Ge(0.3)) perovskite which is a remarkable record in the field of cesium based inorganic perovskite solar cells. At last, all the parameters including short circuit current, V_{OC}, fill factor and efficiency of CsPb_{0.8}Ge_{0.2}I₂Br perovskite solar cells kept nearly no decay when measured more than 7 hours in 50-60% humid air without encapsulation.

9:45 AM *ET04.13.05.5

Hybrid Perovskites: An Ideal Materials Platform with Emergent Properties Aditya D. Mohite; Department of Chemical and Biomolecular Engineering, Rice University, Houston, Texas, United States.

The structure of a material, light and electrical field are fundamental ingredients for any optoelectronic device. In state-of-the-art semiconductors like Silicon and Gallium Arsenide, the crystal structural parameters such as bond length, crystallinity, vacancy and strains are invariant to external stimuli such as electromagnetic radiation and electric fields. However, in sharp contrast, hybrid perovskites exhibit a strong propensity for undergoing structural modifications with light and electric fields. While this raise challenges for elucidating the exact mechanisms of device operation, it also offers opportunities to discover new emergent functionalities. Therefore, a basic principle on the interplay between structure, light and electrical field with in-situ correlated structure-device measurements are critical for understanding optoelectronic transport and determine the design principles for operation of perovskite-based devices.

In my talk, I will focus on understanding these complex behaviors arising from the interaction between structure, light and electric field in both 3D and 2D hybrid perovskite systems by using different device platforms such as photovoltaics, field-effect transistors and light emitting diodes to understand these correlations. Our studies are aimed towards utilizing this fundamental understanding to develop new behaviors and device concepts using perovskite materials.

10:15 AM *ET04.13.06

Physical Properties of 2D and 3D Halide Perovskites—Recent Results Jacky Even; FOTON, UMR 6082, CNRS, INSA Rennes, Rennes, France.

In the past five years, solution-processed organometallic perovskite based solar cells have emerged as a promising thin-film photovoltaic technology. Presently, the intended optoelectronic applications of this class of 3D materials are in the realm of conventional semiconductors. The presentation will present recent theoretical, spectroscopy and diffraction results on monocrystals of halide perovskites, colloidal nanocrystals or thin-films. Related 2D multilayered phases, composed of perovskites multilayers sandwiched between two layers of large organic cations, have recently demonstrated improved solar cells photostability under standard illumination as well as humidity resistance over 2000 hours, leading to a conversion efficiency of 12.5 %. In this case, intrinsic quantum and dielectric carrier confinements are afforded by the organic inner barriers, which lead to a stable Wannier exciton at room temperature. However, solar cells or LED device efficiencies are related to internal exciton dissociation through edge states in layered 2D Ruddlesden-Popper perovskites, as shown from the investigation of both thin films and small exfoliated single crystals.

FOTON, UMR 6082, CNRS, INSA Rennes, Rennes, France;

10:45 AM ET04.13.07

Ion Migration in Triple Mesoporous 2D/3D Perovskite Solar Cells Adam Pockett, Jennifer Baker, Trystan Watson and Matt Carnie; SPECIFIC, Swansea University, Swansea, United Kingdom.

Triple mesoporous layer devices containing a TiO₂ electron transport layer, a ZrO₂ insulating layer and carbon as the hole transporting contact show great promise for scale-up and wide spread implementation. To improve these devices and begin to challenge inorganic PV record efficiencies a deeper understanding of their operation, and in particular sources of performance loss, is needed.

The current state-of-the-art devices use a mixed cation perovskite, consisting of methylammonium and 5-aminovaleric acid (5-AVA). The AVA containing perovskite has been shown to give greater stability and performance – linked to 2D/3D structuring of the perovskite as well as interfacial modifications at the TiO₂ surface. The cells undergo a slow light soaking effect during which time the JV performance of the device is vastly improved. They also show improvement when exposed to a high relative humidity.

A striking feature observed using TPV measurements is the presence of a negative photovoltage transient, comparable to that observed in our previous work on planar TiO₂ devices at low temperature. This behaviour suggests the presence of high rates of interfacial recombination at the TiO₂ surface. In carbon based cells the phenomena is observed at room temperature and is very slow to disappear under continued illumination. For the planar devices the negative transient was shown to diminish over time as ions in the perovskite redistributed, leading to a reduction in the recombination rate. We show that in the carbon devices the exceptionally slow dynamic behaviour observed at room temperature has a similar origin linked to the effects of ion migration – activation energy calculated to be 0.4 eV (in the range of many literature values for iodide migration). However, it takes place at a much slower rate due to the 2D AVA based perovskite hindering iodide ion migration – attempt frequency reduced by several orders of magnitude compared to pure MAPI devices. We show that the inhibited ion migration is the dominant affect rather than the AVA having a direct impact at the TiO₂ interface by adsorption via the carboxylic acid group. This inhibition of iodide migration is also linked to the increased stability demonstrated for these devices.

