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Fabrication of Perovskite Films using Electrostatic Assisted Spray Technique: Effect of Electric Field on Morphology, Crystallinity and Solar Cell Performance

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An electric field assisted spray deposition method employed for improving perovskite films morphology, crystallinity, surface coverage, and further fabricating an efficient solar cell. By applying different voltages ranging from 0.5 to 2.0 kV during spray deposition, we observed large variation in the film morphology and surface coverage as compared to without electric field, which is due to improved atomization from Coulomb fission process. The optimized applied voltage of 1.5 kV during spray led to complete reaction between CH_3NH_3I and PbI_2 on hot substrate for phase pure $CH_3NH_3PbI_3$ thin film formation with improved gain growth and surface coverage. The cells fabricated using perovskite films showed clear applied voltage dependence in energy conversion process and improvement in J-V hysteresis; with 1.5 kV applied voltage average cell efficiency of 8.9% obtained compared to films fabricated without voltage resulted only 6.5 %. The best efficacies are 10.9% and 7.37% for applied voltages of 1.5 kV and 0 kV, respectively. The enhancement in efficiency with applied voltage is due to the formation of more uniform and dense films with large perovskite crystals, which resulted an efficient electron transportation (enhanced photocurrent and modified series and shunt resistances) by minimizing the charge carrier recombination at grain boundaries (resulted enhanced open circuit voltage). With further optimization of perovskite film thickness by adjusting CH_3NH_3I spray volume, the average cell efficiency of ~11.0% was obtained.

1. Introduction

Hybrid organic-inorganic perovskites ($CH_3NH_3PbX_3$, X= Cl^{-}, Br^{-}, or I[-]) have recently emerged as promising light harvesting materials for photovoltaic devices due to strong absorption, bipolar transport and large charge carrier diffusion lengths.[1-3] In a span of less than five years, perovskites made a rapid progress as solar cell materials, the power conversion efficiency (PCE) of perovskite solar cells (PSCs) reached to 17%[4-7], and Yang's group reported the highest PCE of 19.3% based on planar device architecture using mixed halide perovskite ($CH_3NH_3PbI_{3-x}Cl_x$) material.[8] Seok *et al.* also recently achieved a world record PCE of 20.1% based on 85:15 mixture of formamidinium and methylammonium perovskites.[9] Indeed, PSCs are becoming a highly promising next generation photovoltaic devices for harnessing solar energy with an accelerated research and development. But, the PSCs exhibit hysteresis in I-V characteristics, possibly due to defect-assisted trapping, which has been identified as a critical roadblock to commercial viability of perovskite photovoltaic technology.[6]

Therefore, recent research work in this area concentrated on improving perovskite film surface coverage by increasing crystal size and enhancing the crystalline quality of the grains, which is expected to minimize the overall bulk defect density and alleviate hysteresis by suppressing generated charge carrier trapping during solar cell operation.[6]

Since, morphology, crystallinity, thickness and surface coverage of perovskite thin films play a crucial role for obtaining high efficiency PCEs with less hysteresis.[6,7] Various methods have been reported to obtain large crystals with uniform perovskite films such as; solution processing,[10-12] thermal evaporation,[13] and spray coating.[14,15] for reduced charge carrier recombination and improved charge transport. Solvent engineering approach have been also investigated as one step solution and two step sequential deposition technique to fabricate extremely uniform, and dense perovskite films with large grain size for realization of high performance PSC devices.[7,12] Liang *et al.,* demonstrated an improvement in surface coverage and film morphology of perovskites ($CH_3NH_3PbI_{3-x}Cl_x$) by adding a small amount of 1, 8-diiodoocatne to perovskite precursor solution, and also obtained defect free perovskite crystal structure.[16] On the other hand, a modified two-step sequential deposition method (solution-vapour) also employed by spin coating first PbI_2 followed by vapour deposition of CH_3NH_3I, and also the inter diffusion method like spin

coating of a stack of PbI_2 and CH_3NH_3I layers to obtain uniform, large-grain polycrystalline and pinhole-free perovskite films.[17, 18]

