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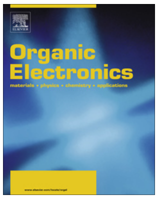

Efficiencies of perovskite hybrid solar cells influenced by film thickness and morphology of $CH_3NH_3PbI_{3-x}Cl_x$ layer

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ABSTRACT

Perovskite hybrid solar cells (pero-HSCs) have been intensively investigated due to their promising photovoltaic performance. However, the correlations between the efficiencies of pero-HSCs and thin film thicknesses and morphologies of $CH_3NH_3PbI_{3-x}Cl_x$ perovskite layers are rarely addressed. In this study, we report the correlation between the efficiencies of "planar heterojunction" (PHJ) pero-HSCs and the thin film thicknesses and morphologies of solution-processed $CH_3NH_3PbI_{3-x}Cl_x$ perovskite layers. Investigation of absorption spectra, X-ray diffraction patterns, atomic force microscopy and scanning electron microscopy images of $CH_3NH_3PbI_{3-x}Cl_x$ layers indicate that the efficiencies of PHJ pero-HSCs are dependent on the film thickness, as the thickness of $CH_3NH_3PbI_{3-x}Cl_x$ is less than 400 nm; whereas the efficiencies are significantly dependent on the film morphologies of $CH_3NH_3PbI_{3-x}Cl_x$ layers as the thickness is larger than 400 nm. Our studies provide a promising pathway for fabricating high efficiency PHJ pero-HSCs.

1. Introduction

Perovskite materials ABX_3, where A is organic cuboctahedral, B is inorganic octahedral, and X is halogens, for example $CH_3NH_3PbX_3$ (X = I, Br and Cl), have recently emerged as a remarkable light harvester for thin-film photovoltaics [1–5]. $CH_3NH_3PbX_3$ are hybrid materials with an ideal bandgap for single junction solar cells [6] due to its broad absorption spectrum with high extinction coefficients [7], large electron-hole diffusion length [8], good electrical transport properties [9]. Currently, over 17% of power conversion efficiency (PCE) has been reported from perovskites hybrid solar cells (pero-HSCs) [10].

The pero-HSCs based on $CH_3NH_3PbX_3$ thin films processed by various methods show quite different device performances [11–14]. High PCEs was observed from pero-HSCs based on high quality vapor-deposited $CH_3NH_3PbX_3$ thin films [15]. Moderate PCEs was observed from pero-HSCs based on low quality solution-processed $CH_3NH_3PbI_{3-x}Cl_x$ layer [16–19]. However, the correlations between the efficiencies of pero-HSCs and the film thicknesses and morphologies of $CH_3NH_3PbI_{3-x}Cl_x$ layers are rarely addressed.

In this study, we investigate the device performance of "planar heterojunction" (PHJ) pero-HSCs correlated with the film thicknesses and film morphologies of solution-processed $CH_3NH_3PbI_{3-x}Cl_x$ layers by investigations of absorption spectra properties, X-ray diffraction (XRD) patterns, atomic force microscopy (AFM) and scanning electron microscopy (SEM) images of $CH_3NH_3PbI_{3-x}Cl_x$ films. The PCEs ranging from 4.88% to 11.88% are observed from PHJ pero-HSCs with the thicknesses of $CH_3NH_3PbI_{3-x}Cl_x$ layers from 270 nm to 670 nm.

2. Experimental section

2.1. Materials

Poly(3,4-ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS) and phenyl-C_{61}-butyric acid methyl ester ($PC_{61}BM$) were purchased from Clevious and 1-Material Inc., respectively and used as received without further treatment. Lead chloride ($PbCl_2$), anhydrous N,N-dimethylformamide (DMF), hydroiodic acid (99.99%), methylamince were purchased from Sigma–Aldrich and used as received without further purification.