11:00 AM ET04.13.08

Charge Transport Mechanisms in Vertically Stacked 2D Ruddlesden-Popper Perovskite Solar Cells—Theory and Experiments Reza Asadpour¹, Hsinhan Tsai^{2,3}, Wanyi Nie², Aditya D. Mohite² and M. Ashraf Alam¹; ¹Purdue University, West Lafayette, Indiana, United States; ²Los Alamos National Laboratory, Los Alamos, New Mexico, United States; ³Material Science and Nano Engineering, Rice University, Houston, Texas, United States.

2D Ruddlesden-Popper perovskites have improved the stability of fabricated solar cells, but their efficiency is reduced compared to 3D bulk perovskite. The improvement in stability is easily understood: 2D perovskite consists of inorganic blocks separated by bulky organic cations. These organic cations act as intrinsic passivation and prevent moisture ingress hence higher stability [1]. Unfortunately, these cations also lead to localized quantum confinement effects that influence the optical and electrical behavior of the material [2]. In this talk, we will discuss how we quantified the transport landscape of electrons, holes, and photons by interpreting the thickness-, temperature-, and illumination-dependent efficiencies of these 2D solar cells. The detailed understanding of optoelectronic and charge transport mechanism in these structures will guide the future efforts in creating perovskite solar cells that are simultaneously highly efficient and highly stable.

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11:15 AM ET04.13.09

Two-Dimensional Tin-Based Hybrid Halide Perovskites for Photovoltaics Zhenyu Wang^{1,2,3}, Alex M. Ganose^{2,3,4}, Chunming Niu¹ and David O. Scanlon^{2,3,4}; ¹School of Electrical Engineering, Xi'an Jiaotong University, Xi'an, China; ²Department of Chemistry, University College London, London, United Kingdom; ³Thomas Young Centre, University College London, London, United Kingdom; ⁴Diamond Light Source Ltd., Diamond House, Oxfordshire, United Kingdom.

The drive towards reduced costs, higher conversion efficiencies and environmentally friendly alternatives to current photovoltaic technologies is immensely important in the search to relieve the world's reliance on fossil fuels and promote sustainable economic development.¹ Since the first reports of solid-state hybrid perovskite solar cells in 2012, power conversion efficiencies (PCEs) have increased dramatically up to 22.7%.² Despite the rapid rise in efficiencies of the hybrid lead perovskite such as CH₃NH₃PbI₃ (MAPbI₃), their poor long-term stability and the toxicity of water-soluble lead compounds, necessitates the development of alternative lead-free halide perovskite materials with improved moisture tolerance.

Although 2D hybrid halide perovskites have been known since they were first synthesized by Mitzi *et al.* in 1994,³ they were not investigated as solar cell absorbers until Smith *et al.* found the 2D perovskites to be more resistant to moisture than their 3D analogues.⁴ Additionally, environmental concerns can be addressed by replacing Pb with less toxic elements, such as Sn and Ge. The band gaps of the 2D series generally decrease monotonically with increasing perovskite-like layer thickness, finally tending to that of corresponding 3D perovskite. In this way, the 2D hybrid perovskites have attracted increasing attention and witnessed a sharp rise in efficiency over the past two years,⁵ with champion devices (containing (PEA)₂(MA)₅₉Pb₆₀I₁₈₁) showing efficiencies of 15.3%.⁶ For the reasons, 2D perovskites are promising candidates for solar cell absorbers.

In this work, we investigate the geometrical, electronic and optical properties of the semiconducting 2D tin-based perovskites (CH₃(CH₂)₃NH₃)(CH₃NH₃)_nSn_nI_{3n+1} (*n* = 1, 2, 3), using relativistic hybrid density functional theory calculations.⁷ We demonstrate that the band gaps of the series decrease with increasing perovskite-like layer thickness, from 1.85 eV (*n* = 1) to 1.38 eV (*n* = 3). We find strong and broad optical absorption across the series, in addition to small effective masses of electrons and holes in the laminar plane. The low *n* tin-based 2D perovskites should possess the best of both worlds, with optimal band gaps but improved moisture stability. Particularly, the *n* = 3 composition displays a high spectroscopic limited maximum efficiency (SLME) of 24.6%. Our results indicate this series of homologous 2D tin halide perovskites are a promising class of stable and efficient light-absorbing materials for photovoltaics.

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11:30 AM ET04.13.10

First Report of More Than 20% Efficient Tin/Lead Perovskite Solar Cells with a Reduced Potential Loss Gaurav Kapil¹, Kengo Hamada², Takeru Bessho¹, Takumi Kinoshita¹, Qing Shen³, Taro Toyoda³, Takuro N. Murakami⁴, Takashi Minemoto⁵, Hiroshi Segawa¹ and Shuzi Hayase²; ¹RCAST, The University of Tokyo, Tokyo, Japan; ²Kyushu Institute of Technology, Kitakyushu, Japan; ³University of Electrocommunication, Tokyo, Japan; ⁴National Institute of Advanced Industrial Science and Technology (AIST), Tokyo, Japan; ⁵Ritsumeikan University, Shiga, Japan.