But, the above mentioned methods have a few disadvantages, such as wastage of precursor materials to some extent, reduced surface coverage by forming island like perovskite structures with pinholes, and also the formation of poor quality perovskite films due to incomplete conversion of PbI_2 precursor. These factors can affect the reproducibility of films, and also above mentioned methods have limitations for large scale fabrication of PSCs. The evaporation based PSCs are going to be more expensive than solution processed cells in a commercial perspective, because of large processing cost and not suitable for manufacturing in large scale. To fabricate cost effective PSCs, recently Lidzey *et al.* have reported a simple ultra-sonic based spray deposition of $CH_3NH_3PbI_{3-x}Cl_x$ films on PEDOT:PSS coated ITO substrates under ambient conditions.[14] Further, Linag *et al.* also reported the spray deposition of different concentrations of $CH_3NH_3PbI_3$ solution on TiO_2 coated FTO substrates.[19] However, with simple spray deposition technique, the disadvantages are small grain size and pin hole formation, and also impurities incorporation during film formation due to incomplete reaction on substrate.[20] So, the morphology and crystallinity of perovskite films need to be improved for better electronic properties and further enhancing the photovoltaic performance using simple spray technique.

To address some of the above mentioned issues, we prepared perovskite films using an inexpensive and simple pneumatic spray deposition method assisted by electric field. In spray process, the most important step is atomization, the crucial parameter is the size of precursor droplets generated at the nozzle and their dispersion over the substrate during the film formation. Apart from air-pressure for the droplet generation at the nozzle, an applied electric field can also play a major role in tuning the droplet size due to the Coulomb fission process,[21] for improving the quality of perovskite films by having complete reaction. We fabricated PSCs by spray deposition of CH_3NH_3I on top of spin coated PbI_2 films, with and without electric field under ambient conditions. We made an attempt to improve crystallinity, crystal size and morphology of perovskite films, and also optimized thickness by modifying electric field during atomization and amount of spray solution for achieving the best PCE from PSCs with minimum hysteresis.

2. Experimental

2.1. Preparation of methylammonium iodide (CH_3NH_3I)

Methylamine (CH_3NH_2) (40 wt% aqueous solution), hydroiodic acid (HI) (57 wt% in water), lead iodide (PbI_2) (98% purity), and *N, N, -*dimethyl formamide (DMF) purchased from Alfa Aesar, and have been used as received. For the preparation of CH_3NH_3I, method described in detail elsewhere are followed.[13] By reacting 30 ml of HI with 30 ml of CH_3NH_2 at 0 °C for 2 h in a three-necked round bottom flask under nitrogen (N_2) atmosphere with constant stirring.

The resultant solution was evaporated with rotary evaporator to get a white precipitate, followed by washing with diethyl ether for several times, finally dried in a vacuum oven for overnight at 60 °C. The obtained white crystalline powder used for preparation of perovskite precursor solution.

2.2. Device fabrication

Fluorine doped tin oxide (FTO) glass substrates having resistivity of <15 Ω sq^{-1} were cleaned sequentially with detergent, deionized water, acetone and ethanol under ultrasonication treatment for 15 min each, and flushed with N_2 gas for 10 min. A thin compact TiO_2 layer (thickness of ~70 nm) on FTO substrates was prepared by spin coating of titanium diisopropoxidebis(acetylacetonate) solution (1 : 39 volume ratio in ethanol) at 2000 rpm for 60 s, followed by drying at 125 °C for 5 min, and annealing at 450 °C for 30 min. The mesoporous active TiO_2 films (thickness of ~500 nm) were prepared by spin coating of 20 nm sized TiO_2 paste (Dyesol, 18NRT, diluted in ethanol with 2:7 weight ratio) at 5000 rpm for 30 s. Then the films were dried at 125 °C for 5 min, followed by annealing at 500 °C for 30 min. The resultant films were subjected to $TiCl_4$ (40 mM aqueous solution) treatment at 70°C for 30 min, washed with deionized water and ethanol and annealed at 500 °C for 30 min again.

