

# Rapid processing of perovskite thin films for applications in PV

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## ABSTRACT

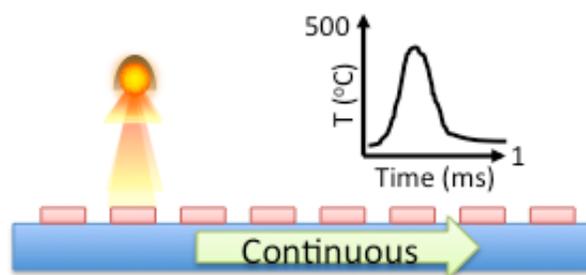
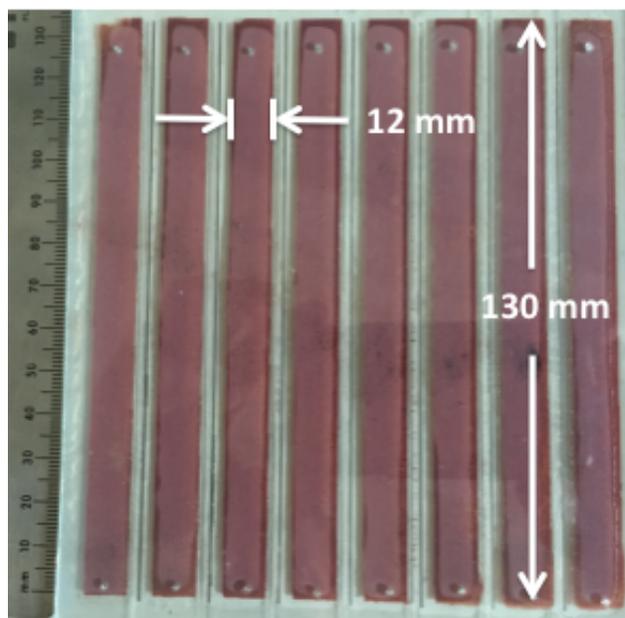
Perovskite solar cells have the possibility of becoming the next generation of industrial solar cells due to their ease of manufacturing, use of common materials, and respectable efficiencies. Since the first report of perovskite solar cells, the technology has evolved to certified power-conversion efficiencies above 20% in a span of only 5 years. The cells are based on organometal halide perovskite materials characterized by high extinction coefficients and carrier mobilities. Unlike traditional semiconductor solar cells, the perovskite solar cell is amenable to changes in the atoms of its crystal structure, which opens up opportunities for low temperature processing techniques. Most solution phase deposition techniques yield a thin film constituted by small grains, which are then relaxed using thermal or solvent extraction techniques. Although, these techniques work very well, they are limited by the low sublimation temperature of the methyl ammonium lead iodide. In this paper, we demonstrate another method to rapidly process the deposited films using intense pulsed light. The film is completely transformed from a deposited cubic structure to a smooth coating with large grain sizes. More importantly, the process occurs in less than 1 millisecond, which is encouraging for continuous manufacturing. In this talk we will describe the evolution of the thin film from deposition to device using scanning electron microscopy, X-ray diffraction, UV-Vis spectroscopy and photoluminescence. We will also demonstrate a working cell and compare to the state of the art production techniques.

**Keywords:** perovskite, photovoltaic, advanced manufacturing, roll to roll, intense pulsed light

## 1 INTRODUCTION

Traditional printing of low cost thin film materials for solar energy applications would transform the power generation landscape. Thin film PVs have been touted as a low cost alternative to the dominant crystalline silicon (c-Si) technology. The costs of c-Si modules in 2010 was estimated to be \$2.25 per watt (/W) compared to \$0.76/W for Cadmium Telluride (CdTe) thin film technology. In the past few years, the costs of c-Si modules have dropped over 80% well below \$1/W due to surplus production and razor thin and often negative margins from manufacturers. Despite these cost reductions, solar still needs further price reductions, especially in the area of installation, in order to be cost competitive with traditional fuels. These cost

pressures have driven a number of thin film manufacturers from the market. Although the materials costs of thin film technologies are low, the high heat, high vacuum, and specialty gas techniques are energy and capital intensive processes that drive up costs. A big challenge for thin film PV technologies is to drastically reduce the manufacturing and capex as well as installed costs to aggressively compete with the falling costs of c-Si. Solution phase printing of thin films has a high likelihood of lowering production costs and providing new designs to reduce installation costs. Recently researchers demonstrated impressive performance of a solution deposited perovskite absorber with dramatic improvement over the past five years.



