Two-step fabrication of MAPbI₃ perovskite thin films with improved stability

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Abstract. Perovskite solar cells (PSCs) are a part of an emerging technology in photovoltaics (PV), which uses perovskite-structured hybrid compounds as light absorbers such as methylammonium lead iodide (CH₃NH₃PbI₃ or MAPbI₃). PSCs with a record certified efficiency of 22.1% are among the fastest advancing PV technology; but PSCs suffer from fast degradation in the presence of moisture. PSCs prepared by a solution process have additional limitation of small device area. In order to improve the stability of perovskite layer, we have used a two-step method for depositing a perovskite layer. First step is the thermal evaporation of lead iodide (PbI₂) and second is dip coating (DC) in methylammonium iodide (CH₃NH₃I or MAI) solution to prepare a MAPbI₃ perovskite. At the same time, we have also used conventional spin coating (SC) for PbI₂ films and DC in MAI to obtain MAPbI₃ for a comparative study. The gradual formation of MAPbI₃ after dipping a PbI₂ film into MAI solution can be seen from X-ray diffraction patterns. Structural, optical and electrical properties of the MAPbI₃ films are also studied. Better stability of perovskite films was observed using vapour-deposited PbI₂ films as compared with spin-coated PbI₂ films.

Keywords. Dip coating; MAPbI₃ perovskite; stability; thermal evaporation.

1. Introduction

Hybrid metal halide perovskites are new promising light-absorber materials that are being widely studied for photovoltaic (PV) application. In less than a decade the recorded efficiency of perovskite-based solar cells (PSCs) has increased from 3.8 to 22.1% [1,2]. The capacity of PSCs to give high open-circuit voltage, $V_{oc} \sim 1$ V [3,4] and short-circuit photocurrent density, $J_{sc} > 20$ mA cm⁻² [5,6] is the most attractive feature. Hybrid perovskite absorber materials have excellent inherent properties such as strong and broad absorption range [7], a long carrier diffusion length of 1 μ m [8], a weak exciton binding energy of 45 meV [9], a high carrier mobility of 25 cm² V⁻¹ s⁻¹ and a low charge recombination rate of microseconds time scale [10], which are the essential properties for solar cell application. It is reported that the carrier lifetime for a single-crystalline MAPbI₃ perovskite is up to a few hundred microseconds with the corresponding diffusion length of > 175 μ m [11]. Also, defect density of single-crystalline MAPbI₃ is as low as $\sim 10^{10}$ cm⁻³, in comparison with $\sim 10^{16}$ cm⁻³ in polycrystalline perovskite thin films [12]. Another attractive feature of MAPbI₃ perovskite material is that it has ambipolar transport property, therefore it can also transport holes [13]. Researchers all over the world have shown a huge interest in perovskites in recent years due to their above-stated excellent PV properties and facile fabrication method. This has led to tremendous research in this

field giving improved efficiencies. The major advantage of PSCs over conventional inorganic solar cells is that, these can be fabricated by a simple solution processing technique such as spin coating (SC) and dip coating (DC). Therefore, PSCs are very promising for future PV technology as they can be fabricated at low temperatures using low-cost solution process methods. However, the stability issue of perovskite materials is the main bottleneck for commercialization and a wide range of applications of PSCs. Since the first report of PSCs, there have been many developments and modifications in the fabrication techniques of PSCs which enhanced the efficiency and the stability in recent years. Basically there are two methods for depositing perovskite films for device fabrication; these are one-step or single-step and two-step or sequential deposition techniques. In one-step method, a perovskite (e.g., CH₃NH₃PbI₃) is deposited using two precursors (e.g., PbI₂ and CH₃NH₃I) at a time. Whereas, in a two-step method two precursors are used separately; PbI₂ is first deposited and then CH₃NH₃I is deposited subsequently to obtain CH₃NH₃PbI₃. In one-step method there are issues with stoichiometry and crystallinity control. The two-step method provides better control compared with the one-step method on the crystal growth of perovskite films. Thus, the fundamental issue of morphology control in a perovskite layer for PSCs can overcome using a two-step process. The film morphology significantly influences the device performance, as the properties such as light harvesting, charge carrier transport

and diffusion length are affected by film crystallinity and morphology [14].

In this work we present study on morphology, optical properties, electrical properties and stability of MAPbI₃ perovskite thin films using two-step methods. The effects of depositing a PbI₂ film in two-step methods by thermal evaporation (TE) and SC on the quality of perovskite films are discussed in the third section of the paper.

