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Twice Deposition of Lead Iodide in Perovskite Solar Cells

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Abstract: This article brings up some explanations and clarifications about twice deposition of lead iodide written in the previous article [1], after looking into the twice deposition of lead iodide and carrying on the improving by a layer of $PbBr_2$ instead of PbI_2, the short circuit current density (J_{sc}) has decreased, allowing to explain the twice deposition is, in fact, one deposition. The absorbance of perovskite will be discussed. The substrate temperature is the most important parameter because it can improve the efficiency of the perovskite solar cells, the substrate temperature should be about 100 °C at the deposition of lead iodide, and when the deposition of methylammonium iodide is done when the substrate is still hot, the efficiency is also improved. The temperature during the preparation is less important than the humidity, but the preparation in the glovebox allows that the environmental conditions be controlled.

Key words: Deposition, perovskite, efficiency.

1. Introduction

Perovskites of the form AMX_3, where A is an organic cation, M is a metal cation, and X is a halide anion, have emerged as promising new materials for photovoltaic cells. The interest of perovskites for use in photovoltaics lies in their unique chemical and physical properties and their relative ease of synthesis [2, 3]. The methylammonium lead triodide ($CH_3NH_3PbI_3$) has become the material most frequently used in high-performing perovskite solar cells [4, 5]. X-ray diffraction measurements and calorimetric studies have reported a phase transition from tetragonal to cubic to occur at 57.3 °C upon heating. A room-temperature stabilized tetragonal phase was calculated to have a band gap of 1.51 eV, which was in good agreement with the observed value [6, 7].

2. Experimental

2.1 Fabrication of Perovskite Solar Cells

Solar cells were fabricated on fluorine-doped tin oxide glass substrates with a sheet resistance of 15 Ω/square (Pilkington). FTO substrate was patterned by chemical etching with Zinc powder and HCl aqueous solution. The conductive substrates were cleaned with detergent solution, de-ionized water and ethanol. A thin dense compact TiO_2 layer (c-TiO_2) was deposited on the etched FTO substrate by spin coating (3,000 rpm, 30 s) using a titanium diisopropoxide bis(acetylacetonate) solution in ethanol and HCl at a volumetric ratio of 0.35:5:1 followed by annealing at 500 °C. Porous TiO_2 films got by commercially available TiO_2 paste (30-NR-D, Dyesol, average particle size ~ 20 nm) diluted in ethanol (1:3.5 weight ratio) were directly deposited on top of the c-TiO_2 by spin coating at 5,000 rpm for 30 s and annealed at 500 °C. PbI_2 solution is diluted in DMF (dimethylformamide) or DMSO (dimethylsulfoxide) (462 mg/mL) and was kept at 70 °C. Thus, the

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prepared mesoporous TiO_2 films were loaded with PbI_2 for 30 s and then spin-coated at 5,500 or 6,000 rpm for 30 s after that dried 2 min and finally annealed at 70 °C during 30 min. For twice deposition of lead iodide, the PbI_2 is recoated, dried and annealed, same as the first step. After drying, the films were spin coated at 5,500 or 6,000 rpm at 30 s after they were loaded a solution of CH_3NH_3I in 2-propanol (13 mg/mL) for 30 s. The HTM (hole-transporting material) was deposited by spin-coating at a solution of spiro-MeOTAD, tert-butylpyridine, lithium bis(trifluoromethylsulphonyl)imide and tris (2-(1H-pyrazol-1-yl)-4-tert-butylpyridine)cobalt(III) bis(tri-fluoromethylsulphonyl)imide in chlorobenzene. Silver (Ag) was thermally evaporated on top of the device to form the back contact.

2.2 Characterization

The photocurrent density-voltage characteristics of the perovskite solar cells were evaluated by a source meter (Keithley 2400) under a solar simulator (Oriel 92250A-1000, Newport, 100 mW cm^{-2}). The absorption of different films was measured using a UV-visible Spectrophotometer (UV-2450, Shimadzu). The crystal structure was examined using X-ray Diffractometer (XRD, D8 ADVANCE, Cu Kα radiation, λ = 1.54 Å, tube voltage = 40 kV, tube current = 30 mA).

