Large-area hysteresis-free perovskite solar cells via temperature controlled doctor blading under ambient environment

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Abstract

Hybrid perovskites have emerged as the most promising thin-film photovoltaic technology with efficiencies exceeding 20% merely in the last five years. Most high-efficiency perovskite solar cells reported in the recent years have relatively small device area in comparison to that required for commercial photovoltaic modules. While these results are excellent from an academic perspective, scaling up the overall cell device area is crucial for achieving practical utility for hybrid perovskite based thin-film solar cells. In this paper, we present a comprehensive study on the use of temperature-controlled doctor blading technique for the growth of large island, crystalline perovskite thin-films. Specifically, we elucidate the physical conditions such as substrate temperature, solution volume, and blade speed under ambient conditions that control the growth of large area perovskite thin-films with desired island size, thickness, uniformity and crystallinity. Using these doctor-bladed thin-films we fabricated devices of $\sim 1 \text{ cm}^2$ area in air that yielded an average efficiency of 7.32% with negligible hysteresis in the current-voltage scans. Further improvements in efficiency can be expected by reproducing the perovskite thin-film growth using doctor-blading in a controlled environment, through compositional tuning of the band-gap, or by selecting electron and hole transport layers with better band alignment with the perovskite electronic energy level.

1. Introduction

Hybrid perovskites have emerged as near-ideal material system for low-cost solution processed optoelectronic applications such as solar cells, detectors, light emitting diodes due to their excellent optical and electrical properties[1-4]. They are direct band-

gap semiconductors with high absorption coefficient and long diffusion lengths ($>1\text{ }\mu\text{m}$) for both electrons and holes[5-7]. Merely in a few years, power conversion efficiency (PCE) has reached 20%, thus making perovskite solar cells one of the most promising low-cost alternatives in comparison to other thin-film technologies[8]. Progress has also been made using different film growth techniques, such as spin-coating, doctor blading, and spray-coating, to develop small-area proof of principle devices[9-12]. However, practical dimensions require the ability to make large-area devices compatible with the development of modules. Moreover, it is critical that these devices do not show hysteresis and are reproducible from batch to batch. Few reports have demonstrated module level large-area perovskite thin-films but the these devices exhibit hysteresis and non-reproducibility[13,14]. Recently, we demonstrated a new approach termed as “hot-casting” for making highly crystalline perovskite thin-films with large grains that produces hysteresis free devices with a high degree of reproducibility[12]. However, spin-coating is not a commercially viable approach for producing solar cells with large dimensions. In contrast, doctor blading is compatible both roll-to-roll manufacturing processes and also well suited for fabricating large area devices as it provides good control of thickness and temperature potentially over foot-scale dimensions with negligible wastage of material[15,16].

Here, we show that doctor blading can be used to produce highly crystalline films with large island sizes over large substrates. In contrast to the hot-casting technique that leads to bulk crystalline grains, doctor blading leads to visually large islands with apparent grains that are composed of small perovskite crystallites. We present a comprehensive

study on the growth of large island perovskite thin-films as a function of substrate temperature, solution volume, and blade speed. Large area (1 cm^2) photovoltaic devices fabricated using these films under ambient conditions leading to an average PCE of 7.32 %, with no hysteresis and high degree of cell-to-cell reproducibility. We attribute this to the superior crystalline quality of these thin-films, which exhibit a bimolecular recombination of photo generated charge carriers verified using the light intensity dependence of the short-circuit current (J_{sc}) and open circuit voltage (V_{oc}). These results elucidate the first step towards the scientific understanding of the physical parameters that control the growth of highly crystalline growth of large-area perovskite thin-films using a practical viable thin-film deposition approach like doctor blading.