Lead (Pb) based perovskite solar cells (PSCs) are now showing reproducible efficiencies more than 20% [1]. Although Pb-PSCs are quite efficient; however, because of the toxicity concern due to presence of Pb²⁺, some research groups started looking for other bivalent cations in ABX₃ (where A is monovalent cation, B is bivalent cation, and X is halide anion) perovskite structure and tin²⁺ (Sn²⁺) came out as a potential candidate [2]. Interestingly, a reduction in band gap was observed in case of ASnX₃ with photon harvesting until 900 nm. But owing to the high oxidation possibilities of Sn²⁺ to Sn⁴⁺, research was directed in mixing of Pb²⁺ and Sn²⁺ at B position, which reduces the formation of Sn⁴⁺ and increases the absorption more than 1000 nm [3, 4]. This increased photon harvesting in Sn-Pb PSCs grabbed the attention of researchers working in PSCs and so far, best PCE of 17.6% has been reported [3, 4] with PSCs containing mixture of Sn-Pb.

The highly efficient Pb containing PSCs are now exhibiting a potential (Voc) loss of approximately 0.4 V from the optical band gap [1] and an average incident photon to current conversion efficiency (IPCE) of 90% leading to the photocurrent densities (Jsc, mA/cm²) equal to 25 mA/cm². In contrast, Sn-Pb PSCs still suffer from higher Voc loss, which could be due to the existence of high trap states in bulk or could be interfacial loss. In our previous work [4], we tried to solve the interfacial losses with the introduction of a spike energy concept and reduced the Voc loss to 0.5 V for FA_{0.5}MA_{0.5}Sn_{0.5}Pb_{0.5}I₃ (1.25 eV) PSC, and achieved a Voc of 0.75 V. Undoubtedly, these PSCs are exhibiting the high Jsc approaching to 30 mA/cm² (with an average 80% IPCE). In this work, we will report the further reduction of Voc loss to approximately 0.45 V- 0.4 V (same as Pb-PSCs), with an enhanced PCE of 20.4% by stoichiometrically doping with Cs⁺ to fabricate the (Cs)_x(FAMA)_{1-x}Sn_{0.5}Pb_{0.5}I₃ based PSC. The role of Cs addition on PSC performance will be discussed in detail by X-ray diffraction, X-ray photoelectron spectroscopy along with the charge carrier dynamics study using photoluminescence and transient absorption spectroscopy.

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11:45 AM ET04.13.11

In Situ Investigation of Wide and Tunable Bandgap MAPbBr_{3-x}Cl_x Hybrid Perovskite Films and Their Application in Solar Cells with Voc > 1.6 V Ming-Chun Tang³, Sehyun Lee¹, Dounya Barrit³, Ruipeng Li², Detlef-M. Smilgies², Dong-Yu Kim¹, Thomas D. Anthopoulos³ and Aram Amassian³; ¹Gwangju Institute of Science and Technology (GIST), Gwangju, Korea (the Republic of); ²Cornell High Energy Synchrotron Source (CHESS), Ithaca, New York, United States; ³King Abdullah University of Science and Technology (KAUST), Thuwal, Saudi Arabia.

Organic-inorganic lead-based halide hybrid perovskites have attracted immense attention because of their extraordinary optoelectronic properties. Beyond the traditional low bandgap hybrid perovskite solar cells, namely MAPbI₃, the wide bandgap MAPbBr_{3-x}Cl_x hybrid perovskite is demonstrated to realize a wide and tunable bandgap ranging from 2.3 eV to 3.1 eV ($x = 0$ to 3), leading it suitable not only for semitransparent and transparent perovskite solar cells, but also blue and ultraviolet light emitting diode and photodetector applications. In this contribution, we compare and contrast the crystallization kinetics and growth behaviors of wide and tunable bandgap MAPbBr_{3-x}Cl_x to conventional MAPbI₃ from precursor inks to solid-state thin films using the one-step spin coating approach. We employ a multi-probe *in situ* investigation method consisting in grazing incidence wide-angle x-ray scattering (GIWAXS) and time-resolved UV-Vis absorbance complemented with *ex situ* characterization of wide and tunable bandgap hybrid perovskite thin film morphology and solar cell performance. Obtained results reveal that the tunable and wide-bandgap MAPbBr_{3-x}Cl_x perovskite phase forms directly from disordered solvate during solution processing, while MAPbI₃ ink tends to form intermediate ordered phases requiring further thermal annealing to form perovskite phase. Furthermore, we disclose the role of anti-solvent dripping is to not only benefit the morphology of perovskite thin film but also pre-nucleate and promote wide-bandgap MAPbBr_{3-x}Cl_x perovskite phase formation. We use this insight to develop a solvent engineering protocol suitable for depositing fully cover and pin-hole-free high-quality MAPbBr_{3-x}Cl_x hybrid perovskite thin films and present working single junction photovoltaics with high open circuit voltage > 1.6 V and promising future for transparent hybrid perovskite solar cells.