2. Experimental

2.1 Materials

Thin films of MAPbI₃ were prepared using two precursors, PbI₂ (99.99%, Alfa Aesar) and CH₃NH₃I or methylammonium iodide (MAI). Dimethylformamide (DMF) solvent (anhydrous, 99.8%, Sigma-Aldrich) is used for dissolving PbI₂ while 2-propanol (anhydrous, 99.5%, Sigma-Aldrich) is used for preparing MAI solution. MAI was synthesized by reacting 12 ml of hydroiodic acid (55%, Himedia) with 10 ml of methylamine (40% in water, Spectrochem) in a round-bottom flask placed in an ice bath at 0°C for 2 h with continuous stirring. The mixture was dried carefully in a rotavap under reduced pressure at 50°C and then a white precipitate (MAI) was obtained. The precipitate was washed three times with diethyl ether; soon after that it was again recrystallized with absolute ethanol (Merck) under stirring for 30 min. Finally, white shiny crystals are collected after removing ethanol. It was then dried in a vacuum at 60°C for 12 h.

2.2 Sample preparation

MAPbI₃ perovskite thin films were deposited in two steps. In the first step, PbI₂ thin films were deposited using either TE or a solution process using SC. In the second step, PbI₂ films were subsequently dip coated in MAI solution in 2-propanol with a concentration of 10 mg ml⁻¹ and annealed to obtain MAPbI₃. Prior to deposition, the corning glass substrates of size 1.5 × 1.5 cm were cleaned with mild soap solution, then sonicated in deionized water, acetone and 2-propanol for 15 min each. Finally, the substrates were dried under a fast flow of dry nitrogen gas. The two methods used for preparing perovskite film are discussed below.

2.2a TE and DC: For preparing thin films of MAPbI₃, PbI₂ was thermally evaporated (Thermal Evaporator system from Hind High Vacuum, Model-12AD) on a corning 1737 glass substrate at a temperature of 100°C and process pressure of $\sim 2 \times 10^{-5}$ mbar to obtain PbI₂ thin films of thickness 200 ± 10 nm. A molybdenum boat source with a secondary low tension supply of 33 A was used to evaporate the PbI₂ powder. In the second step, the PbI₂ films were dipped in MAI solution. Soon after a few minutes, the films were annealed at 100°C for 10 min and eventually dark perovskite

films of thickness 395 ± 18 nm were obtained. The DC step was performed under an ambient atmosphere (relative humidity $\sim 50\%$ and temperature $\sim 28^\circ\text{C}$) and/or inside a dry nitrogen-filled glove box (pressure ~ 1010 mbar and temperature $\sim 28^\circ\text{C}$).

2.2b SC and DC: In addition, for a comparative study, we have also fabricated MAPbI₃ thin films in a dry nitrogen-filled glove box (pressure ~ 1010 mbar and temperature $\sim 28^\circ\text{C}$) by SC PbI₂ and DC in MAI. For SC, 1 molar PbI₂ solution was prepared using DMF solvent by stirring at 70°C for 12 h. The PbI₂ solution was spun on cleaned corning glass substrates at 3000 rpm for 30 s and then transferred to a hot plate and dried at 70°C for 30 min. In the next step, the spin-coated PbI₂ films of thickness 190 ± 18 nm were dipped in MAI solution to form MAPbI₃ and annealed at 100°C for 10 min to obtain perovskite layers of thickness 390 ± 21 nm, similar to that for thermally evaporated PbI₂ films.

2.3 Characterization

X-ray diffraction (XRD) was performed using a Rigaku, TTRAX III equipped with CuK α radiation of 1.54 Å, in thin film mode. Optical absorption spectra were recorded using a Lambda 950 (Perkin-Elmer). Surface morphology images of thin films were taken using a field emission scanning electron microscope (FESEM) (Zeiss, Sigma). Surface topography was measured using atomic force microscope instrument (Cypher, Oxford). Electrical measurements on the perovskite layer were performed under vacuum using a Keithley-2450 source-meter to avoid surface-related processes induced by chemisorption and desorption of oxygen [15]. Prior to measurements, silver (Ag) electrodes of about 100 nm thickness were deposited using TE on the MAPbI₃ films in a co-planar geometry having 1 mm separation. Photocurrents were measured under illumination of a 100 W halogen bulb to calculate electrical conductivity. Film thickness was measured using a DEKTAK 150 profilometer by Veeco. Stability studies were conducted on the perovskite thin films prepared by the two-step methods (TE + DC and SC + DC) using UV-Vis absorbance and electrical measurements as a function of time. All measurements were performed immediately after sample preparation as the film degrades on exposure to moisture.

