

Roll to Roll Processing of Perovskite Materials for Solar Cells

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Abstract

The performance of the perovskite material in solar cells has garnered a fair amount of interest because it is solution processable and thus a prime target for roll-to-roll coating. The precursor materials are typically prepared in solutions and deposited using common evaporative techniques, some that can be adapted to roll-to-roll manufacturing. However, there are some difficulties that must be overcome to allow for the films to be stable in ambient conditions such that they can be deposited more cost effectively. In this work, we report on solution engineering that enables both the deposition of the perovskite in ambient environments using roll-to-roll applicable technologies. These engineered chemistries also designed to enable rapid post processing steps to limit the web length within a conventional oven. Scanning electron microscopy and X-ray diffraction analysis shows that the films achieve consistent morphology and crystallinity and perform well in solar cell devices. Results of several chemistries and processes will be presented.

Introduction

The perovskite solar cell (PSC) has seen impressive improvements in efficiency and durability in a very short period. These are encouraging for the commercial success of this technology which utilizes low cost absorber materials. The bulk of work has focused on the absorber, with photovoltaic conversion efficiencies (PCE) over 20%.^[1] This rapid growth in the PCE is attributed to the excellent material properties of organometallic halide materials such as high light absorption coefficients^[2], longer diffusion lengths^[3], and high charge transfer capabilities.^[4] The organometallic halides are represented by the AMX_3 structural formula where A denotes the organic cations such as methylammonium, butylammonium and formamidinium; M represents metal cations such as lead (Pb) and tin (Sn); and X corresponds to halide anions such as iodine (I), chlorine (Cl), and bromine (Br). The precursor solutions are deposited using solution phase processes that are amenable to roll-to-roll techniques.

[†] Unpublished. ISCST shall not be responsible for statements or opinions contained in papers or printed in its publications.

Typical roll-to-roll processes utilize solution based inks followed by a thermal post-deposition step to evaporate solvents, initiate chemical reactions and sinter materials. The residence times of post deposition processes is considerably longer than deposition and hence the ovens dominate the production line. Although this accepted protocol has been established over decades of operations, it does incur inefficiencies, downtime and yield issues. Technologies that can reduce the habitual reliance on large scale ovens will improve the throughput and reduce costs of advanced roll-to-roll manufacturing. This is of importance for the scalability of the perovskite solar module, which requires deposition of at least four distinct thin films with morphology changes post-deposition. Opportunities to reduce the residence times in these processes will improve the commercial relevance of this technology. Radiant heating technologies such as intense pulsed light (IPL) focus energy into the thin films reducing dwell times to less than a second and allowing for higher temperatures on thermally unstable substrates.

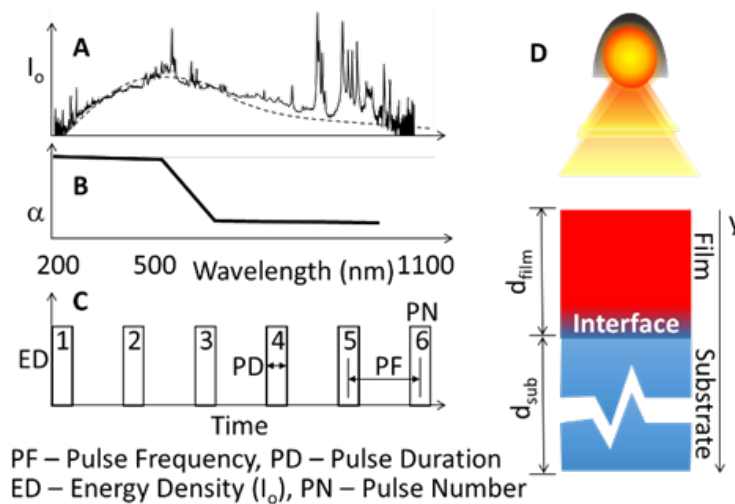


Figure 1. Schematic of radiative process (A) shows the representative wavelength behavior of a light source; (B) is the absorptivity of the film; (C) the parameters from the light source, (D) view of the IPL process orthogonal to the film in the direction of the light energy. (from Druffel et al [5])