SESSION ET04.14: Interfaces, Film Formation and Transporting Materials

Session Chairs: Luis Ono and Jeremie Werner

Friday Afternoon, November 30, 2018

Hynes, Level 3, Room Ballroom C

1:30 PM ET04.14.01

Carbon Nanotubes as Effective P-Type Contact for Perovskite Solar Cells Severin N. Habisreutinger; Chemistry and Nanoscience Center, National Renewable Energy Laboratory, Denver, Colorado, United States.

The enormous strides researchers have made in advancing perovskite based photovoltaics in the past few years are fueling the dream of a rapid entry of this highly promising technology into the global energy market. This seems like serendipitous timing since solar power has gained an enormous momentum over the past decade exceeding all projections. This expansion in solar power is driven by an increasing understanding that climate change requires immediate action, in particular with regards to power generation; and simultaneously, the price for photovoltaic modules has remarkably quickly fallen to make solar power generation competitive vis-à-vis conventional technologies.

Compositional tuning of the perovskite absorber has led to immense improvements in stability and efficiency of perovskite solar cells leading to a certified efficiency of 22.7% for a single-junction laboratory device. The successful transition of a photovoltaic technology from the lab into the field requires, however, two additional important parameters aside from efficiency which are essential for real-world deployment: stability and scalability.

We propose using single-walled carbon nanotubes (SWCNTs) as an alternative p-type layer for future application in perovskite solar cells. Carbon nanotubes combine several highly attractive characteristics such as chemical inertness and mechanical resilience with intrinsically high charge-carrier mobilities endowing them with a unique potential for a much more stable dopant-free charge-selective contact. Furthermore, the SWCNT deposition techniques for large-scale use, such as spray coating, are already well-established opening clear avenues for direct implementation in a real-world industrial setting.

Finally, we demonstrate that employing SWCNTs as hole-transporting material can yield steady-state efficiencies of close to 21% for alloyed narrow bandgap perovskites, and of over 7% for wide-bandgap perovskites, illustrating the versatility and excellent performance of SWCNTs as contact material.

1:45 PM ET04.14.02

Enabling Room-Temperature Processed Highly Efficient and Stable 2D Ruddlesden–Popper Perovskite Solar Cells with Eliminated Hysteresis Shuang Yu¹, Yajie Yan¹, Yani Chen¹, Pavel Chábera², Kaibo Zheng³ and Ziqi Liang¹; ¹Fudan University, Shanghai, China; ²Chemical Physics, Lund University, Lund, Sweden; ³Chemistry, Technical University of Denmark, Kongens Lyngby, Denmark.

Two-dimensional (2D) Ruddlesden–Popper (RP) perovskites have sparked great research interest for their appealing ambient stability. However, their random crystal packing and impeded charge transport in vertical direction restrict the enhancement of photovoltaic performance. These issues have been successfully resolved by employing hot-casting method during the film casting to re-orient the crystal packing. Alternately, we have developed a range of approaches to enable room-temperature fabrication of high-efficiency and air-stable 2D RP perovskites based solar cells. We firstly found that by replacing the conventional linear butylamine (n-BA) to shorter branched butylamine (iso-BA) as spacing cation, preferential out-of-plane orientation can be achieved, which led to significantly enhanced charge transportation in solar cells.^[1] As a result, a high PCE of 8.82% was obtained for (iso-BA)₂(MA)₃Pb₄I₁₃ based solar cells processed at room temperature. Intriguingly, we observed the spontaneous formation of 3D phases in such iso-BA perovskites, which can serve as charge reservoirs to inhibit excitonic recombination and facilitate carrier transport.^[2] Second, we demonstrated the favorable effects of NH₄Cl additive and DMSO solvent on 2D RP perovskites, which remarkably improved both film morphology and charge transportation at room temperature. Integrated 3D phases were identified within either NH₄Cl or DMSO treated perovskites. Dual treatments synergistically

yielded the maximum PCEs over 13% and 10% in planar solar cells processed in N₂ and air, respectively, with eliminated hysteresis. Our results may pave up a way for the industrialization of highly efficient and stable perovskite photovoltaic devices on flexible substrate.

