

Perovskite Solar Cells—Towards Commercialization

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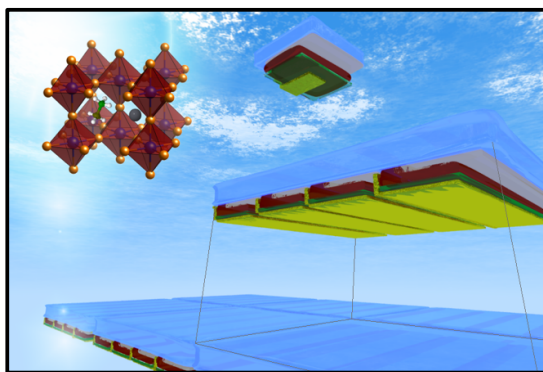
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The Symposium ES1 – “*Perovskite Solar Cells—Towards Commercialization*” held at the 2017 Materials Research Society (MRS) Spring Meeting in Phoenix, Arizona (April 17 – 21, 2017) received ~200 abstracts. The 23 invited talks and 72 contributed oral presentations as well as 3 poster presentation sessions were organized into thirteen principal themes according to the contents of the received abstracts. This article provides a concise summary on the opinions from the scientists and engineers who participated in this symposium regarding the recent progresses, challenges, and future directions for perovskite solar cells as well as other optoelectronic devices.

In Arizona, with an average of 300 sunny days a year, the Agua Caliente Solar Project employing CdS/CdTe materials made fame. *What does perovskite photovoltaic (PV) technology*

need the most? Within merely a few years, surprisingly high solar-to-electricity power conversion efficiencies (PCEs) have been achieved for lead-halide perovskite solar cells. However, many of these state of the art perovskite solar cells with the highest efficiencies were obtained on relatively small active areas ($\sim 0.1 \text{ cm}^2$). Substantial progress has been made and much more efforts are still needed for the development of large-area perovskite solar cell fabrication processes aiming at high PCE, high-throughput, and minimum batch-to-batch variation. Based on the presented works, the number of perovskite solar cells employing active areas larger than 1 cm^2 is still a minority but certainly increasing. On the other hand, an area of 1 cm^2 is only considered “intermediate size” in industrial standards. Therefore, there is still plenty of room for further improvements and developments of techniques to fabricate large area perovskite solar cells. Two invited talks highlighted two webpages (i) Perovskite-Info (<http://www.perovskite-info.com/>) and (ii) International Technology Roadmap for Photovoltaic (ITRPV) (<http://www.itrpv.net/Home/>), which provide the current status on the commercialization of perovskite solar cells and crystalline-Si solar cells, respectively. There are already a few companies that focus on the development of perovskite solar products such as Oxford PV, Dyesol, Saule Technologies, Microquanta Semiconductor, and Solar-Tectic. Oxford PV showed a perovskite solar cell with an area of $156 \times 156 \text{ mm}^2$, which corresponds to a size that is sufficient to integrate with Si solar cells (e.g., 6” wafer size) in a tandem configuration. The development of large-area fabrication techniques relies on (i) *a priori* understanding of complex nucleation and growth processes of perovskite films, (ii) perovskite film deposition methods (solution process or vacuum deposition) with a high degree of controllability to ensure low cell-to-cell and batch-to-batch variation, and (iii) *a posteriori* spatially resolved chemical

composition distribution and morphology characterization of the entire perovskite films as well as when incorporated in complete devices.

Monitoring perovskite film quality during spin coating was achieved by *in situ* time resolved grazing incidence wide angle X-ray scattering (GIWAXS) measurements to investigate the origins of detrimental effects of incomplete lead precursor conversion, inconsistent crystallite formation/film uniformity, and precursor-solvent coordination. In addition, strategies such as electroluminescence (EL) imaging of the complete cell was shown to be helpful to visualize spatially present defects and/or (dust) particulates that lead to shunting pathways. Compositional uniformity is equally important for attaining optimum performing cells, and X-ray fluorescence (XRF) and Rutherford backscattering spectroscopy (RBS) was shown to be effective for depth profiling. Considering up-scaling, the first step is fabrication of large-area perovskite solar cells with high quality (i.e., high film uniformity, reduced roughness across the whole area, reduced density of defects, etc.). Once the first step is attained, it can be followed by the second step of fabrication of a module and the third step of integrating the modules into a panel (Figure 1).