The use of light energy to induce a rapid thermal response through IPL has been used in the PV industry.[5] In these processes, light energy produced from lamps is absorbed by the thin films and subsequently released as heat. Most of the functional materials used in photovoltaics absorb light energy; and for this reason the IPL process has ample opportunities to displace traditional thermal processes. The incident radiation $I_o(\lambda)$ is directly related to the spectrum of light ($S(\lambda)$) a fixed property of the lamp

(with a representative shape shown in figure 1A) and the energy density (ED) of the light can be manipulated through voltage control. Light with energies in the range of absorptivity (λ) of the thin film are absorbed (figure 1B), which results in the production of heat as excited electrons release the energy. The depth of absorption is also a function of the film thickness (t). The transfer of the energy can be conducted further into the film/substrate, or convected/radiated from the surface. The application of the light energy can also be controlled through varying the pulse duration (PD) and frequency (PF) (figure 1C), thus the operational parameters of the technique are considerable. The IPL process delivers high intensity light that can result in very rapid changes in temperature over wide areas making them applicable to roll-to-roll production. The rapid processing also allows the IPL to be done in ambient atmospheres as the interaction with oxygen and moisture is limited.

In this paper we give several examples of how changes in formulation can assist with the IPL processing of perovskite solar cells. Results from 2 step deposition and single step deposition are given. The deposited films are analyzed using X-ray diffraction (XRD) and scanning electron microscopy (SEM). Sample devices are built and tested using standard I-V characterization.

Discussion

In a first demonstration of the IPL process on a perovskite absorber involved the two step deposition of a perovskite material prior to IPL.[6] The SEM images of the as deposited material (figure 2) show that the film is rough and does not penetrate the underlying mesoporous TiO_2 layer. The IPL process smooths the film and results in a good penetration of the mesoporous layer. Finite Element Analysis (FEA) of the IPL process determined that the film reached temperatures in excess of $700\text{ }^\circ\text{C}$; however, XRD demonstrated a decrease in the PbI_2 peak. The resulting solar device had an efficiency of over 12%. In this work the perovskite was deposited in a controlled environment but the IPL process was carried out in an ambient atmosphere. This demonstrated that the speed of the thermal response was too rapid to induce degradation that would normally occur.

