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The effect of ALD-ZnO layer on the formation of $CH_3NH_3PbI_3$ with different perovskite precursors and sintering temperatures

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ZnO films deposited by atomic layer deposition at 70 ℃ were used to fabricate perovskite solar cells, and a conversion efficiency of 13.1% was obtained. On the ZnO layer, $CH_3NH_3PbI_3$ was formed at room temperature using CH_3NH_3I and $PbCl_2$ precursor, which is in contrary with the reported results.

Hybrid organic–inorganic perovskites based on organolead halides have been given a great deal of attention in the field of solar cells. A power conversion efficiency (*PCE*) of 16.7 % has been obtained using perovskite as light absorber[1]. This dramatic improvement in efficiency has occurred over a mere five years, and some reports suggest that solar cells with efficiencies of 20% could be achieved[2]. Commonly, for perovskite solar cells, the underlying TiO_2 compact layer requires high-temperature sintering at 450–500 ℃ [1, 3], which limits its compatibility with plastic substrates. Therefore, low-temperature processing is the most important aspect of solar cell research and could allow for commercialization by reel-to-reel processing and the development of new multi-junction device architectures. ZnO is a viable alternative to TiO_2 for perovskite solar cells with high PCE because it has energy levels comparable to those of TiO_2 as well as having good electron transport properties[4]. Additionally, ZnO layer can be deposited easily and requires no high-temperature sintering step. Solar cells based on a ZnO nanoparticle layer have already achieved high performance[5].

Although the nanocrystalline ZnO electron collection layer, forming an intimate junction of large interfacial area with the $CH_3NH_3PbI_3$ film, is much more effective in extracting electrons from the perovskite than a planar ZnO film, the ZnO film fabricated by atomic layer deposition (ALD) method has many merits, such as large-scale, low-temperature fabrication and high repeatability[6]. In this study, compact ZnO layers were deposited by ALD method at 70 ℃. These ZnO layers were then used to fabricate perovskite solar cells by a single step method.

High purity diethylzinc and H_2O were used as the Zn and O precursors to deposit 30 nm thick compact ZnO layers onto FTO glass. A 350 nm thick mesoporous Al_2O_3 layer composed of 30 nm sized particles was then deposited by spin-coating. After that, in a N_2-purged glove box, the precursor solution containing CH_3NH_3I and PbI_2 was spin-coated onto the mesoporous Al_2O_3 layer at room temperature, followed heating at 100 ℃ for 10 min. Subsequently, the spiro-OMeTAD-based hole-transfer layer was deposited. Finally, a 120 nm thick silver layer was thermally evaporated onto the hole-transfer layer, forming the back contact of the device.

Fig.1 (a) shows the scanning electron microscope (SEM) images of a compact ZnO layer fabricated on a FTO substrate using the ALD method. The resultant thin ZnO layer replicates remarkably well the underlying FTO relief morphology. It is apparent in the SEM images that the surface lacks any visible pinholes. The compact ZnO layer acts as a hole-blocking layer that avoids intimate contact between the FTO and perovskite. As the ALD-ZnO layer is more compact than that of solution-based ZnO layers, it will efficiently suppress charge recombination inside the cells. The *J-V* curve of the best-performing device is shown in Fig.1 (b). Values of 20.4 mA cm^{-2}, 976 mV and 0.66 were obtained for the short circuit current (J_{sc}), open circuit voltage (V_{oc}), and fill factor (*FF*), respectively, yielding a *PCE* of 13.1% under standard AM1.5 illumination. This demonstrates that the ALD method can prepare compact ZnO layers at low-temperature and, allowing for large-scale fabrication, has broad prospects in the domain of perovskite solar cells with the potential to meet commercial demand.
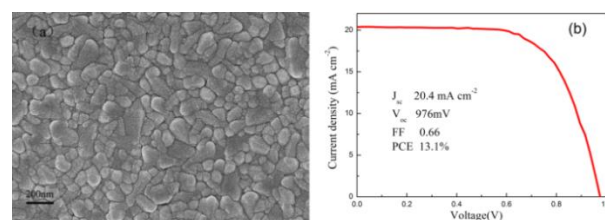

Fig. 1 (a) Top-view FE-SEM images of the surface of 70℃-ALD-ZnO compact layer on FTO glass; (b) *J-V* curves for the best-performing cell measured at a simulated AM1.5G solar. The effective area of the cell was defined as 0.04 cm^2 using a non-reflective metal mask.