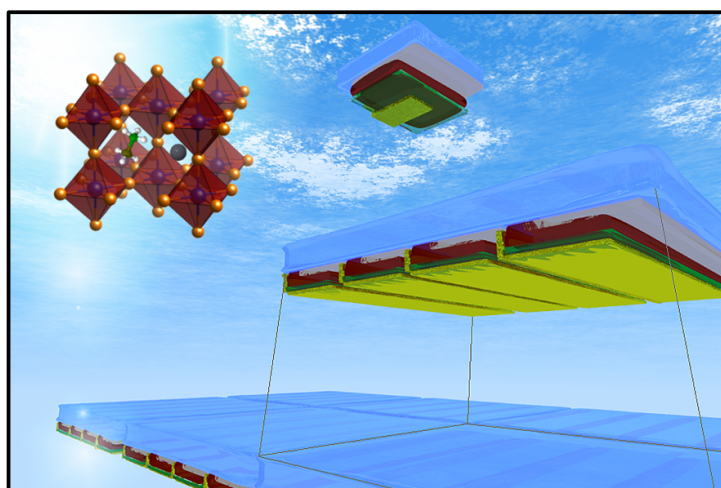


Figure 1. Up-scaling laboratory-scale perovskite solar cells to modules and panels.

Preferentially oriented perovskite film growth, discussed by at least six talks, was one of the topics that attracted attention in this symposium. It has been highlighted that controlling crystal orientations of perovskite films is vital for the preparation of polycrystalline perovskite films with enhanced electronic/electrical properties. Thin-film deposition strategies such as (i) *thermal-gradient-assisted directional crystallization* method, (ii) addition of *rationally selected chemical additives* in precursor solutions, and (iii) *topotactic-oriented attachment* method were some of the techniques to fabricate uniaxial-oriented perovskite films on different substrates. It has been demonstrated that certain crystallographic orientations of perovskites grains can lead to enhancement in carrier mobility and impact significantly the open circuit voltage (Voc) and PCE.

The processes based on the more basic chemical components of methylamine (CH_3NH_2) and formamidine (CH_2N_2) (as opposed to *methylammonium iodide* $\text{CH}_3\text{NH}_3\text{I}$ or *formamidinium iodide* $\text{CH}_2\text{NH}_2^+\text{I}^-$) were another highlight in this symposium. These processes can “heal” defects leading to high quality perovskite films. Methylamine gas treatment not only can improve morphology, but also promote the melting and re-growth of perovskite crystallites into preferred crystal orientations. These preferred orientations lead to significant enhancements in photoluminescence properties. Based on a total of at least seven talks, a series of synthetic routes by either adding (i) methylamine in the precursor solution or (ii) as post-treatment processes to prepare perovskite films with desirable morphologies (e.g. ultra-smooth, large grain sizes, etc.) and chemical compositions showed exceptional promise for up-scaling perovskite solar cells. Furthermore, the methylamine gas exposure post-treatment also led to remarkable advances in $\text{CH}_3\text{NH}_3\text{PbBr}_3$ -based light emitting diode (LED) devices.

In the field it appears that the proposal that ion migration is the major cause for current-voltage hysteresis has been gaining pre-dominance. On the other hand, during this symposium, a vivid

discussion was brought in by at least three talks suggesting that ion migration is not all that matters and other factors predominantly lead to hysteresis in some cases. Based on the observation that hysteresis is absent in certain perovskite solar cells, the fabrication processes seem to be crucial. It has been shown that if properly fabricated hysteresis-free perovskite solar cells can be obtained and the electronic characteristics of these cells can be nicely represented by equations well established to describe conventional inorganic semiconductor solar cells (Si cells with a p-i-n structure). It has been shown in another talk that hysteresis is solely induced by contact issues without the need of ion migration. An analog electronic circuit (composed of a few diodes, capacitors, inductors, and resistors) was proposed as the equivalent circuit to model the interfaces of TiO₂/perovskite/hole transport layer (HTL) and was shown to reproduce well the hysteresis behavior in I-V curves. Electron microscopy studies suggest that the fundamental origins come from the lattice mismatch or empty voids at the interface of perovskite and TiO₂ that can be generated upon e.g., heat-induced volume expansion. Based on this symposium, the discussions on the origin(s) of hysteresis have not ended, and new studies will likely provide more interesting insight.

Organic-halide perovskites are “soft” crystalline materials, and their crystal structure forms at room-temperature by combined ionic and hydrogen bonds maintaining structural equilibrium. Because of thermodynamics as well as imperfect crystal growth, formation of bulk defects is unavoidable, which influences device performance. Furthermore, another limiting factor to high device performance is the presence of surface defects. Although much more effort is needed to unravel the nature of these bulk and surface defects at a microscopic level, they have been reported to influence significantly the optoelectronic properties. As an example presented at this symposium, photoluminescence (PL) properties of CH₃NH₃PBr₃ single crystals and

polycrystalline films were revealed to be highly sensitive on the environment; vacuum *versus* air. Oxygen and water molecules were shown to effectively decrease the sub-band gap trap states enhancing the optoelectronic properties of perovskites. A key response to the question *what is essential to improve solar cell performance and stability* seems to lie in the engineering and management of the interfacial structure and electronic properties at the heterojunctions. The interfaces between the two functional layers (e.g., between the absorber and selective contact) play a key role in facilitating charge transfer and minimizing recombination losses. Twelve talks reported *surface and interface passivation strategies* by employing interfacial organic semiconductor molecular doping, self-assembled monolayers (SAMs), nanoparticles or quantum dots, gradient interlayer, which showed not only solar cell performance improvement but also solar cell stability enhancement by filling surface trap states. Although device applications have demonstrated the effectiveness of these surface passivation strategies, the central question *what is the nature of these trap states* still remains.