2.2. $CH_3NH_3PbI_{3-x}Cl_x$ precursor preparation

Methyl ammonium iodide (CH_3NH_3I) was prepared following the previous literatures [20,21]: hydroiodic acid (114 mmol, 15 mL, 57 wt%) and methylamine (140 mmol, 70 mL, 2.0 M in

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methanol) were reacted at 0 °C with stirring under nitrogen atmosphere for 120 min. The resultant solution was evaporated to give a white precipitate, and then the precipitate was washed with diethyl ether for several times until the diethyl ether was completely colorless. The white precipitate was dried under vacuum for 48 h and used without further purification. And the precursor solutions of $CH_3NH_3PbI_{3-x}Cl_x$ was prepared by dissolving $PbCl_2$ and CH_3NH_3I (with a molar ratio of 1:3) in DMF with different concentrations of 0.44, 0.66, and 0.88 mol/L.

2.3. Thin film preparation

The $CH_3NH_3PbI_{3-x}Cl_x$ films were prepared by spin-casting the precursor solution on the top of PEDOT:PSS coated indium tin oxide (ITO) substrate (for device fabrication and AFM measurement), quartz glass substrate (for absorption measurement) and polyethylene terephthalate (PET) substrate (for XRD measurement), respectively, followed with thermal annealing at 90 °C for 2 h. The thickness of $CH_3NH_3PbI_{3-x}Cl_x$ perovskite films was controlled by using different precursor concentrations and spin-speed.

2.4. Thin film characterization

The absorption spectra of perovskite films were measured by HP 8453 UV-vis spectrophotometer. The SEM images were obtained by using a field emission scanning electron microscope (JEOL-7401). The AFM images were obtained by using a NanoScope NS3A system (Digital Instrument) to observe the surface morphologies of various thin films. The film thicknesses were measured by Dektak 150 surface profilometer with scan rate 0.06 mm/s. XRD patterns of perovskite films coated on PET substrates were obtained by using a Bruker AXS Dimension D8 X-ray System.

2.5. PHJ pero-HSCs fabrication

All PHJ pero-HSCs were fabricated on pre-cleaned ITO coated glass substrates. After ITO glass substrates were treated with UV-ozone for 20 min under an ambient atmosphere, a ~40 nm thick film of PEDOT:PSS was spin-coated on the top of ITO glass substrates, followed with thermal annealing at 150 °C for 10 min. After that, the $CH_3NH_3PbI_{3-x}Cl_x$ thin films with different thickness were spin-coated on the top of PEDOT:PSS from $CH_3NH_3PbI_{3-x}Cl_x$ precursor solution, followed with thermal annealing at 90 °C for 2 h. The thickness was controlled by using $CH_3NH_3PbI_{3-x}Cl_x$ precursor solution with different concentrations (0.44 mol/L, 0.66 mol/L, and 0.88 mol/L) and different spin-rates (2000 rpm, 2500 rpm and 3000 rpm). The thicknesses of $CH_3NH_3PbI_{3-x}Cl_x$ thin films are ranged from 270 nm to 668 nm. Then ~200 nm thick $PC_{61}BM$ was deposited from the chlorobenzene solution. Finally, ~100 nm thick Aluminum (Al) was thermally deposited on the top of $PC_{61}BM$ layer in the vacuum with a base pressure of 6×10^{-6} mbar through a shadow mask. The device area was measured to be 0.16 cm^2.

2.6. PHJ pero-HSCs characterization

The current densities versus voltage (J–V) characteristics of pero-HSCs were obtained by using a Keithley model 2400 source measure unit. A Newport Air Mass 1.5 Global (AM1.5G) full-spectrum solar simulator was applied as the light source. The light intensity was 100 mW cm^{-2}, which was calibrated by utilizing a monosilicon detector (with a KG-5 visible color filter) of National Renewable Energy Laboratory to reduce the spectral mismatch. The incident photon-to-electron conversion efficiency (IPCE) was measured through the IPCE measurement setup in use at ESTI for cells and mini-modules: a 300 W steady-state xenon lamp provides the source light; up to 64 filters (8–20 nm width, range from 300 to 1200 nm) are available on four filter-wheels to produce the monochromatic input, which is chopped at 75 Hz, superimposed on the bias light and measured via the usual lock-in technique; bias light is necessary to put the device under examination close the operating irradiance condition. After collecting the IPCE data, the software also integrates the data with the AM1.5G spectrum and gives the calculated J_{SC} value, which is helpful for checking the accuracy of the measurement.