In addition, a precursor solution containing CH_3NH_3I and $PbCl_2$ was used to prepare perovskite films by a single-step method. It was found, on the ALD-compact ZnO film, $CH_3NH_3PbI_3$ was completely formed at room temperature in just a few minutes, which is in contrary with the reported results[7]. For comparing, two other compact layers, TiO_2 layers deposited by ALD method and ZnO layers deposited by sol-gel method on FTO/glass substrate, were also used to deposit perovskite films. Moreover, glass and FTO/glass were also used.
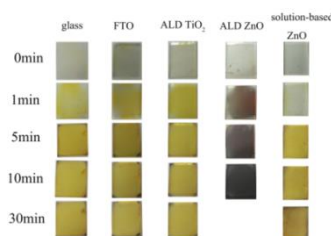

Fig. 2 Photo images of the perovskite films prepared with precursors containing $PbCl_2$ and CH_3NH_3I on different layers (as indicated) and placing at room temperature in the glovebox with varying duration (as indicated)

Fig.2 shows the appearance of the perovskite film deposited by spin-coating onto different substrates after various standing times (0-60 min) at room temperature. All the thickness of the TiO_2 and ZnO layers are about 30 nm. It is observed that on glass, FTO/glass, TiO_2/FTO/glass, the colour of the spin-coated film always remains yellow corresponding to the colour of PbI_2. This indicates that, in this case, the perovskite was not been formed. However, it is amazing to notice that the colour of perovskite film formed on the compact ZnO layer deposited by ALD was changed in a few minutes. The metachromatism of the perovskite film indicates the formation of the perovskite according to regular observations of the colour change of perovskite film with heating, and X-ray diffraction (XRD) measurements of the film provides evidence for the complete formation of $CH_3NH_3PbI_3$ without the appearance of PbI_2 as shown in Fig.3(a). The SEM image (Fig.3b) also presents the typical perovskite structure with a crystalline particle size of approximately 1 μm, similar to that of previous work[8]. Fig.2 indicates that the formation of perovskite film on ALD-ZnO is not only different from that on TiO_2 compact layer, but also different from that on solution-method ZnO layer.
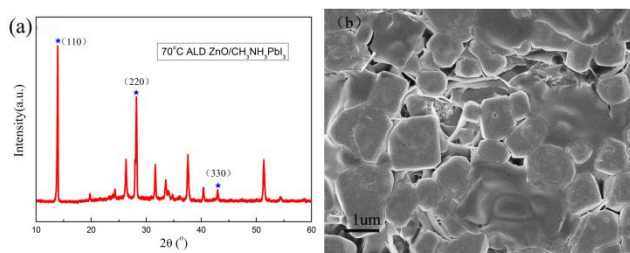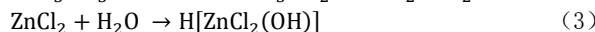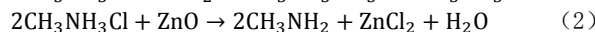

Fig.3 (a) XRD of the $CH_3NH_3PbI_3$ on ALD-ZnO film;(b) SEM micrograph of the surface of the ALD-ZnO/$CH_3NH_3PbI_3$.

However, all previously reported perovskite formation methods using either a single step or sequential deposition required heating to form the perovskite[7, 9], and have confirmed that using a precursor containing $PbCl_2$ and CH_3NH_3I will slow down the rate of reaction, which will improve uniformity, controllability and crystallinity of perovskite films, compared to those prepared with precursors free from chloride ions[7].

The formation of a perovskite film on ALD-compact ZnO layers deposited at 70 ℃ after standing for a few minutes at room temperature probably due to the reaction of CH_3NH_3Cl and ZnO. At room temperatures, the conversion to the perovskite dominates following Reaction (1), and the rate is very slow, however if CH_3NH_3Cl is depleted, the Reaction (1) will be promoted[7]. According to the metachromatism of the perovskite film on ALD-ZnO, so it was speculated that ZnO will react with CH_3NH_3Cl, as shown in reaction (2). The energy dispersive spectra (EDS) measurements as shown in Fig.5 confirmed a large number of chloride ions, which suggest the existence of $ZnCl_2$. To avoid the residual chloridion in the formed perovskite, before the EDS measurement, the samples were heated at 200 ℃ for 3 h in order to completely decompose the perovskite. But Reaction 2 did not happen for solution-method ZnO film. The difference between ALD-ZnO and solution-ZnO is that there are a large number of oxygen vacancies in ALD-ZnO[10]. We thought the oxygen vacancies in ALD-ZnO enhance its reaction activity, which is commonly accepted in the photocatalytic field[10]. In this study, the existing of oxygen vacancies promotes the reaction of ZnO and CH_3NH_3Cl. Nevertheless, ZnO did not react with CH_3NH_3I for the different electronegativity of chlorine and iodine. Of the products of Reaction (2), CH_3NH_2 is in the gas phase and H_2O can be absorbed by $ZnCl_2$ because $ZnCl_2$ is extremely deliquescent in air (Reaction 3).The

appearance of H_2O will therefore not lead to the decomposition of $CH_3NH_3PbI_3$. For ALD-ZnO, due to the existence of Reaction (2), Reaction (1) will continue unless $CH_3NH_3PbI_3$ is totally formed.