The interplay and balance between various structural components in *lead* halide based perovskites generate optimum optoelectronic properties for photovoltaic applications. So far the overall consensus reflected by the majority of presentations is that lead based perovskite solar cells outperform substantially lead-free perovskite solar cells, which makes replacement of lead challenging. The photovoltaic community is well aware of the toxicity issues associated with lead and the anxiety that poses for the public, which are among the major factors influencing the ultimate fate of this technology. Therefore, it has been regarded as a strong motivation spurring more research effort to develop lead-free based perovskite solar cells. Although more research need be done regarding the toxicity of Sn, at least four talks were presented on Sn-based perovskite solar cells showing great promises in terms of efficiency. A major enhancement in

efficiency came after the fundamental understanding of chemical processes taking place at the interface between TiO₂ electron transport layer and Sn-based perovskite; it is important to avoid the direct contact between TiO₂ and Sn-based perovskite. Solvents commonly employed for perovskite synthesis were also pointed out as a source of concern due to their toxicity. The situation is expected to be aggravated when considering large area fabrication processes due to large volumes of solvent vapors. Alternative solvent systems with low toxicity will be an important consideration.

Encapsulation of perovskite solar cells is an important strategy, which is essential to protect not only perovskite solar cells from external environment, but also reciprocally protect environment from lead-based perovskite solar cells. The long-term stability (e.g., >20 years which has been achieved in silicon PV technology) of perovskite solar cells is a grand challenge. Specifically, perovskite solar cells will need to sustain the thermal stress testing conditions following the IEC 61646 protocol. For attaining certification relevant for industry, solar modules must operate successfully in the temperature range between -40 °C and +85 °C. Corning Willow Glass sheets with thickness of 100 or 200 μm (<https://www.corning.com/worldwide/en/innovation/corning-emerging-innovations/corning-willow-glass.html>) was shown to be compatible with roll-to-roll coating processes to fabricate large area, light-weight, and flexible solar cells. It has been emphasized that polymer sheets such as PET and PEN allow easy ingress of water molecules through the material. In this regard, glass would be a better choice to achieve high stability. Alternatively, metal sheets were used as substrates to fabricate flexible solar cells. A few talks discussed the preferential ingress of moisture through the grain boundaries in perovskite polycrystalline films as the main cause for degradation of perovskite solar cells. Naturally, a question arises whether a perovskite solar cell based on thin-sliced “perfect” single crystals (i.e.,

grain boundary-free) would show both enhanced PCE and stability? Efforts are being made towards this direction as presented in two talks.

Recycling of degraded perovskite solar cells was introduced from the perspectives of environment and cost-effectiveness. It has been proposed that the reuse of gold electrodes and transparent conducting glass substrates, e.g. fluorine-doped tin oxide (FTO) could lower the environmental impacts and price per watt for perovskite photovoltaic modules. Strategies to dismantle degraded perovskite solar cells to allow recovery of major components will be beneficial for saving raw materials, energy, and production time. In a particular example, it was demonstrated that the PCE of perovskite solar cells fabricated from recycled substrates can generate a similar level of solar cell performance as those fabricated from new materials.

Operando measurements on perovskite solar cells by synchrotron radiation (SR) techniques was discussed as a useful method to study photovoltaic device dynamics under a number of different stimuli such as cooling/heating, current/voltage, light, and environmental stressing conditions. In particular, an example of *operando* measurements was accomplished on a $\text{CH}_3\text{NH}_3\text{PbI}_3$ -based solar cell by designing a sample stage for simultaneous current-voltage curves dependent measurements on temperature and SR X-ray diffraction. A detailed correlation between perovskite crystal structure and current-voltage profiles were established on the same device sample, revealing insights into tetragonal-to-cubic phase transition temperature (60.5–65.4 °C). Such *operando* measurements provide further fundamental insights into the dynamics of perovskite solar cells under operation conditions. The earned knowledge is expected to stimulate a new wave of technological advances in perovskite solar cells.

AUTHOR INFORMATION

Notes

The authors declare no competing financial interest.

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