A Novel Single-Step Growth Process for the Deposition of $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ Perovskite Films from $\text{CH}_3\text{NH}_3\text{Cl}$ and PbI_2 Precursors

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Abstract: The primary synthesis process for organolead mixed halide thin films for solar cell applications involves a two-step process, where $\text{CH}_3\text{NH}_3\text{I}$ is synthesized first, which is then reacted with PbCl_2 to form $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$. However, the synthesis of $\text{CH}_3\text{NH}_3\text{I}$ is quite expensive and laborious. In this work we present a single-step solution approach to prepare perovskite $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ films by the direct reaction of commercially available $\text{CH}_3\text{NH}_3\text{Cl}$ (or MACl) and PbI_2 . Formation of the mixed halide perovskite phase is facilitated by the confinement of reactants to micro droplets that enhanced reaction kinetics. The growth process includes the nebulization of a stoichiometric mixture of MACl and PbI_2 dissolved in DMF, and injection of the aerosol into a low-pressure chamber and deposition onto a substrate. Our results show that the enhanced perovskite film crystallinity and the formation of multiple phases depend strongly on the precursor concentration and the deposition temperature.

Key words: Organolead halide perovskites, spray deposition, X-ray diffraction (XRD), optical properties.

1. Introduction

Organometal halide perovskites have been extensively investigated in the last few years [1-13]. Interest in organometal halide perovskite as a solar absorber continues to increase due to its appealing features that include low material cost, ease of synthesis, suitable direct bandgap with high light absorption, band gap tunability, ultra-fast charge carrier generation [14], slow electron-hole recombination [15], low temperature processability ($\sim 100^\circ\text{C}$) [16], long electron and hole diffusion lengths [17], microsecond-long balanced ambipolar charge carrier mobility [15], excellent thermal stability, and small exciton binding energy. Methylammonium lead halides were confirmed as photoactive materials for the first time in 2006 and power conversion efficiency (PCE) of perovskite solar cells increased rapidly from 3.13% [1] in 2009 to

20.3% [18] confirmed efficiency in January 2015.

Perovskite is a mineral belonging to a larger family of ABX_3 material where A is an organic cation, B is a metal cation and X is a halogen or oxygen anion. In the case of organolead halide perovskites, A is methylammonium, ethylammonium, or formamidinium, and B is lead and X is chloride, bromide, or iodide. The most widely studied methylammonium lead halides include $\text{CH}_3\text{NH}_3\text{PbI}_3$, $\text{CH}_3\text{NH}_3\text{PbI}_2\text{Cl}$, $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$, $\text{CH}_3\text{NH}_3\text{Pb}(\text{I}_{1-x}\text{Br}_x)_3$, $\text{CH}_3\text{NH}_3\text{PbBr}_{3-x}\text{Cl}_x$ and $\text{CH}_3\text{NH}_3\text{PbBr}_3$. Among these, $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ mixed halide perovskite is under intensive study for solar cell applications due to its ideal band gap (1.55 eV) and long electron and hole diffusion lengths.

Spin coating, doctor blading, slot-die coating, gravure coating, knife-over-edge coating, off-set coating, spray coating, ink jet printing, pad printing and screen printing are a few techniques being used to fabricate solution-processed solar cells. The characteristics of fabricated films such as film

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morphology, density, crystallinity, roughness and structure depend on the technique being used. Among aforementioned methods, film growth by spray coating is very attractive since its capability of making large area coatings. The main step of spray coating is the atomization of a liquid precursor solution to generate microdroplets. Transportation of microdroplets to the substrate followed by droplet impact on a heated substrate, droplet spreading, solvent evaporation, drying, solute adhesion, and bonding to itself and to the substrate leads to the formation of a thick coating. One-step precursor solution deposition [19], two-step sequential deposition [20], dual-source vapor deposition [21], and vapor assisted solution process [22] are the reported fabrication techniques for organometal lead halide perovskites. Herein, we adopt a low pressure spray deposition method to fabricate highly crystalline perovskite $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ films. The standard method of preparing methylammonium lead halide ($\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$) perovskite precursor solution is mixing the powder of methylammonium iodide (MAI) with lead chloride (PbCl_2) at the 3 : 1 molar ratio in Dimethylformamide (DMF). But MAI is commercially not available and one must synthesize it first, which is a tedious process involving multiple steps. Also, the chemicals being used to synthesize MAI (hydroiodic acid and methylamine) are quite expensive. In this work, we report a very convenient, single step, low-cost method to fabricate perovskite $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ films, starting from methylammonium chloride ($\text{CH}_3\text{NH}_3\text{Cl}$ or MACl) and lead iodide (PbI_2). To the best of our knowledge this is the first reported successful growth of $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ films starting from MACl and PbI_2 precursors. By eliminating the intermediate step of synthesizing MAI, this approach makes the growth process simple and cost effective. Controlling the film morphology and crystal structure is very crucial for the fabrication of high quality films. We find that the precursor concentration of MACl and PbI_2 in DMF

and the deposition temperature are the main factors that affect the formation of highly crystalline pure perovskites with intense absorption. Under the optimum conditions, MACl and PbI_2 not only improve absorption of $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ but also enhance the $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ film crystallinity. This paper presents results from a systematic study carried out to determine the optimum precursor concentration and the growth temperature to produce films with best crystallinity and morphology.