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2:00 PM ET04.14.03

Enhancement of Film Quality and Photovoltaic Performance of Organic-Inorganic Halide Perovskite via Polycaprolactone Polymer Dopants Induced Heterogenous Nucleation and Defects Passivation Yuchen Zhou¹, Yifan Yin¹, Anisa Prasad², Sirina Prasad², Aum Upadhyay³, Thomas Chen⁴, Byron Phan⁵, Chang-Yong Nam⁶ and Miriam Rafailovich¹; ¹Stony Brook University, Stony Brook, New York, United States; ²Staples High School, Westport, Connecticut, United States; ³Interlake High School, Bellevue, Washington, United States; ⁴Mission San Jose High School, Fremont, California, United States; ⁵Hunter College High School, New York, New York, United States; ⁶Center for Functional Nanomaterials, Brookhaven National Laboratory, Upton, New York, United States.

Organic-inorganic halide perovskite solar cells (PSCs) have been considered a viable member of next generation photovoltaics, which can address the scalability changes with a low-cost solution process. The perovskite layer is the main source of photogenerated electron-hole pairs in PSCs. The energy loss in the hybrid system has been approved to be principally caused by traps at grain boundaries and surfaces as well as point defects such as interstitial defects or vacancies in the perovskite compounds crystal lattice. Therefore, the premier concern in PSCs is constructing a highly crystallized and defect-free perovskite thin film with full surface coverage, smooth, and ordered crystallites with big crystal grains. In this study, we observe a significantly enhancement in power conversion efficiency (PCE) of photovoltaic device by incorporating a small amount of polycaprolactone (PCL) into the perovskite layer. The long-chain PCL polymer can serve as an efficient passivating agent in the bulk film, due to the formation of weak coordination bonds between Pb²⁺ and the O in the ester group of PCL. Furthermore, the PCL polymer with small volume can participate in the nucleation step as heterogenous nucleus and help reduce interfacial energy, which eventually promotes the growth of each crystal grain. As evidenced from the surface scanning electron microscopy (SEM) images, the average crystal grain size of the perovskite layer with PCL addition increases significantly, as compared with the PCL free sample. The enhanced absorption intensity from UV-vis spectra after the incorporation of PCL indicates the increase of film thickness as well as the light absorption ability. X-ray diffraction (XRD) results prove the purity and high crystallinity of tetragonal (I4/mcm) MAPbI₃ perovskite phase of the PCL passivated perovskites with no sign of PbI₂ peaks, while signal of trace amount PbI₂ are seen on the PCL free perovskite layers. Moreover, provided by steady-state and time-resolved photoluminescence (TRPL) results, addition of PCL increases the emission intensity and prolongs the charge carrier lifetime of the perovskite layer, which largely results from reduced surface/boundary defects/traps as well as minimized corresponding non-radioactive recombinations due to the passivation of the crystal grains by PCL. As a result, the perovskite thin films with proper amount of PCL addition exhibits superb device performance with PCE of the champion device surpassing 18%, indicating a more than 20% enhancement to the original devices. (This work was supported by the Morin Foundation Trust and the NSF, Inspire program #1344267)

2:15 PM ET04.14.04

SnO₂ Quantum Dot Electron-Selective Layer for High-Performance Perovskite Solar Cells Zhiliang Chen, Guang Yang and Guojia Fang; Wuhan University, Wuhan, China.

The carrier concentration of the electron-selective layer (ESL) and hole-selective layer can significantly affect the performance of organic-inorganic lead halide perovskite solar cells (PSCs). Herein, a facile yet effective two-step method, i.e., room-temperature colloidal synthesis and low-temperature removal of additive (thiourea), to control the carrier concentration of SnO₂ quantum dot (QD) ESLs to achieve high-performance PSCs is developed. By optimizing the electron density of SnO₂ QD ESLs, a champion stabilized power output of 20.32% for the planar PSCs using triple cation perovskite absorber and 19.73% for those using CH₃NH₃PbI₃ absorber is achieved. The superior uniformity of low-temperature processed SnO₂ QD ESLs also enables the fabrication of ~19% efficiency PSCs with an aperture area of 1.0 cm² and 16.97% efficiency flexible device. The results demonstrate the promise of carrier-concentration-controlled SnO₂ QD ESLs for fabricating stable, efficient, reproducible, large-scale, and flexible planar PSCs.

2:30 PM ET04.14.05

Photovoltaic Efficiency of CsPbI₃ QDs-Based Solar Cell Exceeding 13% Yueli Liu; State Key Laboratory of Silicate Materials for Architectures, Wuhan University of Technology, Wuhan, China.

The emergence of organic-inorganic hybrid lead halide perovskites has received the impressive power conversion efficiency (PCE) over 22% within a few years [1]. However, the long-term stabilities of perovskite materials, including the durability under humid, thermal, UV radiation and other environmental conditions, are still poor due to the organic components, which are becoming to be the major challenges for their commercialization [2]. α -CsPbI₃, as an all-inorganic lead halide, has been reported recently and exhibited excellent optoelectronic property and good stability, which is regarded as an outstanding alternative to organic-inorganic hybrid lead halide perovskites and a promising light-harvesting absorber for solar cell application [3]. Quantum dot-induced phase stabilization is believed to be an effective procedure to get α -CsPbI₃ and suppress the formation of orthorhombic phase (δ) CsPbI₃. Protesescu et al. have provided a hot-injection method for the preparation of high quality α -CsPbI₃ quantum dots (QDs) [4]. α -CsPbI₃ QDs based solar cells are reported by Luther and co-workers subsequently, which receive a high PCE over 13% [5]. However, the short-circuit current density (JSC) is still low at present, which restricts the performance of CsPbI₃-based solar cells.