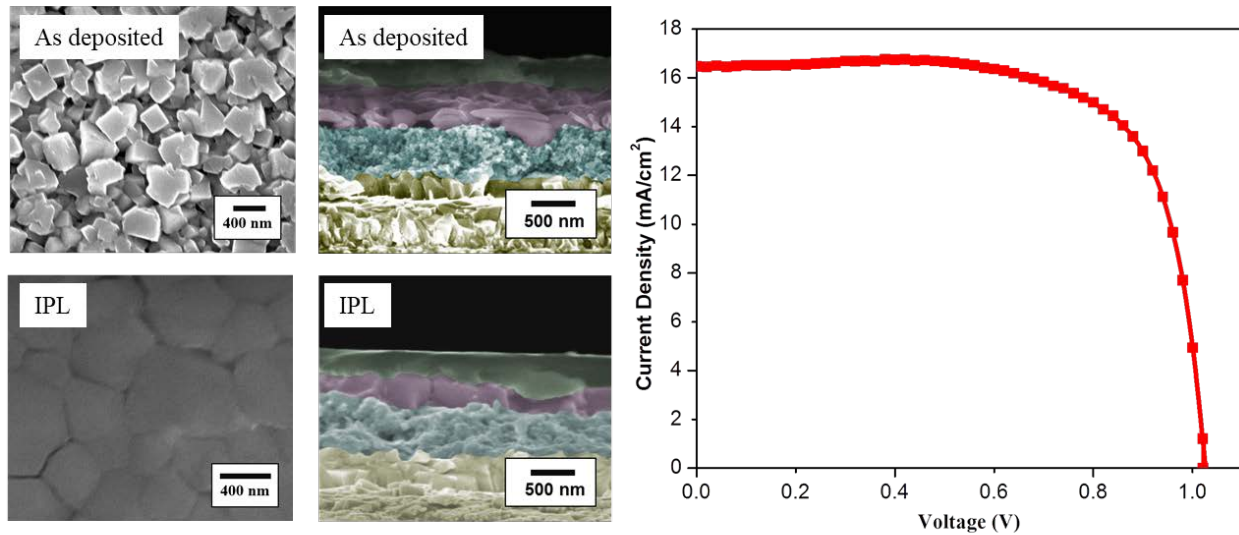


Figure 2. Scanning electron microscope images of the top surface (left) and cross-sections (middle) of the as-deposited and IPL processed perovskite absorber layers. I-V characterization of a solar device manufactured from an IPL processed perovskite layer. (from Lavery et al [6])

In a second attempt to utilize the IPL process a film was deposited in a one-step spin coating technique outside of a glove box.[7] In order to improve the surface morphology of the deposited film a binder was added, Polyvinylpyrrolidone (PVP). PVP was chosen as in our earlier work had been shown to interact with the IPL radiation when utilized with a copper nanoparticle. As can be seen in figure 3, the effect of the PVP was to improve the morphology of the perovskite absorber and this was also confirmed by optical images of the film that showed the PVP addition improved the color of the perovskite.

Unfortunately, the PVP films were not photo-active. However, the films without the PVP that were processed in ambient conditions did have a photovoltaics performance.

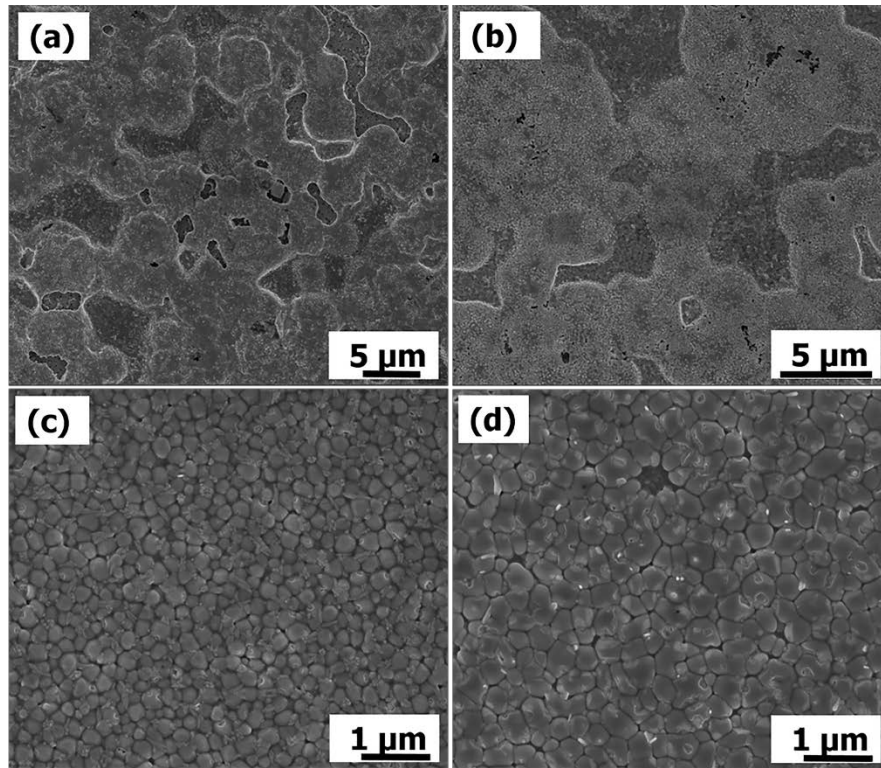


Figure 3. Surface morphology of no-PVP-added and PVP-added films processed with different IPL pulses with 2 ms pulse duration and 26.5 mJ/cm^2 energy density. (a&b) no-PVP added films treated with 5 and 20 pulses, respectively (c&d) PVP added films treated with 5 and 20 pulses, respectively. (from Ankireddy et al [7])