2. Materials and Methods

2.1 Device Fabrication

Lead iodide (PbI_2) and Methyl Ammonium Chloride (MACl) were dissolved in dimethylformamide (DMF) solvent at 1:1 molar ratio. The solution was stirred at 70 °C. We observed that a stirring for at least 2 days is necessary to obtain optimum perovskite phase conversion in our doctor blade films. ITO coated glass slides (3 inch) (Kintec, $15\ \Omega/\square$) were rinsed in isopropanol and cleaned using oxygen plasma. A thin layer of PEDOT:PSS (40 nm) was coated on the substrates and heated at 120 °C for 30 min. The PEDOT:PSS coated substrates were kept on a hot-plate and the temperature was varied between 125 °C and 165 °C. Apart from substrate temperature, solution volume and blade speed were also varied. The precursor solution was coated on hot substrates by doctor blading technique during which the solution color changes from yellow to reddish-brown. The coated substrate is immediately taken off the hot plate and placed on a cold metal base to quench

the heat. All this processing was performed in ambient conditions. Subsequent layers such as C60 (135 nm, 1 Å/s) and Al (120 nm, 1.5 Å/s) were thermally evaporated in a high vacuum chamber (5E-7 torr).

2.2 Thin Film and Device Characterization

Optical microscope images of the perovskite films were taken using an bright-field microscope (Olympus BX51M). The thickness and roughness of these films were obtained by averaging 20 readings along the 3-inch substrate. The current-voltage characteristics of the devices were obtained under AM 1.5G spectrum using a solar simulator (Oriel LCS-100) along with a source meter (Keithley 2400). The distance between light source and device was varied to obtain data for various light intensities. At each distance, NIST calibrated mono-crystalline silicon solar cell of 1 cm² area (Newport532, ISO1599) was used for light intensity calibration. The external quantum efficiency was measured using a NIST calibrated monochromator (PV Measurement INC, QEX10) at a frequency of 151 Hz.

3. Results and Discussion

3.1 Perovskite Film Morphology

A schematic of doctor blading technique for coating thin-films from solutions is illustrated in Fig. 1(a). Here, 100-200 µL of precursor solution is dropped at one edge of the substrate and a linearly translating blade is used to drag the solution uniformly over the entire substrate. Temperatures of the substrate as well as that of the solution are critical parameters that have a significant influence on the crystallinity and morphology of the perovskite thin-film. The efficient conversion to the perovskite phase and the island growth is strongly correlated to the substrate temperature, which is consistent with our recent work with spin-coated devices[12] and recently also reproduced by Zheng et al[17]. In

addition, the thickness and overall crystalline quality of the thin-film can be controlled by tuning the distance between substrate and blade (blade height), precursor solution volume, blade raster speed, and the viscosity of the solution. By controlling these parameters, thin-films with large perovskite island sizes were obtained.

Figure 1. (a) Schematic of the doctor-blade setup including a hot plate to control substrate temperature during coating. (b) Typical optical microscope image of the resulting perovskite thin-films with apparent large grains. (c), (d) and (e) Cross-section SEM images of the perovskite film at magnifications of 6,500x, 65,000x and 100,000x respectively.

A representative optical image of a film with large islands (diameter > 450 μm) is illustrated in Fig. 1(b). Cross-sectional SEM image of one such film deposited on Glass/PEDOT:PSS (30 nm), at a magnification of 6,500X is illustrated in Fig. 1(c). The thickness of the film obtained from this SEM image was 526 nm. The apparent boundary

between two islands can also be seen in this image and a magnified image is illustrated in Fig. 1(d). It can be observed that the film is continuous at these island boundaries but the thickness is approximately one-third (~ 140 nm) at these locations in comparison to the centre of the islands. We also emphasize that in sharp contrast to the hot-casting approach the islands of the perovskite film are comprised of smaller crystallites reminiscent of the two-step post annealing process of conversion to the perovskite phase (see Fig. 1(e)). This suggests that the mechanism of crystal growth is significantly different from that of the hot-casting approach and can be qualitatively explained as follows.

3.2 Effect of Temperature on Perovskite Crystal Growth

The major difference in both the processes is rate of evaporation of the solvent above the crystallization temperature of the perovskite. In the case of the doctor-blading, the thin-films are grown on a substrate maintained above the perovskite phase formation temperature. As a result most of the solvent evaporates almost instantaneously as the solvent is dragged across the substrate thus inhibiting the diffusion of perovskite molecules and resulting in spontaneous crystallization of the perovskite film with small crystals. This is consistent with the absence of a low angle peak at 6.25° that has been attributed to the perovskite-solvent (DMF) intermediate phase (Fig. 2(a)), which is observed for the hot-casting process¹². We note that this observation is also similar to the growth of perovskite thin-films using the conventional two-step post-annealing process where crystallization occurs spontaneously as the spin coated film of PbI_2 -MAI is post annealed above the perovskite crystallization temperature. However, in the case of hot casting method, there is an excess of the solvent present above the crystallization temperature, which slowly evaporates as the substrate and solvent cool with spin-coating. The presence of the solvent

for a longer duration allows for the efficient diffusion of the perovskite molecules and facilitates growth of large grains.