In the work, α -CsPbI₃ QDs were prepared by hot-injection method, and high performance inorganic perovskite quantum dot-based solar cells over 13.78% was fabricated, and the optimized device achieved a highly reproducible champion PCE of 13.05% with a high short-circuit current density (18.68 mA cm⁻²). This work provides an effective strategy for boosting high performance for all-inorganic lead halide PSCs.

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2:45 PM ET04.14.06

Hygroscopic Polymer Passivation Improving Durability of Perovskite Solar Cells Min Kim², Silvia G. Motti^{2,1}, Roberto Sorrentino^{2,1} and Annamaria Petrozza²; ¹Physics, Politecnico di Milano, Milan, Italy; ²CNST, Istituto Italiano di Tecnologia, Milan, Italy.

Long-term device instability is one of the most critical issues that impede perovskite solar cell commercialization. Here we show that a thin layer of a functional hygroscopic polymer on top of the perovskite thin film can make perovskite-based solar cells highly stable under illumination and in a humid atmosphere. We prove that the oxygen atoms in hygroscopic polymer chemically interact with lead ions on the perovskite surface, thus passivate undercoordinated defect sites. Importantly, the defect healing effect leads to an improved photo-voltage and photo-stability. Overall, such interface engineering leads to highly durable perovskite solar cell, which, in the presence of polymer passivation, retained more than 95% of initial power conversion efficiency over 15-h illumination, under load, in the ambient atmosphere without encapsulation. Our findings experimentally reveal the role of defects in triggering the instability of perovskite materials and propose a general approach for improving the reliability of perovskite-based optoelectronic devices.

3:00 PM BREAK

3:30 PM ET04.14.07

A Simple Molecular Reactive Force Field and Its Application to Perovskite Nucleation [Henry C. Herbol](#)¹, Gregory Case², Oluwaseun Romiluyi², Wang Gao¹, Jeet Chaudhuri³ and Paulette Clancy²; ¹Materials Science and Engineering, Cornell University, Ithaca, New York, United States; ²Chemical Engineering, Cornell University, Ithaca, New York, United States; ³Chemical Engineering, National Institute of Technology, Jaipur, India.

In recent years, research into Hybrid Organic-Inorganic Perovskites (HOIPs) has led to numerous experimental and computational insight into the effects of composition, stoichiometry, and solution processing on the overall Photo Conversion Efficiency (PCE) and stability of HOIP thin-films. Computationally, effort has been primarily focused towards time-intensive Density Functional Theory (DFT) simulations: due to the lack of Force Fields for Molecular Dynamics (MD) studies. As such, some of the benefits of a computational approach, such as atomistic revelations on nucleation, have been hindered. An easy to parameterize reactive force field would empower computationalists to probe these nucleation mechanisms, and help validate/guide experiments; however, as of yet none exists.

In this talk, we present updates to the Simple Molecular Reactive Force Field (SMRFF), and demonstrate initial capabilities as applied to Nanoparticle nucleation (PbS). Further, we illustrate the ease of use, parameterization procedure, and how the force field can be extended. SMRFF takes the idea of hybridizing force fields to the next step, and elaborates on how to smoothly transition between force fields based on interatomic distances. Further, it allows for as many transitions as possible, implying a fully extensible and customizable approach to force field development. A pair style, written to work in the popular LAMMPS codebase, implements the procedure, and an accompanying python script automates the process of developing new parameters.

3:45 PM ET04.14.08

Tandem Hybrid Organic-Inorganic Photocathode-Perovskite Solar Cell for Unassisted Solar Fuel Production [Antonio Alfano](#)^{1,2}, Alessandro Mezzetti¹, Francesco Fumagalli¹, Chen Tao¹, Maria Rosa Antognazza¹, Annamaria Petrozza¹ and Fabio Di Fonzo¹; ¹Istituto Italiano di Tecnologia, Milano, Italy; ²Physics, Politecnico di Milano, Milan, Italy.