**Figure 1.** Schematic of the proposed IPL method processing full cells in a continuous manufacturing platform.

The perovskite solar cell since its introduction in 2010 has received a great deal of attention with efficiencies exceeding 20%, the highest for a solution deposited device. This is significant since typical manufacturing of solar cells requires high temperatures and expensive vacuum processing greatly increasing costs. The perovskite avoids these expensive processes, although current state of the art techniques will be difficult to scale, especially into a continuous roll-to-roll manufacturing platform. However, the deposition and heat treatment of the perovskite solar cell as currently described is very difficult to scale. A new technique, intense pulsed light (IPL) is very scalable and has been shown to improve the crystallinity of semiconductors.[1, 2]

In the past decade, the IPL technique has gained a large amount of interest within the printed electronics industry. The IPL technique delivers high-energy light in a very short duration over a large processing area, heating thin films containing photosensitive materials. The method is analogous to additive manufacturing techniques that utilize infrared lasers to locally sinter powders; however, IPL uses a broader spectrum of light and the processing area is far larger improving the feasibility for manufacturing economically. A module of series connected perovskite solar cells could include multiple rectangular cells in series similar to a dye-sensitized solar cell shown in Figure 1. The IPL processing area is 20 mm x 300 mm, and anneals the perovskite absorber in approximately 1 millisecond; therefore is ideally suited for implementation into a continuous roll-to-roll platform of series connected cells.

## 2 PEROVSKITE PROCESSING

As mentioned previously, the perovskite solar cell has seen a tremendous amount of improvement in a very short period of time. Much of the effort towards the perovskite layer has focused on 1) the underlying device physics, 2) the thermodynamics of the perovskite morphology and 3) new materials development. Very little of the research to date has emphasized the scalable manufacture of the devices, despite the fact that these are solution processed devices.

Perovskite solar cells combine the crystallinity and high charge transfer found in inorganic semiconductors with the cost-effective, low-temperature solvent manufacturing of organic solar cells. Since the first report of perovskite solar cells in 2012, the technology has evolved to over 20% certified efficiency[3]. The cells are based on organometal halide perovskite materials having a formula of  $ABX_3$  with the A site typically referring to an organic group, B representing a metal such as lead, and X being a halide group such as iodide, chloride, or bromide. The often used methyl ammonium lead iodide is represented  $CH_3NH_3PbI_3$ . Unlike traditional semiconductor solar cells, the perovskite solar cell is amenable to changes in the atoms of its crystal

structure. This opens up many possibilities in tuning band gaps, using different cell configurations, and experimenting in processing.

Creating larger perovskite crystals and improving the surface coverage of perovskite films have become great topics of discussion in perovskite research. The deposition of the perovskite layer has been accomplished in one of two routes. The first, and the preferred for scalability, is one-step deposition of the  $CH_3NH_3PbI_3$  which is reacted from  $PbI_2$  and MAI prior to deposition. Initially, this technique led to poor coverage of the surface and non-uniform stoichiometry and was eventually replaced with a two-step method. In this technique, the  $PbI_2$  is first deposited from a solution including DMF and then subsequently dipped into a solution of MAI in isopropanol[4]. Ko, et. al. improved on this method by showing that heating the substrates prior to spin coating the lead iodide solution attributed to better surface coverage and pore filling of the perovskite formed after dipping the films in MAI solution [5]. In the past year, researchers have been turning back to the one-step deposition technique, as it yields greater control of the film and more straightforward manufacturing. The one-step deposition of  $CH_3NH_3PbI_3$  has also been advanced by using solvent-solvent extraction techniques. The techniques utilize high vapor pressure solvents such as diethyl ether to remove low vapor pressure solvents such as dimethylformamide (DMF) from the perovskite films after spin coating [6].

The deposited perovskite films must undergo an annealing process, in which the films are subjected to temperatures of between 80 and 150°C for 10 minutes to several hours. At the lower temperatures, it is very difficult to achieve the film uniformity required for an acceptable device even at very long processing times. On the other hand, at higher processing temperatures the  $CH_3NH_3PbI_3$  decomposes into MAI and  $PbI_2$  as shown in the equation.