3. Results and discussion

3.1 Structural studies

The XRD patterns of the PbI₂ (vapour deposited and spin coated) and MAPbI₃ thin films for different dipping time durations are shown in figure 1a and b. The indexed XRD patterns confirm complete formation of MAPbI₃ ($\text{PbI}_2 + \text{MAI} \rightarrow \text{MAPbI}_3$) perovskite films after dipping PbI₂ films in MAI

Figure 1. XRD patterns of PbI₂ and MAPbI₃ thin films with increase in dipping time of PbI₂ in MAI solution: (a) thermally evaporated PbI₂ and MAPbI₃ thin films and (b) spin-coated PbI₂ and MAPbI₃ thin films.

Figure 2. FESEM images of MAPbI₃ films by two-step methods: (a) TE of PbI₂ and DC in MAI solution and (b) SC of PbI₂ and DC in MAI solution.

solution for about 2 min, as the observed peaks correspond to the pure tetragonal (β) phase of MAPbI₃ for both the methods (TE + DC and SC + DC) [16,17]. The perovskite films prepared at 100°C have high purity with very less fraction of intermediate phases. A preferred orientation along the (110) direction was observed in the MAPbI₃ films prepared by both methods. From figure 1a and b, it is observed that the intensity of PbI₂ signature peak at a 2 θ value of 12.6° has decreased after dipping the film in MAI solution. After 2 min of dipping the PbI₂ peak almost disappeared and MAPbI₃ peaks became prominent for both TE and SC PbI₂ films. For vapour-deposited films, there remains a small peak at a 2 θ value of 12.6° even after 2 min of DC, which could be because of a small fraction of unreacted PbI₂ in the bottom layers as the PbI₂ films obtained by vapour deposition are more dense and compact in nature as compared with spin-coated films. However, for spin-coated films there is no PbI₂ peak

after 2 min of dipping, as the film gets fully converted to a MAPbI₃ perovskite. However, depending on the batch of sample preparation, the vapour-deposited PbI₂ films sometime require a slightly longer time up to 3 min to fully react with MAI to form MAPbI₃ depending on the density and compactness of the films.

Figure 2 shows the FESEM images of MAPbI₃ films synthesized using two-step methods. From the images it can be clearly seen that the vapour-deposited PbI₂ (figure 2a) gives perovskite films with large grains of size up to 1 μ m, whereas the spin-coated PbI₂ films (figure 2b) give smaller grain-sized perovskite films. It can also be noticed from figure 2b that there are small pin holes in the film along with small grains. This results in limitation for fabrication of large-area devices using the SC technique. It has been reported that the large grain-sized perovskite films exhibit improved transport properties due to decrease in grain boundary density [18].

Figure 3. AFM topography images of PbI_2 and MAPbI_3 thin films by DC of PbI_2 in MAI solution: (a) thermally evaporated PbI_2 film, (b) spin-coated PbI_2 film, (c) MAPbI_3 thin film by vapour-deposited PbI_2 film and DC and (d) MAPbI_3 thin film by spin-coated PbI_2 film and DC.

The observation indicates that vapour-deposited+dip-coated perovskite films are likely to have advantage of showing better device performance.

Atomic force microscope (AFM) topography images ($5 \times 5 \mu\text{m}$) of PbI_2 and MAPbI_3 films are shown in figure 3. In figure 3a and b, it is seen that the vapour-deposited films of PbI_2 are smoother than the spin-coated films. The vapour-deposited films have uniform coverage and a lower root mean square (RMS) roughness of $2.28 \pm 0.40 \text{ nm}$, whereas the spin-coated films have the RMS roughness of $16.35 \pm 3.27 \text{ nm}$. The spin-coated films are non-uniform and have pinholes in between, which is not suitable for a large area device. These voids in the films are created after the solvents get evaporated during annealing. On the other hand, for MAPbI_3 films in figure 3c and d, the TE and DC films show uniform coverage with larger grain size compared with SC and DC films, as also seen in the FESEM images. The RMS roughness is higher in TE and DC ($49.63 \pm 8.57 \text{ nm}$) films due to large grain size

than that in SC and DC films ($33.39 \pm 6.16 \text{ nm}$). In the case of TE, due to an elevated substrate temperature (100°C) the surface energy gets enhanced and hence uniform nucleation and growth of PbI_2 takes place throughout the substrate leading to large grain size perovskite films with full surface coverage, whereas, in the spin-coated films the substrate was kept at room temperature.

