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Parameters affecting morphologies and efficiencies of mesoporous perovskite solars cells

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Abstract. The mesoporous perovskite morphologies and optical and electronic properties are influenced by many parameters with which the device performance could be affected. Firstly, the working temperature can be mentioned. Secondly the substrate temperature which combined with spin coated speed could permit to load perovskite inside the mesoporous independent to working temperature. And other factor as the methyl ammonium iodide (CH₃NH₃I) solution concentration could be temperature dependent on the lead iodide, means the reaction is most probable done when the concentration increase with the increasing temperature, whereas the reaction between lead iodide and methyl ammonium can be decrease with lead iodide thickness. It is most probable that the solution concentration also has a significant effect on the morphology of the perovskite that is confined in the pores of the mesoporous TiO₂. It is most probable also the spin coating speed has added at this decreasing, meaning the large size of crystal decreased the transformation lead iodide to Perovskite. Andhere it will try to explain thickness of capping layer can improve the short-circuit photocurrent (J_{sc}) but this enhancement decrease with high working temperature.

1. Introduction

Several perovskite morphologies are been reported to date solvent or deposition dependent [1, 2, 3] and the optical and electronic properties of perovskite materials have been also studied thoroughly in recent decades as the band gap [4, 5], the absorption coefficient [2], and the carrier mobility [6]. The reaction between PbI₂ and CH₃NH₃I can be increased the optical absorption due to the formation of the perovskite. The increase can be observed at different wavelengths. In general, the hybrid perovskites have a very strong tendency to form and crystallize, even at room temperature. Due to the high energy of formation, the hybrid perovskites form even in a solid-state reaction, when the two precursors are brought into contact. Whilst, Poglitsch et al. reported that the position of the CH₃NH₃⁺cation in CH₃NH₃PbI₃perovskite is only fixed in the orthorhombic phase at low temperature and could not be fixed at room temperature due to the cubic symmetry requiring eight identical positions for the cations [7]. As a result, the tetrahedral-coordinated C and N atoms exhibit a disordered state inside the eight tetrahedral of the cuboctahedron around the normal A positions (1/2, 1/2, 1/2) of the ABX₃ perovskite. Therefore, the CH₃NH₃PbI₃ perovskite has tetragonal phase, with a slightly distorted PbI₆ octahedra around the c axis at room temperature [7, 8]. Recently, the crystal chemistry of $CH_3NH_3PbI_3$ was studied in detail [9]. Using a differential scanning calorimeter, a reversible phase transition was found from the tetragonal to cubic transition occurring at 57.3 °C upon heating and a cubic to tetragonal transition at 56 °C upon cooling. A low-temperature stabilized orthorhombic phase was detected at 100 K, where its crystal structure was investigated. A room-temperature stabilized tetragonal phase was calculated to have a band gap of 1.51eV. Otherwise at which temperature limit we could see a real

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variation of J_{sc} of perovskite solar cell. Also the rate of conversion could be depending on the concentration of the CH₃NH₃I solution, so a lower solution concentration leads to slower reaction kinetics, it could have that the reaction kinetics were temperature dependent.

This is not a real study leading to proving the decrease the J_{sc} with the temperature but the observations after many making the devices perovskite solar cells. This investigation is leaded by using AFM, XRD and I-V test. There are many parameters which could decrease the J_{sc} , among them, hole transporting material (HTM) which has played an important role in the decreasing of J_{sc} . But high working temperature decreased the J_{sc} with thickness of perovskite in depositing twice lead iodide. And this article will try to explain this phenomenon in basis on optical and electronic properties.

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 15Ω /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-TiO₂) was deposited on the etched FTO substrate by spin coating (3000 rpm, 30s) using a titanium diisopropoxidebis (acetylacetonate) solution in ethanol and HCl at a volumetric ratio of 0.35:5:1 followed by calcinations at 500 °C. Porous TiO₂ films got by commercially available TiO₂ paste (18-NR-T, Dvesol, average particle size ~ 20 nm) diluted in ethanol (1:3.5 weight ratio) were directly deposited on top of the c-TiO₂ by spin coating at 5000 rpm for 30s and annealed at 500 °C. Thus, the prepared mesoporous TiO₂ films were infiltrated with PbI₂ by spincoating at 5500 rpm or 6500 rpm for 30s and dried at 70 °C. PbI₂ solution is diluted in DMF (dimethylformamide) (462mg/ml) and was kept at 70 °C. After drying, the films were spin coated at 5500rpm or 6500rpm at 30s after loaded 80µl for each substrate a solution of CH₃NH₃I in 2-propanol (18mg/ml) for 30s. After drying, the hole-transporting material (HTM) was deposited by spin-coating 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 (66nm) was thermally evaporated on top of the device to form the back contact.

