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$CH_3NH_3PbBr_3$ nanocubes-array for solar cell application

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ABSTRACT

Methyl-ammonium lead bromide ($MAPbBr_3$) is currently studying due to its potential application to high open circuit voltage photovoltaic device. Due to the limited solubility of methyl ammonium bromide (MABr) in isopropyl alcohol (IPA), the $MAPbBr_3$ was only fabricated by one step (1-step) spin coating process. In this article, we alternatively used ethanol and methanol as solvent to dissolve MABr to fabricate $MAPbBr_3$ films by two steps (2-steps) spin coating process. As a result, we observed a dense, closed stacked and aligned perovskite nanocubes array using a varying concentration of MABr and waiting time. Our best device with an architecture of FTO/TiO_2/$MAPbBr_3$/Spiro-OMeTAD/Au shows a current density of 9.31 mA/cm^2, open circuit voltage of 1.05 V, and fill factor of 0.58 with a power conversion efficiency of 5.70%. We were optimistic that these $MAPbBr_3$ nanocube arrays would be applicable to solar cell as well as other optoelectronic devices such as photodetector, light emitting diode and X-ray scintillator.

1. Introduction

It has been almost eight years past to research on methyl ammonium metal halide ($MAMeX_3$) as a solar absorber materials (M: Methyl, A: NH_3, Me: Pb and Sn, X: Cl, Br, or I) [1]. But in recent years, methyl ammonium lead bromide ($MAPbBr_3$) has been studied due to its potential application to high open circuit voltage (V_{oc}) photovoltaic device [2–16], light emitting diode (LED) [17–20], and X-ray scintillator [21,22]. Fabrication of single crystalline perovskite layer which has free of grain boundary and defect, facilitate higher carrier diffusion length, superior to the polycrystalline counterpart [23,24]. Micron size or millimeter size $MAPbBr_3$ crystal has already been fabricated and their optoelectronic properties have been addressed elsewhere [23,24]. The $MAPbBr_3$ films were previously fabricated by one-step spin coating method using $PbBr_2$ and methyl ammonium bromide (MABr) in N,N-Dimethylmethanamide (DMF), dimethyl sulfoxide (DMSO) or mixed DMF/DMSO [2–24]. Furthermore, the morphology and crystallinity were improved by the anti-solvent treatment during the spin-coating process [10,25]. Zhang et al. fabricated $MAPbBr_3$ films by spin coating of $PbBr_2$ and vapor deposited MABr, and observed that the $MAPbBr_3$ film has a better surface morphology than the one-step spin coating fabricated $MAPbBr_3$ films [9]. In order to fabricate high quality uniform and compact $MAPbBr_3$ films, an alternative solvent is needed to dissolute the higher concentration of MABr for complete conversion of $PbBr_2$. It is well known that MABr is highly soluble in H_2O. However, H_2O cannot be used as solvent for preparing $MAPbBr_3$ films. Controlling the crystallization process by adding H_2O and HBr with DMF, pure $MAPbBr_3$ films were fabricated by Heo et al. [2]. Lafalce et al. studied the optoelectronic properties of $MAPbBr_3$ nanocrystals and its application to lasing and LED application [25]. Peng et al. demonstrated monocrystalline $MAPbBr_3$ perovskite solar cell without using a hole transport material (HTL) and achieved a power conversion efficiency of (PCE) of 5.49% [12]. Saidaminov et al. achieved a high-quality bulk hybrid perovskite single crystals within minutes by inverse temperature crystallization [24]. A dense, compact, well-aligned films perovskite films are highly desirable in order to fabricate a highly efficient device. Among many fabrication methods, two step spin coating process found to be beneficial to fabricate dense, compact, pinhole free perovskite films [26,27].

In a recent report, Wu et al. fabricated $MAPbBr_3$ films by two step spin coating process using MABr/IPA solution [28]. In this article, we have alternatively used MABr/ethanol and MABr/methanol onto $PbBr_2$ film to fabricate well aligned $MAPbBr_3$ nanocubes arrays on TiO_2/glass substrate by 2-step spin coating process. We have studied the effect of MABr concentration in ethanol/methanol and also reaction time on microstructure, structural and optical properties of $MAPbBr_3$ films. We also demonstrate a $MAPbBr_3$ nanocube array based solar cell using an optimized MABr concentration.

