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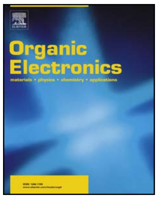

Deciphering perovskite crystal growth in interdiffusion protocol for planar heterojunction photovoltaic devices

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ABSTRACT

Hybrid organic-inorganic perovskites (HIOPs) have increasingly promoted the photovoltaic field due to their excellent semiconductor properties and inexpensive costs. Interdiffusion protocol has been regarded as an efficient approach to deposit high-quality HIOP films. Nevertheless, the underlying mechanism of this protocol remains obscured. In this work, in virtue of vapor-deposited lead halide frame to eliminate solution-driven lead halide effect, we thoroughly studied the evolution of different HIOP films by symmetrically controlling the initial lead halides as well as organic salts. The crystal growth mechanism of the interdiffusion can be drawn in two aspects: 1. CH_3NH_3 (MA)-HIOP shows higher nucleation rate than $(NH_2)_2CH$ (FA)-HIOP; 2. FA-HIOP and $PbCl_2$-HIOP exhibit greater coarsening rates than other colleagues. Most importantly, conflicting lattice with Cl-barren phase and Cl-rich phase is first uncovered for MA-HIOP and FA-HIOP using $PbCl_2$ frame. All the device performances based on these films also prove the potential mechanism, and champion efficiency of 16.01% is achieved based on $FAPbI_3$. This work will provide in-depth insight into the interdiffusion protocol and drive this protocol toward multiple photovoltaic applications by facilely controlling precursor compositions.

1. Introduction

Hybrid organic-inorganic perovskites (HIOPs), overwhelming other semiconductor materials, have tremendously boosted the photovoltaic field in recent years since Miyasaka et al. pioneered promising devices by simple solution method [1–3]. Moreover, the excellent photo-physical natures (such as tunable bandgap, high absorption coefficient, and long carrier diffusion length) make HIOPs increasingly intriguing [4–9]. The key for realizing highly efficient device lies in depositing high-quality polycrystalline HIOP films with lower roughness, higher film coverage, homogeneity and more favourable crystallinity. Multiple deposition protocols, proposed by many groups, have been applied for yielding high-quality films especially toward planar heterojunction (PHJ) architecture [10–20]. Among these approaches, interdiffusion of stacking layers, initially proposed by Xiao et al., became the most prevailing pathway to deposit uniform HIOP films [14]. Unfortunately, the individual roles of different halides in the initial lead halide (PbX_2) layer and different organic cations in the upper layer still remain unclear during interdiffusion process. First of all, various solubility of different PbX_2 compounds in particular solvent makes it difficult to deposit high-quality spin-coated matrix film to study halide-induced effect. Impressively, vapor deposition with higher accuracy is regarded as a beneficial method toward uniform lead halide films under low temperature irrespective of the PbX_2 [21–23]. Additionally, thanks to the easily processing various organic cations within HIOP structure [24–27], versatile bandgaps could be readily achieved by employing different PbX_2. However, the different ionic size between $CH_3NH_3^+$ (MA^+) as well as $(NH_2)_2CH^+$ (FA^+) will lead to distinct crystal growth kinetics, so as to the resulting films [2,28–30]. Consequently, the underlying growth mechanism of polycrystalline HIOP films driven by interdiffusion, based on varying PbX_2 matrixes and organic components, is an imperative issue to be addressed. Especially, when $PbCl_2$ is firstly served as the lead source, whether Cl^- inclusion in the final HIOP lattice or not is still under debate, indicating more complicated reacting mechanism compared to pure I^- phase during the conversion process [31–34].

In order to best comprehend the interdiffusion deposition for PHJ devices, we should analyze the independent role in nucleation as well as coarsening stages of the beneath PbX_2 layer and the upper organic salt (MAI/FAI) layer. In this work, we focus on the evolution process of the

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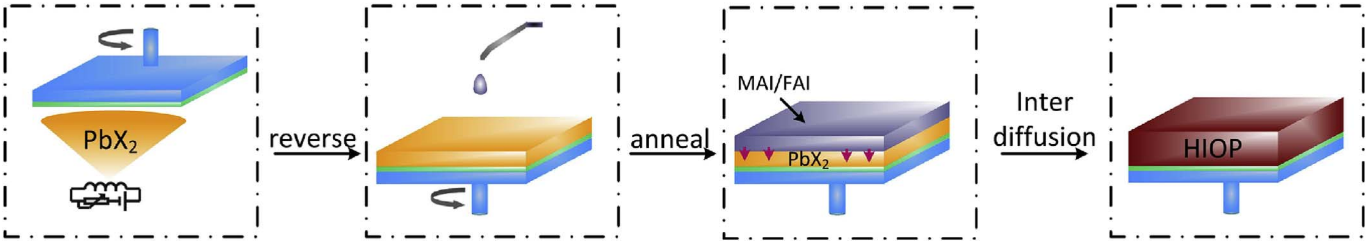

Fig. 1. Process of the vapor-solution interdiffusion protocol.

HIOP films via vapor-solution interdiffusion of vapor-deposited PbX_2 (including PbI_2, $PbBr_2$ and $PbCl_2$) and solution-deposited MAI/FAI layer. By thoroughly studying the optical properties, crystallinities, chemical components within the corresponding films and the prepared devices, potential crystal growth mechanism of the interdiffusion protocol is well explained: 1) In terms of nucleation stage, denser crystal seeds are formed in MA-HIOP than FA-HIOP due to higher nucleation rate of MA^+ ion. Particularly, using $PbCl_2$ matrix, Cl-barren phase and Cl-rich phase is first revealed for MA-HIOP and FA-HIOP, respectively. 2) As for coarsening stage, the growth rate of crystal grain in FA-HIOP surpasses that in MA-HIOP. Meanwhile, $PbCl_2$-HIOP shows greater crystal growth rate with heterogeneous phase. The best PHJ device exhibits an efficiency of 16.01% with $FAPbI_3$. We believe that this work would be a guiding light of the interdiffusion method toward further HIOPs' optoelectronic applications, such as solar cells, light-emitting diodes and lasers.