The deposition of perovskite layer was made by using electric field assisted spray technique inside the gas leak-proof spray chamber.[21,23] The CH_3NH_3I spray solution was prepared in 2-propanol with a concentration of 8.0 mg/ml, and the other optimized spray deposition parameters are; deposition temperature of ~70 °C, solution flow rate of ~0.5 ml/min, nozzle to substrate distance of 18.0 cm. The atomization of solution was made by N_2 gas with flow rate of 10 l/min. and at pressure of 1.5 kgf/cm^2. Initially, PbI_2 solution (1.25 M PbI_2 in DMF) was spin coated on mesoporous TiO_2 films with a spinning rate of 4000 rpm for 40 s followed by annealing at 70 °C for 30 min. In second step, CH_3NH_3I solution (100 µl) was sprayed on PbI_2 films without and with different applied voltages. For an electrostatic assisted spray deposition, an additional electric pressure on N_2 gas generated droplets were produced by applying high voltage between spray nozzle (+ve) and an annular metal electrode (–ve) placed beneath the nozzle at a distance of ~4.0 mm as shown in Fig.1. The deposition was carried out by spraying the CH_3NH_3I solution on PbI_2 coated substrates, by applying D. C. voltages from 0.5 to 2.0 kV with an interval of 0.5 kV between nozzle and metal electrode, by keeping all other spray parameters same as mentioned above. During the spray deposition, substrate temperature was kept at ~70 °C, after the deposition the substrates were immediately transferred to second hot plate and annealed at 85°C for 45 min in order to improve morphology of perovskite films, all steps were performed inside the spray chamber. The thickness of perovskite films is about 350 nm.

The hole transporting layer (HTL) spiro-MeOTADof~200 nm thickness was deposited by spin coating on perovskite layer at 4500 rpm for 30 s. The spiro-MeOTAD solution contains the mixture of 72.3 mg of 2,2'7,7'-tetrakis(N,N-di-pmethoxyphenylamine)-9,9'-spirobifluorine, 28.8 µl of 4-tert butylpyridine, and 17.5 µl of lithium bis(tri-fluoromethylsulphonyl)imide (520 mg/ml in acetonitrile) in

1.0 ml chlorobenzene. Finally, ~80 nm thin gold electrode was deposited using DC sputtering system having pressure of ~2×10^{-6} mbar. The active area of each perovskite cell is 0.12 cm^2.

2.3. Characterization

The crystal structure of perovskite films was examined by analysing the X-ray diffraction (XRD) patterns recorded using Rigaku Ultima*IV*X-ray diffractometer equipped with a Cu Kα X-ray tube (λ = 1.54056 Å) operated at 40 kV and 40 mA. Scanning electron microscopy (SEM) micrographs were acquired using Carl Zeiss, EVO-18 microscope to study the surface morphologies. Surface roughness factor of perovskite films were analyzed using Bruker's Dimension icon atomic force microscope (AFM). Absorbance spectra were recorded using Perkin Elmer Lambda (1050) UV-Vis-NIR spectrophotometer. Photoluminescence (PL) spectra of spray deposited perovskite films were recorded using an Edinburgh instruments with an excitation wavelength of 530 nm. The photovoltaic parameters were recorded by using a Keithley 2440 source meter under a simulated sunlight (AM 1.5G, 100 mW/cm^2) from an Oriel class 3A solar simulator. For the measurements, first devices was allowed to stabilize (20 s), and then the cyclic J–V was swept toward forward bias and return at 150 mV/s. External quantum efficiency (EQE) measurements were performed by using a lock-in amplifier coupled with a monochromator from ReRa systems, The Netherlands, light source was 150 W xenon lamp with chopped frequency of 20 Hz, in addition bias light of 10 mW was also applied during IPCE measurements.

3. Results and discussion

The perovskite films preparation without and with electric field assisted spray deposition method is schematically presented in fig. 1, along with SEM micrographs, which are showing the effect of applied voltage on perovskite films morphology. Usually, in normal spray deposition method (without electric field) generate a large droplet size, and it leads to the slow evaporation of solvent, resulting the formation of voids in the film, and also incomplete chemical reaction for desired compound material.[20] To minimize this, the electric field (pressure) applied, in addition to gas pressure during atomization, which will lead to formation of finer droplets of uniform size distribution, for complete reaction between chemical species on the hot substrate.[20-23] The existed electric field at the nozzle will develop some type of polarization effect in droplets, which will increase droplet surface area for improving the rate of evaporation, and results a better surface morphology of films.[20] The application of electric field also minimizes droplets coalescence before reaching the hot substrate due to the electrostatic repulsion between charged droplets. Isolated and fine charged droplets have an advantage for growing thin films with good optical and electronic properties. The distance between nozzle and substrate also alters the morphology of perovskite films. The optimized nozzle to substrate distance of 18.0 cm gives the best film morphology, for other distances poor film morphology was observed, the distance dependent films morphologies are presented in Fig. S1 as in electronic supplementary information (ESI).