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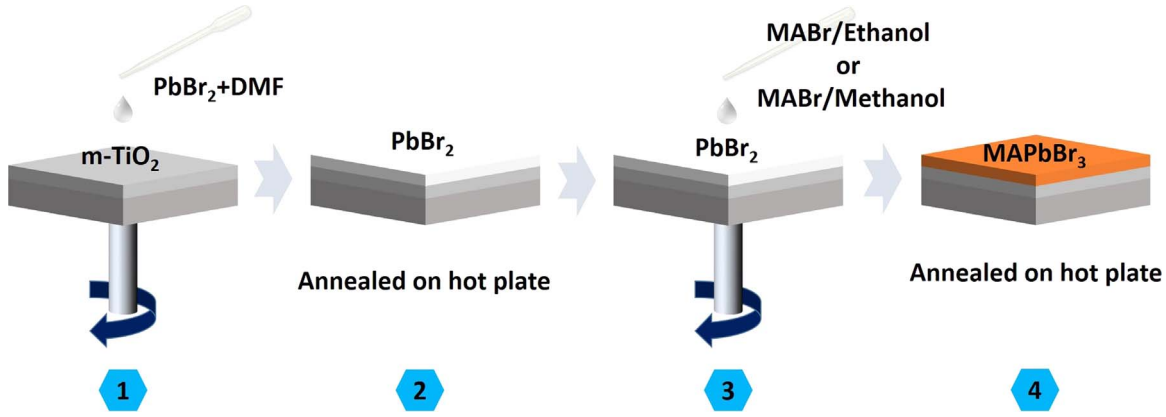

Fig. 1. Schematic of two-step deposition process used in our experiment.

2. Experimental

2.1. Fabrication of solar cell

All chemicals were commercially purchased and used as such without purification. Lead bromide ($PbBr_2$) of 0.36 g was dissolved in 1 ml of DMF and stirred on a hot plate at 120 °C for 30 min. MABr solution was prepared using three different solvent iso-propyl alcohol (IPA), ethanol and methanol at room temperature. We observed that the solubility of MABr in IPA is nearly 5 mg/ml in IPA. However, we observed that the solubility of MABr is up to 75 mg/ml and 90 mg/ml in ethanol and methanol, respectively. Fig. 1 shows the schematic two-step sequential deposition process used in our experiment. The $PbBr_2$ solution was spin coated on to mesoporous titania (m-TiO_2)/glass at a typical process condition (3000 rpm/30 s) and annealed at 100 °C for 10 min on a hot plate. The fabrication of mesoporous titania (m-TiO_2) films is discussed in the following. MABr solution was spin coated at a typical condition (1500 rpm/30 s) and annealed at 100 °C for 5 min. In order to fabricate solar cell, we used fluorine-doped tin oxide (FTO) as a transparent electrode. The FTO glass was cut into 2 cm × 2 cm and etched by ZnO powder and 50% HF solution and cleaned with acetone, deionized (DI) water and ethanol, each for 30 min followed by nitrogen blowing. Commercially available m-TiO_2 paste (Dyesol) of 20–30 nm particle size was dissolved in ethanol with a ratio of 1:3.5 and spin coated onto an FTO/glass substrate at typical condition (3000 rpm/30 s). The resulted films were annealed at 500 °C for 1 h in the ambient air atmosphere. The perovskite active layer films were fabricated as discussed above. We choose Spiro-OMETAD as HTM, was deposited at 3000 rpm for 30 s. The hole transport layer material was composed of 30 mg of 2,2′,7,7′-tetrakis-(N,N-di-p-methoxyphenyl-amine) − 9,9′-spirobifluorene (Spiro-OMeTAD) (Aldrich, Korea) was dissolved in 0.25 ml of chlorobenzene and 85 mg of bis(trifluoromethane)sulfonimide lithium (Li-TFSI) salt was dissolved in 0.5 ml of acetonitrile and the both solutions were stirred for 30 min. 12 mM of 4-tert-Butylpyridine (TBP) was added to Spiro-OMeTAD followed by 10 ml Li-TFSI salt. 80 nm of Au was used as counter electrode, deposited by thermal evaporation at the deposition rate of 5 Å/s. Except the Au deposition, all experiments were carried out in the ambient air atmosphere.