2.2. Characterization

The morphology of films was characterized by scanning electron microscopy (SEM, SU8010), we have also used atomic force microscopy (AFM) for getting more information about perovskite morphologies. The crystal structure was examined using X-ray Diffractometer (XRD, D8 ADVANCE, Cu K α radiation, λ =1.54Å, tube voltage = 40kV, tube current = 30mA). 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, 100mWcm⁻²). The absorption of different films was measured using a UV-visible Spectrophotometer (UV-2450, Shimadzu). Incident photon-to-current conversion efficiency (IPCE) spectra were recorded using the QE-R (Enlitech) quantum efficiency measurement system. A calibrated silicon solar cell was used as reference.

3. Results and discussion

3.1. Top-view SEM images and cross-sectional

Firstly in Figure 1 is shown the different morphologies with variation loading content, PbI_2 film becomes dense with increasing loading content. Secondly, in figure 1(d) and 1(e) are shown the variation of perovskite morphologies using same CH_3NH_3I solution concentration but different PbI_2 loading content. Perovskite crystal size increases also with increasing PbI_2 loading content.



Figure 1. (a), (b) and (c) PbI_2 deposited into TiO_2 at different loading content, (d) and (e) perovskite on TiO_2 with different volume loading of PbI_2 .



Figure 2. Cross-sectional SEM of a complete photovoltaic device FTO/c-TiO₂/m-TiO₂/ CH₃NH₃PbI₃/spiro/Ag

Figure 2 shows cross-sectional SEM of a photovoltaic device. The pore filling of TiO₂ with perovskite increase with TiO₂ thickness but Power Conversion Efficiency (PCE) is best with the thinner TiO₂ layer about 260 nm still have large capping layer of perovskite[10]. It's also confirmed that the pore filling of TiO₂ depend with temperature of substrate when the substrate temperature is above 100 $^{\circ}$ C before PbI₂ deposition, the J_{sc} and PCE become strongly better [11, 12].

3.2. Atomic Force Microscopic (AFM)

The investigation with AFM is allowed to show that the capping layer decrease with decreasing the content of PbI_2 as shown in figure 3. (a) and (d) and also with increasing of spin coating speed for this reason there are different views with different speeds deposition as shown in figure 4. (a) and (b). The morphology of perovskite has changed the form in the same substrate at different scales as shown in figure 3. (b) and (c).

Large capping layer of perovskite with thinner layer of TiO_2 is the best architecture device but at room temperature this capping layer of perovskite couldn't be over than 140 nm due to in the triiodide films are limited by about 100 nm diffusion length, so that photogenerated charge in thicker films cannot be efficiently extracted before recombining [13, 14, 15]. Other studies have got results optimum devices performances are obtained for perovskite layer thickness around 210 nm [16] and

300nm [17]. In fact the diffusion length decreases at higher temperature [18], and generally increases charge-carrier recombination rate.



Figure 3.(a) PbI₂ on TiO₂ without capping layer (15µl PbI₂ loading on TiO₂) deposited at speed 6500rpm. (b) and (c) perovskite on TiO₂. (d) PbI₂ deposited twice at 6500 rpm.



Figure 4.PbI₂ deposited on TiO₂ once $(30\mu l)$ with different spin coating speed, (a) with 5500 rpm and (b) with 6500 rpm.