2. Experimental section

2.1. Preparation of materials

Methylammonium iodide (MAI) was synthesized via a previously reported method, in which 10 ml hydriodic acid (57 wt% in water, Sigma Aldrich) and 24 ml methylamine solution (33 wt% in ethanol, Sigma Aldrich) were stirred into 100 ml of ethanol at 0 °C for 2 h. The precipitate of MAI was obtained by a rotary evaporator. Formamidinium iodide (FAI) was synthesized using a previously reported method. 25.2 g and 48 ml of formamidinium acetate and hyriodic acid were mixed into 250 ml of methanol reacted for 2 h at room temperature. The FAI precipitate was collected by a rotary evaporator. The synthesized MAI and FAI were dried in a vacuum oven overnight. PbI_2, $PbBr_2$, $PbCl_2$ (99.999 wt%) were purchased from Alfa. PEDOT:PSS (CLEVIOS PH 1000) solution was from Haraeus and $PC_{61}BM$ (99.5%) were acquired from Haraeus and Solenne, respectively.

2.2. Fabrication of solar cells

ITO glasses were sonicated in neutral detergent and solution of acetone and ethanol for 20 min and the cleaned glasses were treated with ultraviolet ozone plasma for 5 min. PEDOT:PSS solutions were spin-coated at 1000 rpm for 30 s on cleaned ITO glasses and ITO glasses were heated at 120 °C for 20 min PbI_2, $PbBr_2$, $PbCl_2$ films of 120 nm were sublimated under a pressure of 10^{-5} mbar at a rate of 1.0 Å s^{-1} and the ITO/PEDOT:PSS/PbX_2 substrates were placed into a N_2 –filled glovebox at room temperature. MAI and FAI solutions (0.4 mol MAI/FAI in 1 ml of isopropanol (IPA)) were respectively spin-coated at 2000 rpm for 30s on substrates and were driven to interdiffusion at 80 °C for 2 h. Afterwards, the residual MAI/FAI upon the as-formed HIOP films were cleaned by spinning IPA for 2000 rpm for 30 s. Eventually, the devices were completed by consecutively vacuum deposited $PC_{61}BM$ (30 nm), BCP (6 nm) and Ag cathode (120 nm) under 10^{-5} mbar.

2.3. Characterization

The absorption spectra were acquired on a UV–vis spectrophotometer (Fluoromax 4, HORIBA Jobin Yvon, USA). The morphology was investigated by a scanning electron microscopy (SEM) (Quanta 250, FEI). The elemental composition in the corresponding films was measured by Energy Dispersive X-Ray (EDX) Spectroscopy with Standardless Quantification Model. The crystalline structures were performed by a X-ray diffraction (XRD) (D/MAX-2400, Rigaku, Japan) with Cu Kα radiation.

Device characteristics were evaluated in ambient under a AAA solar simulator (XES-301S, SAN-EI Electric. Co. Ltd.), AM 1.5G illumination with an intensity of 100 mW/cm^2. The current density-voltage (*J-V*) curves were measured by a Keithley digital source meter (Model 2602). For the inverted PHJ devices, the scan rates of current-voltage curves were performed by 0.05 V/s starting from −0.1 V to 1.2 V. The Incident Photon-to-current Conversion Efficiency (IPCE) spectra were obtained by the solar cell quantum efficiency measurement system (SolarCellScan 100, Zolix instruments. Co. Ltd). The area of each device, calibrated by the shadow mask, was 9.00 mm^2.

3. Results and discussion

The interdiffusion process of different HIOP films in our work is presented in Fig. 1. In brief, different PbX_2 films with 120 nm were initially deposited by evaporation on ITO/PEDOT:PSS (the abbreviation of poly(3,4-ethylenedioxythiophene) polystyrene sulfonate, a common hole transporting polymer) substrates in a vacuum chamber, which were sequentially transferred into a N_2-filled glovebox. Afterwards, MAI/FAI solutions dissolved in 2-propanol were respectively dripped upon the substrates and then spin-coated to cover the beneath PbX_2 film. Finally, the bilayer films were annealed to form various polycrystalline HIOP films.

We first paid attention to the morphologies as well as the crystallinities of these HIOP films by applying scanning electron microscopy (SEM) (Fig. 2a). The low magnification SEM images are also shown in Fig. S1. Systematically studying the SEM images and the corresponding crystal size distributions (Fig. 2b), we could draw some conclusions as follows: 1) To begin with, diverse crystal morphologies were achieved between different vapor-deposited PbX_2 films, mainly originating from the different bond lengths of Pb-X. Nevertheless, planar and uniform polycrystalline PbX_2 films with negligible defects and voids were readily deposited upon the substrates, which prevailed over the orthodox solution-deposited films. Naturally, the high quality films would provide a superior basic frame for as-forming HIOP films. 2) After completely thermal interdiffusion of PbX_2-MAI/FAI bilayers, the virgin PbX_2 crystals were dramatically enlarged to convert into the final HIOP crystals. More importantly, δ-phase (a non-perovskite lattice) was suppressed for $FAPbI_3$ without high thermo-energy assistance (generally > 160 °C in general 1-step method when preparing $FAPbI_3$). Compared with the coarse morphologies with scattered crystals in conventional 2-step deposition, smooth and continuous HIOP films driven by interdiffusion protocol were composed of massive closely packing crystals, which would be favourable for photo-excited carriers'