2. Experimental Details

2.1 Chemicals

Methylamine hydrochloride (MACl, 99%), lead (II) iodide (PbI_2 , 98.5%) were purchased from Alfa Aesar. Dimethylformamide (DMF, 99%), acetone, iso-propanol were purchased from Sigma-Aldrich.

2.2 Synthesis of $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ Perovskite

The precursors used for the synthesis of $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ were prepared by dissolving $\text{CH}_3\text{NH}_3\text{Cl}$ (or MACl) and PbI_2 with the molar ratio of 3 : 1 in a glove box followed by 2 h sonication. Six different precursors were prepared by dissolving appropriate number of moles of MACl and PbI_2 in 3 ml of DMF. Basically, 0.11, 0.22, 0.275, 0.33, 0.385 and 0.44 M concentrations of PbI_2 and 0.33, 0.66, 0.825, 0.99, 1.155 and 1.32 M concentrations of MACl were used for each precursor solution. Glass substrates were cleaned by sonicating for 10 minutes in liquinox detergent, acetone, iso-propanol, and deionized (DI) water respectively.

2.3 Fabrication of $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ Perovskite Films

The precursors were used in a low-pressure deposition system to fabricate coatings. A schematic diagram of the experimental apparatus is shown in Fig. 1. Films were deposited on glass substrates. First the precursor is nebulized into 4-5 μm aerosols and injected into the low-pressure deposition system using

Fig. 1 Experimental setup for low-pressure spray process.

nitrogen as the carrier gas. The substrate was mounted on a heating block that was placed 6 cm in front of the nozzle and the pressure of the deposition chamber was kept at 550 torr. Deposited films were held at deposition temperature for additional 5 minutes to evaporate any residual solvent. Films were grown at 7 different substrate temperatures and 6 different compositions to investigate the role of temperature and composition on properties.

2.3 Sample Characterization

Powder X-ray diffraction (XRD) was performed by Bruker AXS D8 Focus X-ray diffractometer with graphite monochromatized $\text{Cu K}\alpha_1$ radiation ($\lambda = 0.15406 \text{ nm}$). The accelerating voltage was set to 40 kV with 40 mA flux at a scanning rate of $5^\circ/\text{min}$ in the 2θ range from 12° to 60° . SEM was carried out using JEOL JSM-6390LV Scanning Electron Microscope. The SEM spot size and acceleration voltage was kept at 30 and 20 kV respectively. The magnification was varied from 3000x to 30,000x. It is also equipped with an energy dispersive spectroscopy (EDS) detector from Oxford Instruments INCA X-sight for compositional analysis. A Perkin-Elmer Lambda 950

UV-vis-NIR spectrometer was used to measure the absorption spectra of $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ perovskite films. A Veeco Dektak 3030ST profilometer was used to measure the thickness of $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ perovskite films.

3. Results and Discussion

After a preliminary temperature study to obtain crystalline phase of the film, 120°C was used as the deposition temperature for the concentration study. X-ray diffraction patterns of $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ perovskite films fabricated for six different precursor concentrations of PbI_2 and MACl are shown in Fig. 2. Primary diffraction peaks of the samples appear at 14.20° , 28.58° , 43.27° and 58.88° , which can be assigned to the (110), (220), (330) and (440) planes, respectively, of a tetragonal perovskite structure with lattice parameters $a = 8.825 \text{ \AA}$, $b = 8.835 \text{ \AA}$, $c = 11.24 \text{ \AA}$, in agreement with those reported for $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$. For the PbI_2 and MACl concentration ratio of 0.11 M/0.33 M the film exhibited a strong XRD peak near 12.65° which corresponds to an impurity phase of the unreacted PbI_2 . While X-ray peaks for all other 5 concentrations

Fig. 2 X-ray diffraction patterns of fabricated $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ perovskite films (a) 0.11 M, 0.33 M, (b) 0.22 M, 0.66 M, (c) 0.275 M, 0.825 M, (d) 0.33M, 0.99 M, (e) 0.385, 1.155 M, (f) 0.44 M, 1.32 M PbI_2 and MACl concentrations respectively.

showed strong peaks corresponding only to the perovskite phase, the film corresponding to the 0.33 M/0.99M concentration. Fig. 2d exhibited the narrowest peaks indicating superior crystallinity.

Figs. 3 and 4 show the scanning electron microscopy (SEM) images of the spray deposited perovskite films prepared at 120 °C and annealed for 5 minutes from the 6 different precursor solution concentrations of PbI_2 and MACl . It can be observed from SEM images in Fig. 3 that the crystallinity is not well developed till the concentration ratio approaches 0.33 M/0.99 M. At much higher concentrations the porosity seems to increase. Comparison of the SEM images in Fig. 4 at higher magnification also shows a well-defined grain structure for this concentration.