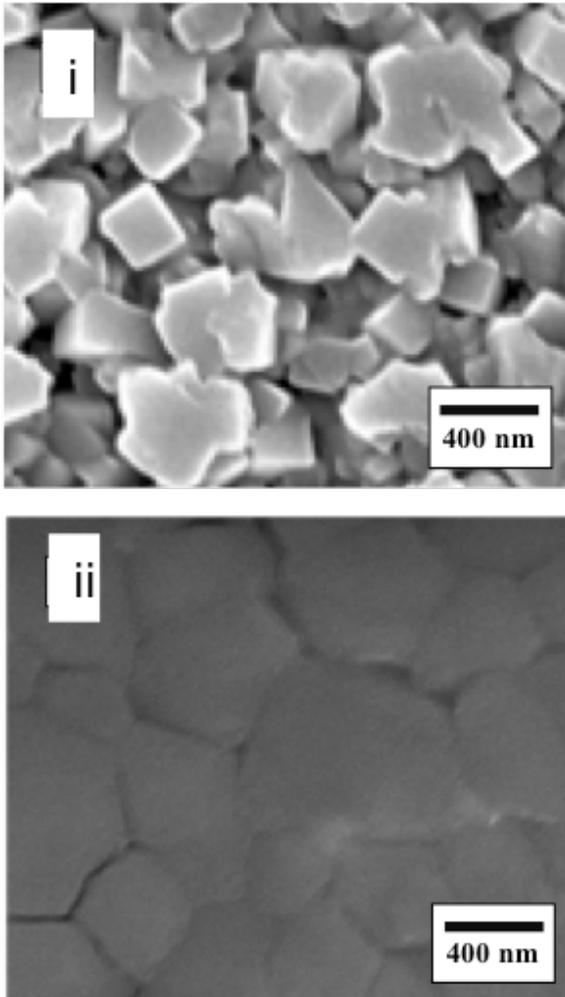


In this case, thermogravimetric analysis (TGA) shows the  $CH_3NH_{2(g)}$  is in the gas phase and escapes the film leaving behind the  $PbI_2$ . Work to improve the surface coverage of the films includes using other precursor chemistries in the two-step technique and adjusting the ratio of the MAI to  $PbI_2$  in the single-step deposition. These accomplish a change in the local vapor pressure of the deposited films, thereby altering the film formation especially during the annealing process.

## 3 RESULTS

As-deposited perovskite films using the two-step method (spin-coating  $PbI_2$  and dip coating MAI) commonly yield poor surface coverage (Figure 2i). These gaps cause lower shunt resistance and hence lower short circuit current densities when the hole transport layer is in direct contact with the electron transport layer. This has spurred research attempts to densify the morphology of the perovskite layer to prevent shunting pathways and improve the fill factor

and reproducibility of perovskite solar cells[7]. Research has shown that increasing the annealing temperature leads to an increase in the efficiency of the perovskite solar cell until 150°C, and then the perovskite decomposes into lead iodide[8]. IPL was applied to as deposited perovskite films as shown in Figure 4 (ii).



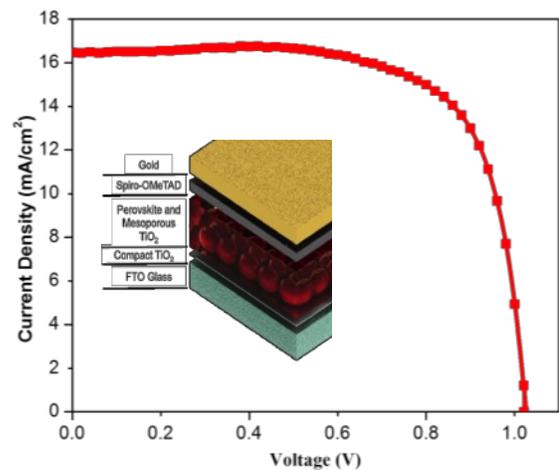
**Figure 2:** Scanning electron microscope image of the top of the perovskite films i) after deposition and ii) after IPL

The SEM images of the top surface of the film demonstrate that there is a remarkable alteration of the film morphology. Prior to this research, densification of this magnitude was accomplished via an extra solvent extraction treatment or using a less scalable chemical vapor deposition process. Figure 2 shows the transition of cubical particles formed during the solvent reaction to large dense particles at 2000 J/Pulse. These images suggest that there is more occurring to the film than just a simple annealing, and in fact look surprisingly similar to the prior results from the in which the IPL induced sintering of CdTe.[1, 9] The perovskite films after IPL processing have in contrary to

thermal annealing, improved coverage as the intensity of the light was increased, and interestingly, this has occurred over a 2 ms time frame.