3. Results and Discussion

3.1 Absorption

The absorption is improved when the methylammonium iodide is deposited when the substrate temperature is hot. The solvent used for dissolving the methylammonium CH_3NH_3I is 2-propanol which has an ebullition temperature around 82 °C while the perovskite temperature annealing used is 70 °C during 30 min so that the hot substrate temperature could be between 50 and 70 °C. Therefore the 2-propanol ebullition point has not reached during the transformation in perovskite. In addition, perovskite cubic phase has gotten at 57 °C. The absorption spectrum increases with the perovskite phase cubic crystallization. That's shown in Fig. 1 where the absorption spectrum has been improved between 500 nm and 700 nm wavelength significantly.

Some studies have already been done about the thickness of perovskite layer [8-10]. Fig. 2 shows the absorbance curves at once deposition and twice deposition and at the different volume that are still identical approximately. That's explained the absorption does not improve by twice deposition of lead iodide.

Fig. 3 shows the difference between the absorbance curves when lead bromide is used as the second deposition instead of lead iodide. The decreasing of absorbance at twice deposition proves the second deposition used $PbBr_2$ has removed the first deposition of PbI_2, so the curve got is different as the perovskite absorbance. Therefore the solvent as DMF or DMSO removed the first deposition. When at the second deposition the solvent chlorobenzene as used to dissolve the $PbBr_2$, the first deposition has not been removed by the solvent, despite the weak dissolution of $PbBr_2$ by the chlorobenzene, the absorbance of twice deposition is more increasing than the absorbance of once deposition shown in Fig. 4.

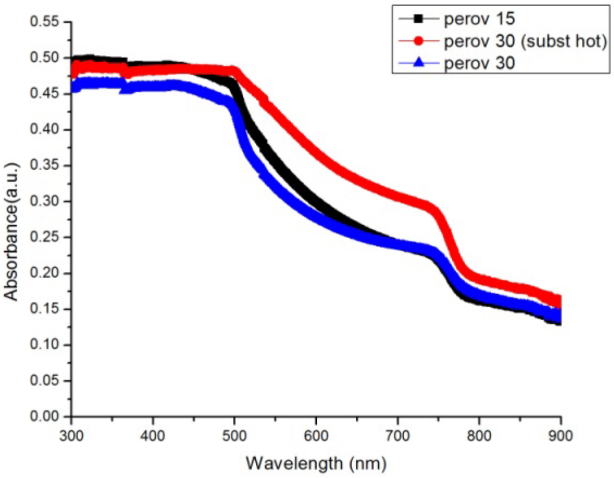

Fig. 1 Absorbance curves with a hot substrate and a normal substrate.

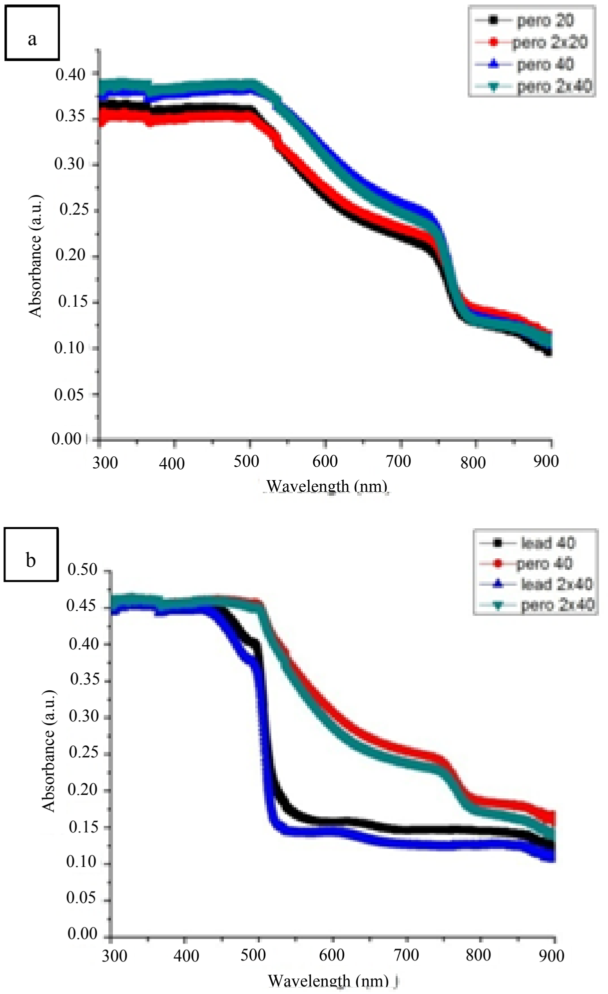

Fig. 2 Absorbance curves at once and twice deposition of lead iodide and perovskite.