3.3. X-Ray Diffraction (XRD)

The curves in Fig.5a show X-ray diffraction spectra measured before the TiO₂/PbI₂ film is brought into contact with the CH₃NH₃I solution with PbI₂ deposited into TiO₂ at different loading volume. Crystal grow in a preferential orientation along the c axis [1, 19, 20], then the main diffraction peak corresponding to the (001) lattice plane. The diffraction peak at $2\theta = 38^{\circ}$ can be attributed to the diffraction from (110) lattice plane of 2H polytype, suggesting that the anatase scaffold induces a different orientation for the PbI₂ crystal growth, but the diffraction peak attributed to the (111) lattice plane doesn't appear in the curve at different loading volume. The curves in Fig.5b show X-ray diffraction spectra measured after the TiO₂/PbI₂ film is brought into contact with CH₃NH₃I solution. The conversion of PbI₂ nanocrystals in the mesoporous TiO₂ film should be practically complete on a timescale of seconds, as is evident from the immediate disappearance of its most intense diffraction peak corresponding to the (001) lattice plane, and the concomitant appearance of the XRD reflections

for the tetragonal perovskite. The peaks at 14.17, 28.47 and 43.27 $^{\circ}$ are respectively assigned to the (110), (220) and (330) planes. The presence of these peaks indicates that the conversion to perovskite, while incomplete, is done. The conversion of PbI₂ to perovskite decreases with film thickness at high working temperature as is shown in Fig.5b.



Figure 5. (a) Spectra of PbI_2 deposited on TiO_2 at once and twice (20µl). (b) Spectra of perovskite with different loading content on TiO_2 .

3.4. Current density-voltage (I-V) characteristics

The current density (J)-voltage (V) characteristics of the solar cells is measured under simulated air mass 1.5 global (AM1.5G) solar irradiation as is shown in Fig.6. The short-circuit current increases at low working temperature but the decreasing of the fill factor (FF) parameter is not only due to high temperature, while open circuit voltage remains same at different working temperature.



Figure 6. J-V curves for photovoltaic devices with same volume of PbI₂ loading at different working temperature.

3.5. Absorption

The optical properties of $CH_3NH_3PbI_3$ have been investigated, where the exciton binding energy and exciton Bohr radius have been determined to be 50 meV and 22 Å. Since the Bohr radii is relatively large and the exciton binding energy small, the excitons from $CH_3NH_3PbI_3$ will be Wannier-type [7]. And a material with a low exciton binding energy, the exciton is rapidly quenched with increasing temperature. Apart from photoluminescence fact, the formation of perovskite could be incomplete and decrease the absorption spectrum. The band gap of PbI_2 is about 2.5 eV corresponding to an absorption onset of about 500 nm. Any wavelength between 500 nm and the absorption onset of the

perovskite absorber (800nm) should therefore be suitable to monitor the formation of $CH_3NH_3PbI_3$. In figure 7 is shown the curves of absorbance spectra which are almost same with a small decreasing between 600 and 800 nm when the thickness of perovskite increases. This means that the transformation of PbI_2 to $CH_3NH_3PbI_3$ isn't complete [11]. It's also most probable that the twice deposition of lead iodide doesn't improve the absorption.



Figure7. Spectra of perovskite absorbance with different volume of PbI₂ deposited on TiO₂.

3.6. IPCE



Figure8. IPCE spectrum of photovoltaic device without capping layer at high-working temperature $(J_{sc}=10.3 \text{ mA/cm}^2)$.

The Equation (1) of IPCE (incident photon-to-electron conversion efficiency) or EQE (external quantum efficiency) corresponds to the internal efficiencies, meaning the electronic processes within the devices, where LHE is the light harvesting efficiency, and η_{inj} and η_{coll} are the electron injection and charge collection efficiencies respectively.

$$PCE(\lambda) = LHE(\lambda) \times \eta_{ini}(\lambda) \times \eta_{coll}(\lambda)$$
(1)

In figure 8 is shown IPCE spectrum as a curve with a maximum around 550 nm, it means that the diffusion length is short due to a high working temperature.

4. Conclusion

XRD spectra have been allowed to see that the conversion PbI_2 to perovskite is incomplete at high working temperature furthermore became insignificant with increase thickness. Capping layer with twice deposition of lead iodide is the best way for improving the J_{sc} but high working temperature is

an inconvenient factor for this enhancement by decreasing the diffusion length. The precise mechanism which working temperature is responsible for reducing the J_{sc} is not fully understood and the parameter such as decreasing the speed coating could decrease the J_{sc} . And the absorption decreases with the conversion PbI₂ to CH₃NH₃PbI₃ which becomes incomplete with the increase perovskite thickness.

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