In Fig. 2, we presented set of SEM micrographs related to perovskite films that show the effect of electric field during spray deposition on surface morphology and coverage, except the Fig. 2(a) which is the surface morphology of spin coated PbI$_2$ thin film having flakes like structure. After the spray deposition of CH$_3$NH$_3$I solution, one can see without applied voltage (Fig. 2b) and with 0.5 kV applied voltage (Fig. 2c) the formation of small size (~100-150 nm) perovskite crystals. Which is due to large size CH$_3$NH$_3$I droplets generation at the nozzle with no/small (<1.0 kV), electric field, and these droplets can't diffuse into PbI$_2$ layer for the growth of large grains, leading to a poor crystallization and non-uniform perovskite films. With the increase in applied voltages to 1.0 kV and 1.5 kV, we observed the formation of well-ordered, large and uniform perovskite crystals (~240 -350 nm), with improved surface coverage in film formation. At large applied voltage (≥1.0 kV), the atomization process improved by generating tiny CH$_3$NH$_3$I droplets through the process of Columb fission, which improves the diffusion of CH$_3$NH$_3$I into the PbI$_2$ layer, leading to a large size (~460 nm) perovskite crystals formation with the complete chemical reaction at optimized spray conditions. However, with 2.0 kV applied voltage, we observed the perovskite films having unreacted CH$_3$NH$_3$I droplets, despite of large perovskite crystals. Fig. 3 show cross-sectional SEM images of glass/FTO/TiO$_2$+CH$_3$NH$_3$PbI$_3$ prepared at voltages of 0 kV and 1.5 kV. At applied voltage of 1.5 kV, once can see the perovskite crystals growth of large size and dense implanted in the mesoporous TiO$_2$ layer (Fig. 3b). The extra perovskite material above TiO$_2$ provides higher pore filling and also acts as a capping layer. Where it acts as both light absorber and hole transporting layer.[24] Thus the higher portion of perovskite reduces the requirement of Spiro-OMeTAD hole transporting layer.

The XRD patterns of perovskite films prepared with different applied voltages from 0.5 to 2.0 kV are presented in Fig. 4. The diffraction peaks at 2θ ≈ 14.02°, 19.98°, 23.38°, 24.42°, 28.38°, 31.83°, 34.92°, 40.53°, and 43.08° are corresponds to the (110), (112), (211), (202), (220), (310), (312), (224), and (314) crystal planes of tetragonal perovskite phase, respectively.[25] The films prepared at applied voltage of 1.0 kV and 1.5 kV showed sharp and intense peaks from crystal planes of (110), (220) and (310), which indicates the formation of well oriented perovskite crystal phases with large grain sizes. Improved crystal structure formation also reflects the formation of fine CH$_3$NH$_3$I droplets at large applied voltages due to improved atomization for an effective interdiffusion of CH$_3$NH$_3$I droplets into spin-coated PbI$_2$ films. Even with high applied voltage of 2.0 kV, we observed pure perovskite crystals formation without any evidence of unconverted PbI$_2$. But the films prepared without voltage, and also with small voltage of 0.5 kV resulted some additional peaks (marked by *) at 2θ ≈12.65°, 12.65° and 12.65° along with tetragonal perovskite phase, which are well matches with PbI$_2$ crystal phase (Fig 2a). At no/small applied voltage, due to larger droplets generation at the nozzle, the perovskite films formation is incomplete due to some unevaporated solvent during film deposition, leading to the presence of trace amounts of unconverted PbI$_2$ crystals. So, these results clearly

showing that the applied electric field playing a prominent role in enhancing crystallinity and morphology of perovskites with the complete reaction between PbI_2 and CH_3NH_3I on hot substrate along with other important spray parameters.