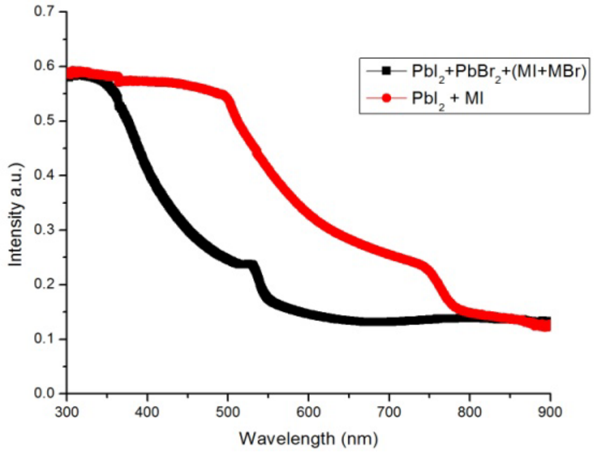

Fig. 3 The twice deposition is done with (PbI_2+$PbBr_2$) with DMSO used as solvent at the first and second deposition.

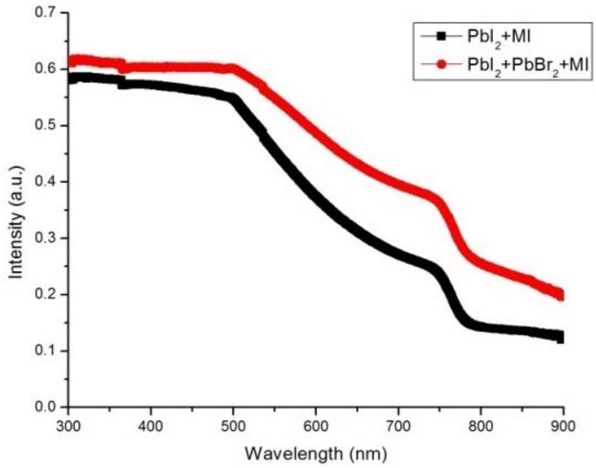

Fig. 4 The twice deposition is done with (PbI_2+$PbBr_2$) with DMSO used as solvent at the first deposition and chlorobenzene used as solvent at the second deposition.

The precursor solvent could influence the morphology of perovskite crystallization, and the absorption spectrum of cubic particles is higher than the absorption spectrum of hexagonal particles [11, 12]. Also, the more polar solvent can dissolve more lead iodide PbI_2, higher polarity solvent leads to the formation of cubic nanocrystals. The using solvent acetonitrile for dissolving PbI_2 at the second deposition of lead iodide also improves the absorption although the particles got with acetonitrile are hexagonal particles.

3.2 XRD

Fig. 5 and Fig. 6 show XRD spectra of lead iodide and perovskite at loading volume of lead iodide at once deposition and twice deposition of lead iodide. All the spectra exhibited characteristic peaks of TiO_2 anatase crystal plane with (101) and (004). The peak intensity of the diffraction peak (101) became larger at twice deposition of lead iodide than at once deposition.

3.3 Current Density-Voltage (J-V) Characteristics

Substrate temperature:

It has been proved that the deposition of lead iodide

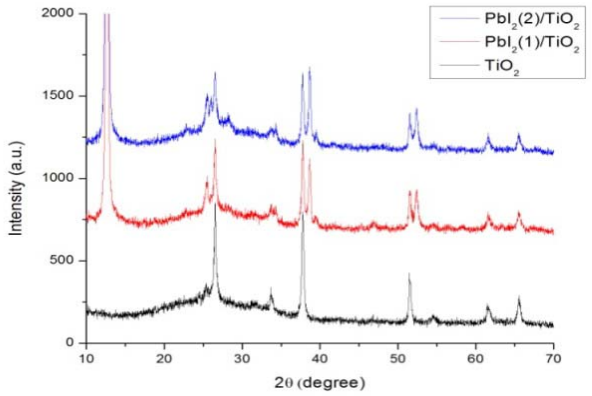

Fig. 5 Spectra of lead iodide at once and twice deposition of lead iodide.