3. Results and discussion

The PHJ pero-HSCs with a p-i-n device structure of ITO/PEDOT:PSS/$CH_3NH_3PbI_{3-x}Cl_x$/$PC_{61}BM$/Al is applied to investigate the device performance influenced by film thicknesses and film morphologies of $CH_3NH_3PbI_{3-x}Cl_x$ layers. In the p-i-n pero-HSCs, the $CH_3NH_3PbI_{3-x}Cl_x$ film being the intrinsic semiconductor acts as the light absorber, PEDOT:PSS being the p-type layer acts as the hole transport layer, and $PC_{61}BM$ being the n-type layer acts as the electron transport layer, respectively. The J–V characteristics of PHJ pero-HSCs are shown in Fig. 1a. Table 1 summarizes the device performance parameters of all PHJ pero-HSCs. For each thickness, over 50 devices were tested for the statistics. The confidence interval is 80% for standard errors. All PHJ pero-HSCs possess a similar fill factor (FF) of ~0.61, and an open-circuit voltage (V_{OC}) of ~0.93 V, but with significantly different short-circuit current density (J_{SC}), consequently significantly different PCEs. As the thicknesses of $CH_3NH_3PbI_{3-x}Cl_x$ layers are gradually increased from 273 nm to 575 nm, and then further increased to 668 nm, the J_{SC} values are gradually increased from 8.45 mA/cm^2 to 19.79 mA/cm^2, and then decreased to 17.26 mA/cm^2, respectively; correspondingly, the PCEs are increased from 4.88% to 11.88%, and then decreased to 9.42%, respectively. The decreased J_{SC} in thicker $CH_3NH_3PbI_{3-x}Cl_x$ films are likely due to the inferior surface quality of $CH_3NH_3PbI_{3-x}Cl_x$ films [22], which will be addressed late (Figs. 5 and 7).

To gain insight into the influence of film thickness on Jsc, the incident IPCE spectra of pero-HSCs were measured and displayed in Fig. 1b. The IPCE specifies the ratio of extracted electrons to incident photons at a given wavelength. The IPCE spectra of pero-HSCs are in good agreement with the absorption spectra of $CH_3NH_3PbI_{3-x}Cl_x$ with different film thicknesses (Fig. 3). The IPCE spectra of all pero-HSCs show a wide photoresponse from 300 nm to 800 nm, which is consistent to absorption spectra of $CH_3NH_3PbI_{3-x}Cl_x$. As the film thicknesses are gradually increased from 270 nm to 607 nm, the photoresponses of pero-HSCs are gradually enhanced from ~40% to ~80%, correspondingly. In specific, as the thicknesses of $CH_3NH_3PbI_{3-x}Cl_x$ are gradually increased from 270 nm to 607 nm, the photoresponses in the region from 550 nm to 800 nm are dramatically enhanced while the photoresponses at the wavelength below 500 nm are moderately enhanced. The different shapes of IPCE spectra are probably due to interactions among photocontribution from $PC_{61}BM$ and from $CH_3NH_3PbI_{3-x}Cl_x$ of different thicknesses. It has been reported that a small amount of photoinduced excitons can also be generated in $PC_{61}BM$ at the wavelength below 500 nm [23]. When the thickness of $CH_3NH_3PbI_{3-x}Cl_x$ is small, the photocontribution from $PC_{61}BM$ is more obvious than that from $CH_3NH_3PbI_{3-x}Cl_x$; while the thickness $CH_3NH_3PbI_{3-x}Cl_x$ is large, the photocontribution from $PC_{61}BM$ is trivial compared with that from $CH_3NH_3PbI_{3-x}Cl_x$ [24,25,23]. The estimated J_{SC} from pero-HSCs with different thicknesses of $CH_3NH_3PbI_{3-x}Cl_x$ layers are 7.24 mA/cm^2 (273 nm), 8.59 mA/cm^2 (296 nm), 11.82 mA/cm^2 (365 nm), 14.05 mA/cm^2 (387 nm), 15.88 mA/cm^2 (401 nm), 17.21 mA/cm^2 (468 nm), 18.13 mA/cm^2 (575 nm), 18.45 mA/cm^2 (607 nm), 15.76 mA/cm^2 (668 nm). These

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