Fig. 5 shows the UV-visible absorption spectra of perovskite films prepared with different applied voltages. The spectra show a broad range of absorption in visible region of the spectrum having absorption band edge around 784 nm (E_g ~ 1.58 eV). The perovskite film prepared without electric field shows relatively less absorption compared to films prepared with electric field. It also may be due to an incomplete conversion of PbI_2 (see Fig. 4), resulting films remain in pale yellow colour. With the gradual increase of applied voltage during spray, the colour of films turned into a dark brown, and led to the improvement of light absorption in entire visible region due to the improved crystallinity and morphology of perovskite films. However, at higher applied voltage (2.0 kV) the amount of light absorption is slightly decreased, which can be due to the modified surface roughness of the film due to the saturation of diffusion rate of CH_3NH_3I into PbI_2 films by leaving unreacted CH_3NH_3I material over the film (see Fig. 2f). Inset of Fig. 5 shows PL spectra of perovskite films prepared without and with 1.5 kV voltage. The PL peak is observed around 780 nm, but we have not seen any enhancement in PL intensity with electric field except the uniform increase in the background. Enhanced background represents modification in surface roughness, which we have verified using AFM analysis. The root mean square surface roughness values of perovskite films are 37.6 nm and 76.4 nm for without and with 1.5 kV voltage, respectively. The AFM micrographs of perovskite films prepared at different applied voltages (0 to 2.0 kV) are presented in Fig. S2.

A series of PSCs are also fabricated using perovskite films prepared under different applied voltages to see photovoltaic performance of device. The fabricated solar cell structure is FTO/bl-TiO_2/m-TiO_2/$CH_3NH_3PbI_3$/Spiro-MeOTAD/Au having an active area of 0.12 cm^2. It was reported that high efficiency PSCs suffers from the hysteresis effect,[7,26] which depends on scan direction, scan rate and TEBBing effect,[27] allthese effectscreate difficulty for determining cell efficiency accurately. The original research paper on the hysteresis effect demonstrated an origin of traps, mobile ions and ferroelectric effects,[28] along with the crystal size effect.[29] Here, we also investigated the effect of hysteresis; since the applied electric field during spray strongly affecting the crystal size.The cyclic J–V characteristics (forward and reverse scan directions) of PSCs fabricated at different applied voltages are presented in Fig. 6 (a-e), and their photovoltaic parameters are summarized in Table 1. The effect of electric field on device performance is clearly observed. The device PCE improved with applied voltage of 1.5 kV and for higher applied voltage it started decreasing. The devices without electric field showed a relatively poor performance due to an incomplete conversion of PbI_2, which can affect the absorption and charge transportation. Hence, resulted a lower short circuit current density (J_{sc}) of 13.64 mA cm^{-2}, open circuit voltage (V_{oc}) of 0.86 V, fill

factor (FF) of 62.86 %, and average PCE of 6.5 %. These devices exhibited high hysteresis index (h-index) of 0.061 due to smaller perovskite crystal size. The h-index values are calculated using the relation (Equation 1) given by Kim *el al.* in the reference 29, they have observed that large J–V hysteresis with small size perovskite crystals and explained that smaller crystals store capacitive charge, which will be released as the crystal size increases. Similar observation we made, as applied voltage inverses crystal size increases by alleviating J–V hysteresis effect. The average PCE of 8.92 % is observed from the cell prepared with perovskite film deposited under applied voltage of 1.5 kV, with J_{sc} of 18.11 mA cm^{-2}, V_{oc} of 0.912 V, FF of 66.0 %. The h-index of device prepared at 1.5 kV is the lowest (0.034), which increases for lower and higher values of applied voltage. With an applied voltage of 2.0 kV average cell efficiency also decreased to 8.06%, because of unreacted CH_3NH_3I droplets, which can act as a thin insulating layer over perovskite films instead of semiconducting. This insulating layer can hinder the charge transportation in perovskite layer resulting either accumulation or recombination near perovskite layer, which is also reflected by increasing the series resistance and decreasing shunt resistance of the device (Table 1).

To evaluate the reproducibility of device performance, ten such devices are fabricated at different applied voltages, the maximum number of devices showed an average PCE of 7-8%. For comparison, we also fabricated device by one step spin coating method, corresponding surface morphology of perovskite film presented in Fig. S3, and J-V graph and cell parameters are presented in Fig. S4. The cell from spin coated perovskite film exhibited a poor performance compared to cells prepared from perovskite films under electric field of 0.5 to 2.0 kV, due to non-uniform film formation and poor crystallization.