$$3CH_3NH_3I + PbCl_2 \rightarrow CH_3NH_3PbI_3 + 2CH_3NH_3Cl \quad (1)$$
$$2CH_3NH_3Cl + ZnO \rightarrow 2CH_3NH_2 + ZnCl_2 + H_2O \quad (2)$$
$$ZnCl_2 + H_2O \rightarrow H[ZnCl_2(OH)] \quad (3)$$

To further investigate the formation mechanism of perovskite on ALD-ZnO films, the sintering of ALD-ZnO films at different temperatures carried out. Photos comparing perovskite films on 70 ℃-ALD-compact ZnO films sintered at different temperatures are exhibited in Fig.4. The subsequent perovskite film formation process became slower when the sintering temperature increased from 70 to 450℃ and the compact ZnO film sintered at 350 and 450℃ for 30 min could not drive perovskite formation at room temperature. This increase in sintering temperature improved the crystallinity of ZnO films and decreases the content of oxygen vacancy, the change in perovskite formation indicates that ZnO sintered at high temperature does not react with CH_3NH_3Cl at room temperature. Subsequently, it was observed that perovskite can be formed at temperatures of 70 and 80 ℃ for ALD-compact ZnO layers sintered at 350 and 450 ℃, respectively. In the standard case, where the precursor containing chloridion is spin-coated onto a compact TiO_2 layer, annealing at 100 ℃ for 45min is required to lead to the formation of the lead-iodide based perovskite material[11]. The EDS (Fig.5) of the layers also confirmed a large number of chloride ions reside at the interface between ALD-ZnO sintered at 450 ℃ and PbI_2, where, no chloride ions were observed in the sample based on an ALD-TiO_2 film. It demonstrated that the ALD-ZnO sintered at high-temperature can react with CH_3NH_3Cl at a higher temperature than as-deposited ALD-ZnO, and at a lower temperature than TiO_2.
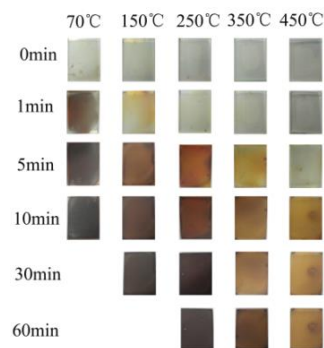

Fig.4 Images of the perovskite films on ALD-method ZnO compact with varying the placing time. ZnO compact film deposited at 70°C were sintered at different temperature.
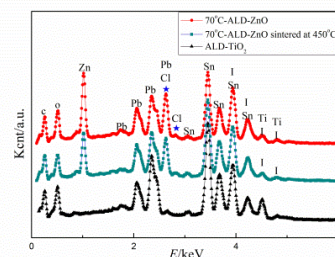

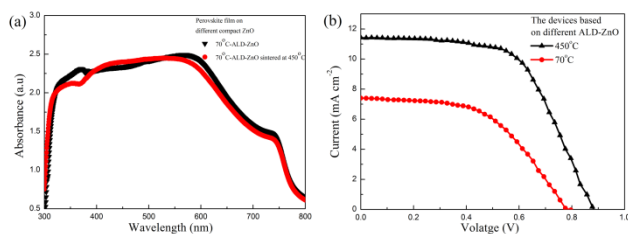**Fig.5** EDS of the samples based on different compact layers after heating at 200 ^{o}C for 3h
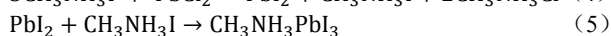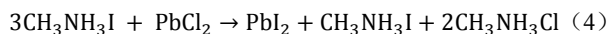
Fig.6 (a) UV-vis absorption spectra of perovskite films on different compact ZnO substrate; (b) *J-V* curves of the best performing solar cells prepared using ALD-ZnO and ALD-ZnO sintered at 450 ℃ processed compact layers.