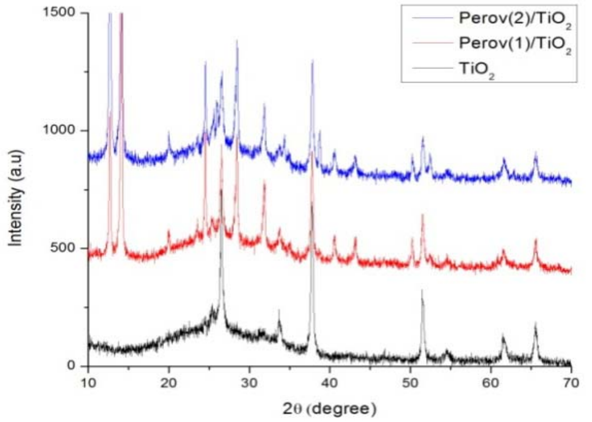

Fig. 6 Spectra of perovskite at once and twice deposition of lead iodide.

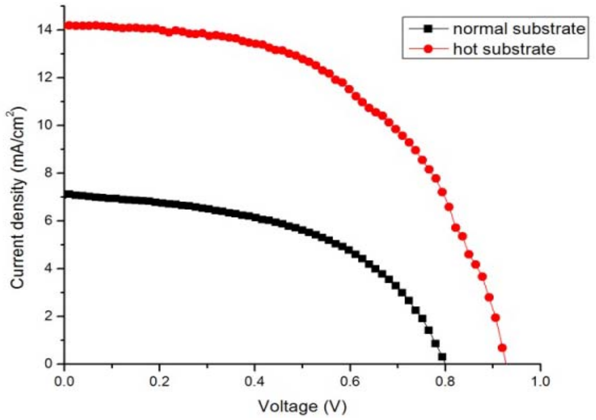

Fig. 7 J-V curves for photovoltaic devices at hot substrate and normal substrate during methyl ammonium iodide deposition.

on the mesoporous TiO_2 at hot substrate temperature improve the efficiency [13, 14], in addition, when the substrate temperature is hot during the loading of methyl ammonium iodide, the J_{sc} is also improved due to a better crystallization.

Table 1 Photovoltaic devices at different substrate temperature.

Device	J_{sc} (mA/cm^2)	V_{oc} (V)	FF (%)	PCE (%)
Hot substrate	14.2	0.92	52.8	6.9
Normal substrate	7.1	0.8	50.8	2.9

Comparison J-V between twice deposition and once deposition of lead iodide dissolved in DMSO.

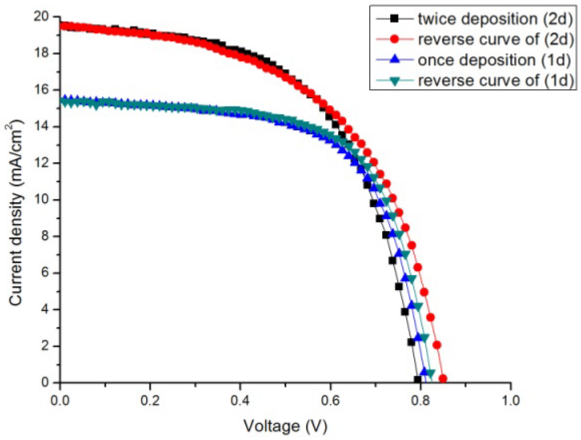

Fig. 8 J-V curves of photovoltaic devices.

Table 2 Photovoltaic devices at once and twice deposition of lead iodide.

Device	J_{sc} (mA/cm^2)	V_{oc} (V)	FF	PCE
Once deposition	15.5	0.81	63.3	7.9
Twice deposition	19.5	0.79	56.8	8.8

Twice deposition of (lead iodide + lead bromide) dissolved in DMSO.

Table 3 Photovoltaic devices at twice deposition with lead bromide.

Device	Jsc (mA/cm^2)	Voc (V)	FF (%)	PCE (%)
Lead iodide+lead bromide +(MI+MBr)	0.6	0.56	65	0.23
Lead bromide +MBr	2.9	0.39	53.5	0.6

The twice deposition of lead iodide has been discussed in the paper [1] previously, in fact after used $PbBr_2$ as the second deposition that's proved the twice deposition is, in fact, one deposition, the solvent DMF or DMSO have removed the first deposition. The thickness of perovskite does not change, but the morphology could have been denser by the twice deposition improving by the way the J_{sc} [15].

4. Conclusion

The twice deposition of lead iodide improves the J_{sc} not by improving the absorption but by new morphology created inside the mesoporous TiO_2 because the second deposition of lead iodide removes the first deposition. The twice deposition improves the absorbance when the solvent as chlorobenzene or acetonitrile is used at the second deposition. The next issue could have been the interface between the two layers of perovskite with different solvents. The substrate temperature improves the efficiency which a better infiltration of lead iodide could explain it, and a quick transformation did in the cubic perovskite phase.

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