3.2 Optical properties

The UV-Vis absorbance spectra of MAPbI_3 perovskite thin films are shown in figure 4a and b for TE + DC and SC + DC films. The measurements were started after 30 min of deposition. From figure 4a and b, it is seen that the MAPbI_3 perovskite films have the sharp absorption edge at around 760 nm , almost covering the visible range which shows the characteristic of the MAPbI_3 perovskite film [16]. This optical absorption is consistent with the XRD patterns, confirming the

Figure 4. UV-Vis absorbance spectra of MAPbI₃ thin films with respect to time: (a) TE of PbI₂ and DC and (b) SC of PbI₂ and DC.

formation of perovskites. The optical bandgap was estimated from the absorbance data by using the Tauc plot $(\alpha h\nu)^{1/n}$ vs. $h\nu$, where α is the absorption coefficient (cm^{-1}), $h\nu$ is the photon energy (eV) and n is $1/2$ for direct bandgap material [19]. The calculated bandgaps (for 30-min MAPbI₃ films) are found to be 1.55 ± 0.02 and 1.54 ± 0.02 eV for TE and DC and SC and DC MAPbI₃ films, respectively. The bandgap values are close to the reported literature value (1.5 eV) [20].

The absorbance spectra were recorded as a function of time to study the degradation of MAPbI₃ thin films by continuously exposing them to air with high relative humidity varying from 76 to 88%. As seen in figure 4a, in the case of TE and DC films their absorbance decreases slowly with time upon degradation and up to 72 h the absorbance spectra still show the characteristics of a perovskite. However, in the case of SC and DC films, the film degraded completely within 12 h. It is remarkable that in TE and DC films even at high relative humidity, the degradation rate is quite slow. This shows that TE and DC films are superior in terms of stability compared with SC and DC films. Eventually, the dark brown fresh samples slowly turn to faded yellowish upon degradation.

3.3 Electrical properties

The current (dark and photo) vs. time measurements of the MAPbI₃ thin films were carried out in a vacuum at a pressure of 0.02 mbar and at an applied field of 2000 V cm^{-1} to calculate electrical conductivity (σ). Equation (1) is used for calculating electrical conductivity of the MAPbI₃ thin films:

$$\sigma = (I \times d) / (V \times l \times t), \quad (1)$$

where I is the measured current, V is the applied voltage, d is the separation between the electrodes, l is the length of the electrode and t is the thickness of the film.

Figure 5. Conductivity of MAPbI₃ layer measured with respect to time. The perovskite thin films were prepared by two different methods: TE and DC and SC and DC.

The measurements were performed for 72 h with 24 h time interval to study the degradation effect on dark and photoconductivity. Figure 5 shows the dark and photoconductivity of MAPbI₃ films as a function of time. It is observed that the TE and DC film has higher photoconductivity as compared with the SC and DC film. It is also observed from the electrical conductivity data that the photoconductivity degrades faster than the dark conductivity for both TE + DC and SC + DC films. However, photoconductivity of the TE and DC films decreases at a slower rate than the SC and DC films, which is consistent with the degradation rate as observed in UV-Vis absorbance spectra. This is because SC and DC films are more porous and easily affect by moisture compared to the compact and dense TE and DC films. This suggests that the TE and DC films are better for device application as they have

better stability and photoconductivity compared with SC and DC films.

4. Conclusion

MAPbI₃ perovskite thin films were successfully prepared by two-step methods. As seen in AFM images, using the vapour technique we could achieve more uniform PbI₂ films with large area compared with the SC technique. Also, the film quality is reproducible by easy control of the deposition parameters. Whereas, using the SC technique, it is difficult to reproduce similar quality of films for each time of deposition. The extra material loss is more in the case of SC technique compared with TE. For TE we need only 50 mg of PbI₂ powder for at least three substrates (size of each substrate = $3 \times 3 \text{ cm}^2$), whereas for SC it requires 50–100 μl of 1 molar PbI₂ solution for the substrate size of $\sim 1.5 \times 1.5 \text{ cm}^2$ (460 mg of PbI₂ to prepare just 1 ml of solution). Moreover, the SC films depend more on the factors such as solution dispensing method on a substrate, solution viscosity, temperature, etc. It was observed from FESEM images that the MAPbI₃ films prepared by TE and DC have uniform coverage over a large area and less porosity compared with SC and DC films. The DC technique is an easy and a quick method for preparing large area films, which is not possible using the SC technique as the film uniformity is limited to a small area. Therefore, we can conclude that the TE and DC method is more preferable for fabrication of large area films compared with the SC and DC method. The perovskite films have strong absorption in the visible region and show good light sensitivity in electrical conductivity measurements. The TE and DC films have better stability in air as compared with SC and DC films. The photoconductivity degrades at a slower rate in the case of TE and DC films and hence the TE and DC method can be adopted for large area PSC fabrication.

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