The applied electric filed improving first the conversion of PbI_2 to $CH_3NH_3PbI_3$, latter the structure and morphology, which clearly reflected in the device performance with improved electronic properties and charge transport. The increase in J_{sc} is attributed to the improvement in carrier mobility with an effective electron transportation, which originated from the improved crystallinity and grain sizes of perovskite, and also improved surface coverage. We also observed the decrease in series resistance and increase in shunt resistance from PSCs with the applied electric filed (see Table 1) during perovskite films preparation. The significant enhancement of open circuit voltage (~60 mV) also clearly reflects the reduced charge carrier recombination at grain boundaries. With smaller applied voltages <1.0 kV, the poor quality crystalline perovskite thin films are obtained with less surface coverage, which clearly reflected with high series resistance and low shunt resistance, which led to the poor cell performance. The EQE spectra as well as integrated J_{sc} calculated from the EQE data are presented in Fig. 6(f), to see the wavelength dependent photo-to-electron conversion. The improvement of EQE in a broad spectral response from 400 nm to 760 nm observed for an applied voltage of 1.5 kV. The spectral response of all devices are in good correlation with

observed absorbance. The integrated J_{sc} calculated from the EQE data also correlated with J_{sc} obtained from the J-V measurements, one can clearly see from fig. 6(f) that the photocurrent density is nearly same.

Based on optimized applied voltage of 1.5 kV for perovskite films growth, we further explored the effect of film thickness on device performance, the film thickness controlled by varying the CH_3NH_3I spray solution volume. Three batches of PSCs are fabricated with volumes of 150, 250 and 350 µl spray solution, which resulted film thicknesses of ~240 nm, ~320 and ~390 nm, respectively. The J-V graphs of PSCs fabricated with different film thicknesses are presented in Fig. 7, and their corresponding photovoltaic parameters are summarized in Table 2. The average cell efficiency of 11.0% was obtained with 250 µl of CH_3NH_3I spray solution having a film thickness of 320 nm, with J_{sc} of 19.38 mA cm^{-2}, V_{oc} of 0.90 V, FF of 63.45%. It is known that an optimized perovskite film thickness absorbs more light and generates higher photocurrent, but with large thickness loss of photovoltage can also occur mostly due to increased charge carrier recombination.[19] With the increase in film thickness by increasing the volume of CH_3NH_3I to 350 µl, the photo-generated charge carriers cannot be extracted effectively from perovskite films due to limited diffusion lengths, which can decreases the device performance. With lower volume (150 µl) of CH_3NH_3I, poor cell performance observed due to insufficient CH_3NH_3I for complete conversion of $CH_3NH_3PbI_3$ from PbI_2 film. Thus the inappropriate amounts of perovskite precursor solution can reduce J_{sc} and FF due to traceable insulating precursors and non-stoichiometric compounds in prepared perovskite thin films.

4. Conclusions

We have investigated the effect of electric field on spray deposited perovskite films and further on solar cell performance. We observed that applied electric field improving the crystallinity, morphology and surface coverage of perovskite films with improved atomization process during spray. With an optimized electric field of 1.5 kV, we obtained pure crystal phase with an average grain size of around 350 nm, which led to the highest PCE of 10.9 % from the cell, compared to without electric field the cell PCE is 6.5 % due to improved charge carrier transportation process. The hysteresis index which depends on crystal size also improves with applied voltage and found minimum for devices fabricated at 1.5 kV. We further optimized the perovskite film thickness of around 320 nm by varying CH_3NH_3I spray solution volume and with an optimized applied voltage of 1.5 kV, we achieved the average conversion efficiency of ~11.0 % from the PSC. Besides this, further investigations on spray deposition of mesoporous TiO_2 and HTM layers are also in progress to boost the cell efficiency using electric field. Our results demonstrate that electrostatic assisted spray deposition method can be considered as one of the low cost techniques for preparing high quality perovskite films of large area

to fabricate photovoltaic devices for harnessing the abundant solar energy.

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