Figure 2. (a) X-ray diffraction data showing <110> and <220> peaks of MAPbI₃ perovskite phase and also the presence of the undesirable PbI₂ and MAPbCl₃ phases can also be observed. (b) Temperature dependence of the relative XRD peak intensities of <110> perovskite phase to PbI₂ and MAPbCl₃ phases.

X-ray diffraction (XRD) pattern of a perovskite thin-film grown at 145 °C is illustrated in Fig. 2(a). The <110> and <220> crystal planes of the desired MAPbI₃ perovskite phase at 2θ angles of 14.25° and 28.50° respectively, which corresponds to d-spacing values of 0.62 nm and 0.31 nm respectively. In addition, a consequence of the stoichiometry of a molar ratio of 1:1 for PbI₂ and MAcl, the presence of an impurity MAPbCl₃ phase was also detected at 15.75° and 31.50°. The band-gap for the pure chlorine perovskite phase has been determined to be close to ~3 eV and has been used to fabricate efficient UV photodetectors[18]. Because of its high band-gap energy, it can prevent efficient charge transport by acting like energy barriers for charge carriers, effectively

trapping them[19]. We also observe the PbI_2 phase at an angle of 12.75° but its intensity is much lower relative to the MAPbI_3 perovskite phase. Fig. 2(b) shows the variation of relative XRD peak intensities with substrate temperature. It can be observed that the optimum temperature to maximize perovskite peak with respect to PbI_2 peak is 145°C , which is close to the boiling point of DMF, the solvent utilized for this study. Below this temperature, the perovskite phase conversion remains incomplete resulting in higher PbI_2 content. At temperatures greater than 145°C , a decrease in the peak ratio of perovskite to PbI_2 is observed. We attribute this to the evaporation of solvent much before the complete conversion of PbI_2 to perovskite phase can take place. On the other hand, the perovskite to MAPbCl_3 peak ratio remains nearly constant at a low value, which is due to the fixed molar ratio in the solution used for casting.

In addition to the effect on relative values of the constituent phases, the substrate temperature also strongly influences the film morphology and apparent island size. The temperature dependence of the size of perovskite islands is illustrated in Fig. 3(a) for a fixed solution volume of $150\ \mu\text{L}$ and a blade speed of $22\ \text{mm}\cdot\text{sec}^{-1}$. It can be inferred that the apparent island size increases quite dramatically above 120°C and reaches a maximum average size of $\sim 293 \pm 0.094\ \mu\text{m}$. The values are lower than those illustrated in Fig. 1(b) because of the lower precursor volume used for blading. Dependence of island size on solution volume is explained in the following section. The temperature dependence suggests that 120°C is the threshold temperature for the perovskite phase formation. Below this temperature, no island formation was observed. At low temperatures, the phase conversion to perovskite is limited due to the lack of activation energy required for promoting forward conversion reaction to the perovskite phase consistent with previous

reports[17]. Corresponding optical microscope images of perovskite films for the different temperatures from 125 °C to 165 °C (from Fig. 3(a)) are illustrated in Fig. 3(b).

Figure 3. (a) Temperature dependence of perovskites optically visual island-size. (b) Optical microscope images taken at 10X magnification of the perovskite films deposited at temperatures ranging from 125°C to 165°C (increasing from left to right).