The concept of depositing the perovskite with a co-solvent or binder that would interact with the IPL radiation was further explored with the single step deposition.[8] The addition of iodine during the annealing of the perovskite would be beneficial to the formation of the layer and should also improve the performance of the device. It so happens that diiodomethane CH_2I_2 is known to degrade into I and CH_2I when exposed to ultraviolet (UV) light. The lamp used in the IPL process has a UV component. The SEM images show that the coverage of the CH_2I_2 IPL processed films is improved (figure 4A & 4B). The XRD spectra indicate that there is no obvious degradation of the perovskite material in the presence of UV (figure 4C & 4D). Finally the performance of the device as built using IPL processing with CH_2I_2 outperforms the device built without the CH_2I_2 (figure 4E).

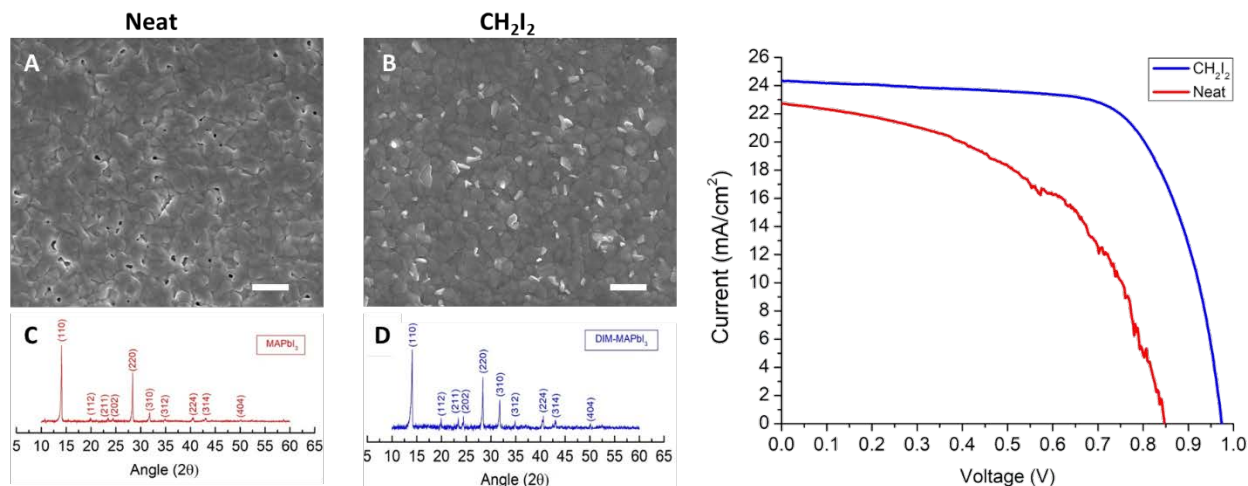


Figure 4. Side by side comparison of results neat (left) and CH_2I_2 additive (right) perovskite films processed using IPL. A,B) SEM images.(Scale bar is 1 micron) C,D) XRD diffraction patterns. E) I-V performance of neat and CH_2I_2 IPL processed perovskites. (from Ankireddy et al [8])

Conclusion

The IPL process has been successfully used in the manufacture of perovskite thin films for photovoltaic devices. The IPL process has been demonstrated using two popular techniques for material deposition including a two step and one step spin coating process. The addition of additives that interact with the UV portion of the IPL have also been shown to improve performance.

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