The absorption spectra of $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ films deposited for the 6 concentrations are shown in Fig. 5. The increase in absorption near 800 nm wavelength

observed for all films is due to the inter-band absorption of the perovskite corresponding to its 1.57 eV bandgap. Comparison of the absorbance at the band edge (~790 nm) to the saturated absorbance at 400 nm for the six samples, which is a measure of the optical quality of the film as an efficient absorber, showed the percentages for the samples (a) to (f) are 36.5%, 48.1%, 66%, 100%, 65.4% and 82.8% respectively. Clearly, the perovskite films grown with 0.33M/0.99M concentration showed the best crystallinity, surface morphology, and the absorption properties.

The optical bandgap (E_g) of $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ of this film was determined from the Tauc plot of the absorption spectrum in Fig. 5d. The Tauc plot follows the expression $(\alpha h\nu) = \beta (h\nu - E_g)^n$, where α is the absorption coefficient, $h\nu$ is the photon energy, E_g is the bandgap, and n is 0.5 for a direct bandgap

Fig. 3 Top view SEM images of fabricated $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ perovskite films on glass substrates at different concentrations (a) 0.11 M & 0.33 M, (b) 0.22 M & 0.66 M, (c) 0.275 M & 0.825 M, (d) 0.33M & 0.99 M, (e) 0.385 M & 1.155 M, (f) 0.44 M & 1.32 M PbI_2 and MACl concentrations respectively.

Fig. 4 Top view SEM images of fabricated $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ perovskite films on glass substrates at different concentrations (a) 0.11 M & 0.33 M, (b) 0.22 M & 0.66 M, (c) 0.275 M & 0.825 M, (d) 0.33M & 0.99 M, (e) 0.385 M & 1.155 M, (f) 0.44 M & 1.32 M PbI_2 and MACl concentrations respectively.

semiconductor. By extrapolating the linear region of the Tauc plot, the bandgap is found to be 1.57 eV, which is consistent with reported bandgap for $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$.

In order to study the effect of the substrate temperature on film crystallinity, morphology, and optical absorption; seven samples with 0.33 M PbI_2 and 0.99 M MACl concentration were synthesized in

the temperature range from 80 °C to 160 °C.

X-ray diffraction patterns and SEM images of those films are shown in Figs. 6 and 7, respectively. X-ray diffraction of the films deposited at low deposition temperatures (80 °C) included all the major peaks corresponding to the perovskite phase. However, presence of other peaks indicates incomplete crystallization. This film also showed needle-like

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Fig. 5 Linear absorption spectra of $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ perovskite films for 6 precursors.

morphology. Such morphology is possible if the aerosol drops hitting the substrate remain as a liquid as a result of slow evaporation of the solvent, and dragged along the substrate due to the low pressure environment. From the 100 °C to 140 °C deposition temperatures, all the deposited perovskite films

showed the same XRD patterns with tetragonal crystal structure. The strongest and the narrowest peak corresponding to the (110) orientation of $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ was observed at 120 °C. Above a temperature of 140 °C the perovskite phase appears to decompose giving the film a yellowish color coming

Fig. 6 X-ray diffraction patterns $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ perovskite films at different deposition temperatures.

Fig. 7 Top view of SEM images of fabricated $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ perovskite films on glass substrates at different deposition temperatures.

Fig. 8 Linear absorption spectra of $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ perovskite films at different deposition temperatures.

from lead iodide precipitation. This study confirms that the optimum deposition temperature is 120 °C for growing perovskite films via low pressure spray deposition.

The linear absorption spectra of fabricated $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ perovskite films on glass substrates

at different deposition temperatures are shown in Fig. 8. The maximum absorption spectrum was observed at 120 °C that indicates the completion of the reaction to form perovskite phase with the best crystallinity, which is in agreement with XRD patterns.

4. Conclusions

In summary, we have presented $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ films with a single-step process, which make it a low-cost and convenient method for synthesizing highly crystalline $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ perovskite films on glass substrates. In this approach we used a low-pressure spray coating technique where aerosol droplets containing methylammonium chloride and lead iodide were generated by an ultra-sonic nebulizer. Formation of pure $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ perovskite films depends on the concentration of methylammonium chloride and lead iodide and deposition temperature. Concentrations of 0.33 M methylammonium chloride and 0.99 M lead iodide deposited at a substrate temperature of 120 °C produced the best quality films of $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ perovskite with enhanced crystallinity and optical absorption near the band edge. Even though, Colella *et al.* [23] and Zhao and Zhu [24] reported adding methylammonium chloride to lead iodide resulted in the segregation of a $\text{CH}_3\text{NH}_3\text{PbCl}_3$ phase indicating low solubility of chlorine in the iodine derivative, under optimum growth conditions, the technique used in this work did not show excess PbI_2 or $\text{CH}_3\text{NH}_3\text{PbCl}_3$ phase. The primary reason for this is that each droplet behaves as a micro reactor that is subjected to a uniform temperature within, and thus facilitating the complete conversion of the stoichiometric mixture.

Acknowledgements

The authors wish to express their appreciation to United States Army for their financial support.

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