Table 1 Photovoltaic performance of perovskite solar cells based on different compact ZnO blocking layers

Different substrate	V_{oc} (mV)	J_{sc} (mA cm^{-2})	FF	R_s (Ω cm^2)	R_{sh} (Ω cm^2)	PCE (%)
ALD-ZnO sinteredat450℃	877	11.4	0.59	934	5864	5.96
ALD-ZnO	796	7.4	0.51	1939	1377	3.02

To study the impact of the metachromatism of the perovskite on the performance of ALD-compact ZnO layers in perovskite solar cell, we fabricated a group of perovskite solar cells with the traditional FTO/ZnO/perovskite/spiro-OMeTAD/Ag structure under identical conditions, but with different compact ZnO films, either ALD-ZnO or ALD-ZnO sintered at 450 ℃, using a precursor solution containing PbCl$_2$ and CH$_3$NH$_3$I. The *J-V* curves of the devices with different ZnO films are shown in Fig.6b, and their corresponding photovoltaic parameters are listed in Table1. Devices fabricated with the 70 ℃-ALD-ZnO layer yielded low performances with a low J_{sc}, V_{oc}, and *FF*. In contrast, the performance was improved, yielding a J_{sc} of 11.2 mA cm^{-2} and a V_{oc} of 877 mV, together with a *FF* of 0.59, by using a ZnO layer sintered at 450 ℃, resulting in a high PCE of 5.96%. In Table 1, the shunt resistance, R_{sh}, and series resistance, R_s, values of the corresponding devices are also listed. R_{sh} is closely related to the interfacial charge recombination inside the device. The ALD-ZnO solar cell sintered at 450 ℃ exhibited far higher R_{sh} than the ALD-ZnO solar cell without sintering, indicating efficient suppression of charge recombination inside the cell, which leads to its higher V_{oc} after sintering. It is suggested that the degree of corrosion of the ZnO sintered at 450 ℃ is lower than that of the ALD-ZnO layer without sintering. The R_s of the devices prepared using ALD-ZnO is large, due to the redundant ZnCl$_2$ at the interface between the ZnO layer and the perovskite and results in a lower J_{sc}. The R_s of the device based on ALD-ZnO layer is higher than that on ALD-ZnO sintered at 450 ℃, this is in accordance with the EDS and R_{sh} values and the observation that reaction of the ZnO sintered at 450 ℃ is lower. Because of the identical absorption spectra of perovskite films on different compact layers (Fig 6a), the J_{sc} of the device based on ALD-ZnO sintered at 450 ℃ was also larger. The higher R_{sh} and lower R_s enabled a larger *FF*. This experiment clearly indicates that the ALD-ZnO at 70 ℃ was more conducive to the formation of the perovskite by Reaction (2) at room temperature, and when it was sintered at 450 ℃, the formation was driven by the combined actions of Reaction (2), (4), and (5). Reaction (4) is the reaction of CH$_3$NH$_3$I and PbCl$_2$ at higher temperature. CH$_3$NH$_3$I and PbI$_2$ can form the perovskite at 70 ℃ or 80 ℃ by a single step method.

$$3CH_3NH_3I + PbCl_2 \rightarrow PbI_2 + CH_3NH_3I + 2CH_3NH_3Cl \quad (4)$$
$$PbI_2 + CH_3NH_3I \rightarrow CH_3NH_3PbI_3 \quad (5)$$

To conclude, we replaced the conventionally used compact TiO$_2$ layer with an ALD-ZnO film deposited at low temperature, and have successfully fabricated an ALD-ZnO-based perovskite solar cell with a high PCE of 13.1% by single step with a precursor containing PbI$_2$ and CH$_3$NH$_3$I. The devices on ZnO compact film using ALD method has equal photoelectrical conversion efficiency to those based on TiO$_2$ compact layer, but the process temperature is lower. It is an irresistible trend of the ALD method that can meet the requirements necessary for commercialization with large-fabrication compared with solution methods, it is very important for the perovskite solar cell into practical application. In addition, we found that the ALD-compact ZnO layer can promote the single step formation of CH$_3$NH$_3$PbI$_3$ with a precursor containing chloridion at room temperature; this is mainly attributed to the reaction of CH$_3$NH$_3$Cl and ALD-ZnO film. Although perovskite formation by the single step containing chloridion method on the ALD-ZnO film at room temperature had a negative impact on the performance of the resulting perovskite solar cells, the compact ALD-ZnO layer also is an ideal substitution to replace TiO$_2$ film in perovskite solar cells using the no-chloridion precursor.

Notes and references

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