Molecular hydrogen produced via solar energy is emerging as a prominent way to convert and store the conspicuous, yet intermittent, amount of energy that the Sun daily irradiates on Earth. Hybrid Organic photoelectrochemical (HOPEC) water splitting is gaining momentum in this field, and various approaches are currently being developed to realize hybrid tandem systems to perform unbiased water splitting. By taking advantage of the organic semiconductors properties such as low cost, stability, tuneable electronic properties and ease of large area production, these materials can help overcoming the limitations of standard inorganic photoelectrochemical water splitting. The potential of hybrid organic systems has been proven by our previous works¹. Indeed, excellent photocurrent performances² or extended operational lifetime³ have been obtained through careful optimization of hybrid photocathodes (PC) architecture. Good results have also been achieved investigating novel materials belonging to the family of transition metal dichalcogenides which fit for hole selective layers (HSL) application, allowing to deliver good performances both on stability and photocurrent.

Our main interest is now to tune the properties of hybrid organic PC acting on their photoactive layer, taking advantage of the latest advancements in the field of organic photovoltaic (OPV). Promising materials from OPV are, among many, the high-performance photo-absorbers PCE11 and PCDTBT, and the non-fullerene acceptors IDTBR and IDFBP, which were found to be responsible of a sharp increase in the open circuit voltage in OPV devices⁴. Their improved electronic properties and optimized band gap are here exploited to realize hybrid PC specifically designed to be coupled in a tandem configuration with a high performing perovskite⁵, realizing a full water-splitting system with cheap, easily processable and suitable for large area production materials. By modifying the hybrid PC, it was possible to extend the absorption range of the stack. Taking advantage of the high V_{oc} of the perovskite and the additional photovoltage coming from the PC, the system efficiently performs the full water splitting reaction without the application of any external bias. The results clearly indicate that the Solar To Hydrogen (STH) efficiency of the system increases sensitively when proper design of the tandem system is achieved, with STH above 2% for the best performing case. These results prove that a tandem hybrid organic perovskite-photocathode stack can be used to realize efficient photoelectrochemical systems for solar fuels production, unlocking a new field of application for these excellent performing class of materials.

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4:00 PM ET04.14.09

Copper Complexes Redox Couple as Solid-State Hole Transporting Material for Perovskite Solar Cells [Iacopo Benesperi](#), Hannes Michaels and Marina Freitag; Institutionen för kemi - Ångström, Uppsala University, Uppsala, Sweden.

Perovskite solar cells (PSCs) have been extensively studied in the past six years. The development of effective deposition methods for this material have led to devices rivaling in efficiency – at least at the laboratory scale – with silicon-based solar cells, at a fraction of the cost. The introduction in recent years of mixed cation perovskite materials has also started to address what is nowadays the main issue of this technology: long-term stability. While there has been an evolution of the perovskite layer in the past lustrum, the same cannot be said about another essential layer in PSCs – the hole transporting one. Spiro-OMeTAD, first introduced in solid-state dye-sensitized solar cells (DSSCs) and then employed at the beginning of the solid-state PSCs era is, in fact, still considered the material of choice for this particular component of a device. This fact is not due to a lack of research effort. In the past four years almost two hundred new hole transporting materials (HTMs) have been developed for PSCs and, despite the fact that some were claimed to perform better than spiro-OMeTAD itself, none managed to become widely employed by the larger research community. Although spiro-OMeTAD's successor has not been found yet, its replacement is paramount for PSC commercialization. Spiro-OMeTAD is known to be very expensive, which in part nullifies the inexpensive nature of the perovskite material. More importantly, however, spiro-OMeTAD is known to introduce stability issues inside PSC devices, greatly reducing their life. This is in part due to spiro-OMeTAD's properties themselves, in part due to all the additives and dopants embedded in the spiro-OMeTAD film

to improve its poor conductivity and film-forming properties.

To date, little research has been focused on transition metal coordination complexes, and especially metal complex redox couples, as HTM for PSCs. Metal complexes are known to be generally conductive and stable compounds, with their energy level easily tuned by changing the metal center or by applying small modifications to the organic ligand. They have been shown to perform very well in liquid DSSCs and they have recently been successfully employed in solid-state DSSCs.^[1,2] A proof of concept, with mixed results, has also been demonstrated for PSCs.^[3] Here, we employ a copper(I/II) complexes redox couple in devices featuring a mixed cation perovskite light absorber. These copper complexes feature good energy alignment with the perovskite material and good conductivity.

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4:15 PM ET04.14.10

Hole Extraction from Lead Halide Perovskite to PDPP-3T Probed by Ultrafast Transient Absorption Spectroscopy Jafar I. Khan¹, Esma Ugur¹, Erkan Aydin¹, Mindaugas Kirkus¹, Marios Neophytou¹, Iain McCulloch^{1,2}, Stefaan De Wolf¹ and Frédéric Laquai¹; ¹King Abdullah University of Science and Technology, Jeddah, Saudi Arabia; ²Imperial College London, London, United Kingdom.