The maximum temperature rise, within the film due to a rapid intense light pulse can be estimated using a model for laser induced temperature rise, which includes the heat capacity and thermal conductivity of the film, the emissivity of the surface and the duration of the pulse. Using this information, the rise in the temperature of the film ranges from a 100°C to a maximum of 800°C. The temperature rise of the semiconducting thin film exposed to IPL was previously confirmed through a simple finite element model with ANSYS using CdS as a model material. This showed that the temperature of the bulk film reached a maximum of several hundred degrees Celcius lasting for nearly 1 ms and returning to the original temperature in less than one second. These results were further confirmed using an experimental setup where the temperature of the substrate was monitored.[2]

Perovskite solar cell devices were fabricated on glass slides using a sequential approach detailed by Graetzel’s group.[10] The device consists of a 50 nm titanium dioxide hole-blocking layer, a 150-250 nm mesoporous titanium dioxide electron transport layer with  $\text{CH}_3\text{NH}_3\text{PbI}_3$  perovskite crystals filling the pores, a 150 nm layer of hole-transport material Spiro-OMeTAD, and an 80 nm layer of gold to make a contact. The device structure is shown in the inset of Figure y. Prior to the deposition of the Spiro-OMeTAD, the perovskite films were subjected to a single 2 ms light pulse at an energy of 2000 Joules over an area of 1.9 cm x 30.5 cm. After the devices were built, they were tested for performance using a standard I-V characterization test. The results of the PV performance are shown in Figure y. The IPL processed solar cells have an average current density of 16.55  $\text{mA}/\text{cm}^2$ , open circuit voltage 1.02 V, and fill factor 0.69. The overall efficiency of the champion IPL processed device was 12.25%.



**Figure 3:** I-V curve of IPL sintered perovskite layer.

## 4 CONCLUSION

In this paper, we have demonstrated the utility of the IPL process on perovskite solar cells. The IPL can quickly increase the crystallite size without inducing sublimation, despite the fact that very high temperatures are achieved. The IPL method was successfully used to produce a functioning solar cell with an efficiency over 12%. The process is extremely fast (ms) over a very large area and so is amenable to continuous manufacturing platforms such as roll to roll coating.

## REFERENCES

1. Dharmadasa, R., B. Lavery, I.M. Dharmadasa, and T. Druffel, *Intense pulsed light treatment of cadmium telluride nanoparticle-based thin films*. ACS Applied Materials & Interfaces, 2014. **6**(7): p. 5034-40.
2. Dharmadasa, R., I.M. Dharmadasa, and T. Druffel, *Intense Pulsed Light Sintering of Electrodeposited CdS Thin Films*. Advanced Engineering Materials, 2014. **16**(11): p. 1351-1361.
3. Green, M.A., K. Emery, Y. Hishikawa, W. Warta, and E. Dunlop, *Solar cell efficiency tables (version 46)*. Progress in Photovoltaics, 2015. **23**(7): p. 805-812.
4. Burschka, J., N. Pellet, S.-J. Moon, R. Humphry-Baker, P. Gao, M.K. Nazeeruddin, and M. Graetzel, *Sequential deposition as a route to high-performance perovskite-sensitized solar cells*. Nature, 2013. **499**(7458): p. 316-319.
5. Ko, H.-S., J.-W. Lee, and N.-G. Park, *15.76% efficiency perovskite solar cells prepared under high relative humidity: importance of PbI<sub>2</sub> morphology in two-step deposition of CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>*. Journal of Materials Chemistry A, 2015. **3**(16): p. 8808-8815.
6. Zhou, Y., M. Yang, W. Wu, A.L. Vasiliev, K. Zhu, and N.P. Padture, *Room-temperature crystallization of hybrid-perovskite thin films via solvent-solvent extraction for high-performance solar cells*. Journal of Materials Chemistry A, 2015. **3**(15): p. 8178-8184.
7. Salim, T., S. Sun, Y. Abe, A. Krishna, A.C. Grimsdale, and Y.M. Lam, *Perovskite-based Solar Cells: Impact of Morphology and Device Architecture on Device Performance*. Journal of Materials Chemistry A, 2015. **3**(17): p. 8943-8969.
8. Dualeh, A., N. Tétreault, T. Moehl, P. Gao, M.K. Nazeeruddin, and M. Grätzel, *Effect of Annealing Temperature on Film Morphology of Organic-Inorganic Hybrid Perovskite Solid-State Solar Cells*. Advanced Functional Materials, 2014. **24**(21): p. 3250-3258.
9. Dharmadasa, I.M., O.K. Echendu, F. Fauzi, N.A. Abdul-Manaf, H.I. Salim, T. Druffel, R. Dharmadasa, and B. Lavery, *Effects of CdCl<sub>2</sub> treatment on deep levels in CdTe and their implications on thin film solar cells: a comprehensive photoluminescence study*. Journal of Materials Science: Materials in Electronics, 2015.
10. Burschka, J., N. Pellet, S.-J. Moon, R. Humphry-Baker, P. Gao, M.K. Nazeeruddin, and M. Graetzel, *Sequential deposition as a route to high-performance perovskite-sensitized solar cells*. Nature, 2013. **499**(7458): p. 316-+.