3.3 Effect of Precursor Solution Volume on Perovskite Crystal Growth

Another important parameter affecting the relative intensities of constituent phases of the perovskite film and the perovskite island size is the precursor solution volume

dropped on the substrate for blading. Fig. 4(a) shows the false colored optical microscope images of the films deposited for different solution volumes ranging from 160 to 200 μL . It can be observed that as the solution volume is increased, the island size also increases. The perovskite island size variation is plotted in Fig. 4(b). Presence of solvent for longer time allows for prolonged growth of the islands, which leads to larger islands. The blade speed used for these films was $13 \text{ mm}\cdot\text{sec}^{-1}$, which is lower than that used for lower volumes. This is because higher volumes require longer time for the solution to reach the equilibrium temperature of the substrate. As illustrated in Fig. 4(c), the MAPbI_3 to MAPbCl_3 peak ratio remains nearly constant at a low value, as was the case with the substrate temperature variation described previously. On the other hand, the perovskite phase peak ratio relative to PbI_2 increases with solution volume. Since higher volumes allow sufficient time for complete phase conversion, the PbI_2 peak diminishes and eventually disappears with increasing solution volume. These results suggest that it is critical to use higher solution volumes to obtain complete conversion to the desired perovskite phase and minimize the undesired phases.

Figure 4. (a) Optical microscope images of the perovskite films deposited at solution volumes ranging from 160 μL to 200 μL (increasing from left to right) (b) Increase in the perovskite island size with solution volume and (c) Dependence of the relative XRD peak intensities of $\langle 110 \rangle$ MAPbI_3 phase to PbI_2 and MAPbCl_3 phases on the solution volume.

3.4 Device Performance

Thin-film thickness is another important parameter that needs to be considered carefully when designing a photovoltaic device. Thus, we measured the effect of blade speed on the thickness and roughness of the film for a fixed solution volume of 200 μL and a substrate temperature of 150 $^{\circ}\text{C}$, these conditions were chosen due to highest

perovskite/PbI₂ peak ratio. We observe that the film thickness increases with blade speed as illustrated in Fig. 5(a). Typically for an ideal doctor blading process with a linear velocity profile, the film thickness (d) equals half the gap (g) between the blade and substrate[16]. However, this relationship holds only for high blade speeds, typically >150 mm.sec⁻¹. For low blade speeds, the film thickness also depends on other parameters such as the viscosity of the solution, density of the film, surface energy of the substrate, and surface energy of the blade. These factors dominate over substrate-blade gap effect thus making it possible to obtain thicknesses that are much lower than this gap. Moreover in our doctor blading setup the blade is maintained at high temperature along with the substrate and the surface energies of both the substrate and blade affect the film thickness. In such cases, predicting the thickness based on standard equations used for a conventional thin-film blading process is non-trivial[15,16]. This is important for perovskite solar cells, which require active layers of sub- μ m thicknesses using substrate-blade gaps of tens of μ m. We also measured the film roughness for each blade speed and these are also plotted in Fig. 5(a). We observe that the roughness of the film becomes higher for faster blade speeds. This increases the probability of voids and pinholes especially when coating thin-films with large areas and is detrimental for achieving high shunt resistances and low series resistance and hence high fill factors.

Figure 5. (a) Dependence of film thickness and roughness on blade speed. (b) Schematic of the solar cell. The area of each cell is 1 cm^2 . (c) Photograph of the solar cells fabricated on a 3-inch substrate. (d) J - V characteristics of the perovskite solar cell with substrate at 150 °C.

Thus considering all of the above factors such as optimal phase conversion, island size, film thickness and roughness from the above studies we fabricated planar, large area (1 cm^2) photovoltaic devices using films with an average thickness of 514 ± 52 nm and the average roughness of 29 ± 10 nm. The device schematic, optical micrograph of the typical devices and the representative J - V curve are illustrated in Figs. 5(b), 5(c), and 5(d) respectively. The peak efficiency of our champion cell under standard AM 1.5G spectrum was measured to be 7.32 %. The average and standard deviation of efficiencies measured

for 12 cells were 6.70% and 0.42% respectively, suggesting that the process of making these large island films was highly reproducible. We also note that for all the devices, the J - V curves were measured after 5 minutes of light soaking, which was required for the device to achieve steady state. Fig. 6(a) shows the external quantum efficiency (EQE) and its corresponding integrated short circuit current density (J_{sc}). The peak EQE obtained for this device is 44% at a wavelength of 610 nm. For different devices, the best values obtained for V_{oc} , fill factor (FF), and J_{sc} were 0.90 V, 68.7%, and 12.5 mA.cm⁻² respectively. In comparison to other recent reports on large area cells[20-23], these values are lower. This is most likely due to the following factors: (a) the processing of the doctor bladed films on ITO/PEDOT:PSS done in air with a humidity of 25-40%. The films remained in a chemical hood for several hours prior to their transfer to an Argon glove box for completing of the device. It is well known that PEDOT: PSS is hygroscopic and absorbs ambient moisture, which might eventually affect the overall contact resistance of the cell. (b) The chosen stoichiometry is expected to yield nearly 33% of the higher band-gap (~2.88 eV) MAPbCl₃ phase, which can act as high-energy barrier for photogenerated charge carriers.