Solution-processed metal-halide perovskite solar cells (PSCs) have received immense attention in the field of photovoltaics due to their high power conversion efficiency (PCE) of now more than 22% reached in a relative short time. Today, various electron and hole transport layers (HTLs) have been implemented to further enhance the device performance and stability. State-of-the-art PSCs use spiro-OMeTAD as HTL in *n-i-p* device structures, however, doping with both tBP and Li-TFSI is required to increase the hole mobility and conductivity of the HTL and achieve optimum performance. Long-term stability of devices is severely limited by Li-TFSI doping because of its hygroscopic nature. Here, as an alternative to spiro-OMeTAD, we used the high molecular weight solution-processed polymer PDPP-3T and demonstrate comparable performance to spiro-OMeTAD. Furthermore, we are interested in the dynamics of hole extraction from the perovskite to the HTL and interfacial recombination of charge carriers at the perovskite/HTL interface, which we studied by ultrafast transient spectroscopy. We show that the ground state bleach of the polymer allows direct optical probing of the carrier extraction and recombination dynamics. Hole transfer takes place from the perovskite to the HTL in tens of nanoseconds when the sample is excited from the perovskite side. By varying the perovskite film thickness from 170 nm to 570 nm, we investigate the diffusion of holes in the perovskite absorber layer, when PDPP-3T is used as HTL. Finally, we discuss the dynamics of carrier recombination at the PDPP-3T/perovskite interface.

4:30 PM ET04.14.11

Modification of TiO₂/CH₃NH₃PbI₃ Interface with KCl, KI, or KBr in Planar Perovskite Solar Cells Amrita Yasin, Adam Pockett, James McGettrick, Stoichko Dimitrov, Catherine S. De Castro, Matthew Davies, Matt Carnie, Trystan Watson and Cecile Charbonneau; Swansea University, Cardiff, United Kingdom.

This work showcases our research on modification of compact TiO₂ electron transport layers (ETLs) at the TiO₂/CH₃NH₃PbI₃ interface for application in planar lead halide perovskite solar cells. Compact TiO₂ ETLs were formed via spraying of a commercially available titanium diisopropoxide bis(acetylacetonate) precursor on fluorine-doped tin oxide (FTO) glass followed by annealing at 550 C. These layers were subsequently spin coated with aqueous solutions of 10mM and 40mM of KX (X = Cl, I, Br, prior to CH₃NH₃PbI₃ deposition. Presence of potassium and the X⁻ ions on the TiO₂ surface is evident via X-ray photoelectron spectroscopy (XPS) analysis, and individual crystals can be seen on the modified TiO₂ films. The absorbance and photoluminescence spectra of TiO₂/KX/ CH₃NH₃PbI₃ films do not show significant difference, however the work function of the modified TiO₂ film decreases. Against a stabilized power conversion efficiency of 8.25% in the reverse direction for unmodified planar devices, KI modified devices reach up to 11.53%, followed by KBr at 11.68%, and finally KCl at 8.09%. The change in efficiency can be correlated with a change in work function of the modified films.

4:45 PM ET04.14.12

Gas-Solid Reaction Based over 1 μm Thick High-Quality Stable Perovskite Films for Efficient Solar Cells and Modules with High Reproducibility Zonghao Liu¹, Longbin Qiu¹, Emilio J. Juarez-Perez¹, Zafer Hawash¹, Taehoon Kim¹, Yan Jiang¹, Zhifang Wu¹, Sonia R. Raga¹, Luis K. Ono¹, Shengzhong Liu² and Yabing Qi¹; ¹Okinawa Institute of Science and Technology, Okinawa, Japan; ²Shaanxi Normal University, Xi'an, China.

Organic-inorganic halide perovskite solar cells (PSCs) have drawn a great deal of attention in the photovoltaic research community due to their high efficiency over 23%. Besides high efficiency, the stability and reproducibility of PSCs are also key for their commercialization.¹ Here, we report a simple perovskite formation method to fabricate perovskite films with thickness over one micrometer in ambient condition on the basis of the fast gas-solid reaction of chlorine incorporated hydrogen lead triiodide and methylamine gas. The comprehensive characterization results reveal that with the synergistic effect of methylamine gas and partial substitution of iodine ions by chlorine ions, the resultant perovskite films with a thickness over one micrometer and low thickness variation exhibit excellent film quality. The resultant PSCs gave an average power conversion efficiency (PCE) of 19.1% and low PCE standard deviation (± 0.4%), which indicates the excellent reproducibility of this method. Meanwhile, this method enables a best active-area PCE of 15.3% for 5 cm × 5 cm solar modules and good reproducibility (13.6± 0.8%). Besides, the un-encapsulated PSCs exhibit an excellent T₈₀ lifetime exceeding 1600 h under continuous operation conditions in dry N₂ environment. Our study not only provides a highly reproducible method to fabricate PSCs and modules with enhanced efficiency, reproducibility and stability, but also offers the in-depth understanding for the underlying mechanisms responsible for device stability improvement. The encouraging results in this work points out a promising direction, *i.e.*, use of thick absorber films to realize PSCs and modules with high efficiency, reproducibility and stability.²

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