2.2. Characterization

The microstructure of $MAPbBr_3$ films was examined with a field-emission scanning electron microscope (FESEM) using a JEOL JSM-6500F operating at 5 kV accelerating voltage. The phase of the perovskite films was analyzed by X-ray powder diffraction (XRD) method (Rigaku, USA, $CuK_{\alpha 1}$ radiation (λ = 0.15406 nm)) in 2θ mode. The absorption spectra were obtained with a Perkin-elmer ultra-violet visible (UV–Vis) spectrophotometer. The current-voltage (*I-V*) characteristics were measured in the dark and under illumination at AM1.5G (100 mW/cm^2) Xenon lamp (Newport, USA) connected with a Keithey-2400 electrometer. The device active area was 0.09 cm^2. The *I-V* characteristics were measured with voltage step 0.025 V from −0.02V to 1.5 V.

3. Results and discussion

3.1. IPA as solvent

Fig. 2(a) and (b) show the microstructure of $PbBr_2$ (1M) film using DMF solution and $MAPbBr_3$ films using 5 mg/ml MABr (MABr is slightly soluble in IPA) in IPA by 2-step spin coating process, respectively. The $PbBr_2$ film has a smooth surface and $MAPbBr_3$ film shows some nanocubes embedded in the film. Fig. 2(c) shows the comparison of XRD spectra of $PbBr_2$ and $MAPbBr_3$ films. The characteristic peaks of $PbBr_2$ were indexed in black color and the characteristic peaks of $MAPbBr_3$ film were indexed in red color, just for clarity. The $PbBr_2$ peaks were well matched with JCPDF card number 84-1181, which is an orthorhombic crystal structure with space group: *pnam*. The XRD spectrum of $MAPbBr_3$ clearly shows the film was not completely converted to $MAPbBr_3$. Fig. 2(d) shows the comparison of the optical absorption spectra of $PbBr_2$ and $MAPbBr_3$ film. The optical absorption edges of $PbBr_2$ and $MAPbBr_3$ film is appeared about 350 nm (3.54 eV) and 530 nm (2.32 eV) respectively, is matched with previously reported values [25].

3.2. Ethanol as solvent

It is well known that the lead halide is slightly dissolved in alkyl hydroxide (C_nH_{2n+1}-OH), does not effect on the conversion of lead halide to perovskite film. Due to the limited solubility of MABr in pure IPA, we alternatively choose ethanol and methanol as a solvent to dissolve MABr. We observed that the MABr is fairly soluble in ethanol as well as methanol. The amount of MABr dissolved in ethanol and methanol is about 75 mg/ml and 90 mg/ml, respectively. Fig. 3 shows the microstructure evolution of $MAPbBr_3$ films fabricated with different concentration of MABr in ethanol on m-TiO_2/glass substrate; (a) 5 mg/ml, (b) 15 mg/ml, (c) 30 mg/ml, (d) 45 mg/ml, (e) 60 mg/ml and (f) 75 mg/ml. A gradual changes in microstructure from micron size cubes to nanometer size nanocubes film was observed with increasing the MABr concentration. Using 5 mg/ml MABr in ethanol, a few numbers of meso to micro-cubes of approximately 500–1000 nm were observed. However, with increasing the MABr concentration to 15 mg/ml and 30 mg/ml, the number density of $MAPbBr_3$ nanocubes was by reducing the particle size of 100 nm. Further increasing of MABr concentration (45–75 mg/ml) provides uniform and compact nanocubes array films with different shapes and sizes.