Figure 6. (a) External quantum efficiency of the device along with integrated short circuit current density (J_{sc}). **(b)** Variation of short circuit current density (J_{sc}) with light intensity. The axes are in log scale. **(c)** Variation of open circuit voltage (V_{oc}) with incident light intensity. The x-axis is in natural log scale. **(d)** J - V characteristics of the perovskite solar cell with substrate at 150°C with different sweep directions showing no hysteresis.

In order to gain insight into the loss mechanisms, we performed light intensity dependence of the J_{sc} and V_{oc} in our devices. The variation of J_{sc} with light intensity (I) in log scale is shown in Fig. 6(b). The slope of a straight line fit to this variation is 0.87.

Reasons for such sub-linear slope include the presence of space charge effects as well as bimolecular recombination losses within the device[24-26]. This shows that the carriers generated in the device are not fully extracted. Fig. 6(c) shows the variation of open circuit voltage (V_{oc}) with light intensity in semi-log scale. For trap-assisted Shockley-Read-Hall (SRH) type recombination, the slope of $V_{oc}-\ln(I)$ curve is expected to be $2kT/q$ [27,28]. For low light intensities, the slope of this curve for our devices equals $2.06kT/q$ suggesting that SRH mechanism dominates. We believe that trap-assisted recombination in our devices arises due to the presence of the insulating MAPbCl₃ phase. At higher light intensities, the slope reduces to $0.95kT/q$ owing to a combination of bimolecular recombination and space charge effects. Such lower slope values were reported by other groups as well where, in addition to the previously mentioned reasons, passivation of trap states at the grain boundaries by PbI₂, and enhanced surface recombination at the hole contact have been attributed to the reduction in slope[25,29]. The V_{oc} eventually tends to saturate to its maximum value. However, in spite of the low efficiency, an advantage of our devices, which is critical for stable solar cell operation for the perovskite based solar cells has been the ability for the devices to work without showing any hysteresis when sweeping the current and voltage in forward and reverse directions[30,31]. We found that these solar cells show negligible hysteresis and is illustrated in Fig. 6(d). At a scan rate of 50 mV/sec, the difference between forward and reverse sweep efficiencies is less than 0.11%.

4. Conclusion

In summary, we present a detailed investigation of growth of perovskite films in ambient conditions using a scalable doctor-blading technique. We observed the formation of islands that are comprised of closely packed crystallites. The size of the islands increases

with the solution volume as well as substrate temperature. The residual insulating PbI_2 phase in the perovskite film could be minimized by performing synthesis of films close to the boiling point of the solvent as well as ensuring presence of excess solvent during the growth. Due to the presence of MACl in the solution, we observed the presence of MAPbCl_3 phase via XRD, however the ratio of the phases $\text{MAPbI}_3/\text{MAPbCl}_3$ is independent of growth temperature, volume of solvent or doctor blade speed. Thickness as well as roughness of the films is directly proportional to the blade speed. After optimization of all parameters we synthesized large area photovoltaic devices with an average area of 1 cm^2 . These solar cells have an efficiency of 7.32 %, with high degree of reproducibility and importantly negligible hysteresis. In addition, the variation of short-circuit current density and open circuit voltage of these devices with light intensity show that the device efficiency is limited by Shockley Read Hall recombination. Further improvements in the overall efficiency of these large area devices can be improved by tuning the composition and stoichiometry, performing doctor blading in controlled environments and using electron and hole transport layers with better alignments. We anticipate that these results will aid in obtaining a thorough understanding of the kinetics of film growth and will pave the way to achieve large-scale production of highly efficient perovskite solar modules.

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