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Low Temperature Aqueous Solution-Processed ZnO/TiO_x bilayer Electron-Transport Layer for Highly Efficient Planar Perovskite Solar Cells

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Abstract

ZnO has been considered as a potential electron transport layer due to its high charge carrier mobility and low temperature processability. However, due to the poor chemical compatibility between ZnO and perovskite materials, there is still a challenge to obtain high efficient and stable perovskite solar cells (PSCs). In this study, PSCs with efficiency of over 19% has been realized with low temperature aqueous solution-processed ZnO/TiO_x bilayer as electron transport layer (ETL).

1. Introduction

As one of the promising alternatives to silicon cells, perovskite solar cells (PSCs) has been developed rapidly in recent years due to their ideal material properties.[1] The certified power conversion efficiency (PCE) of PSCs has reached up to 24.22 % in early 2019.[2] In order to further promote the PSC commercialization, the poor stability issue should be resolved. Besides, the intrinsic property of perovskite materials and the contact at interfaces have been considered as the major cause for the stability problem.[3] Therefore, various materials have been developed recently. Among them, inorganic interlayers have received much attention due to their high optical transmittance, high charge carrier mobility, and good air stability. ZnO, TiO_2 and SnO_2 ETLs were also developed to form good contact for efficient electron extraction and transport.

Among these ETL materials, ZnO has excellent optical and electrical properties to become an outstanding electron transport material (ETM) in PSC structures.[4] Besides, the fabrication methods for ZnO film are simple and compatible with low temperature fabrication process. However, ZnO based devices achieved limited progress compared to TiO_2 and SnO_2 based devices, which could be due to the poor chemical stability between ZnO and perovskite caused by the reverse reaction at interface. It has been reported that residual solvent and hydroxyl groups at the ZnO surface could deprotonate the MA cation in perovskite thin films and decompose the perovskite when the temperature is higher than 90 °C.[5]

In this study, we proposed a low-temperature aqueous solution zinc-amine complex for ZnO layer deposition and low-temperature aqueous $TiCl_4$ solution treatment to passivate the ZnO surface to form ZnO/TiO_x bilayer as the electron transport layer. The upper TiO_x layer could passivate the ZnO surface and stabilize the ZnO/perovskite interface. Meanwhile, the bottom ZnO could enhance charge transfer process.[6] Finally, a high PCE of 19.34 % was achieved based on low temperature all aqueous solution processed ZnO/TiO_x bilayer ETL.

2. Results and Discussions

To evaluate the effect of bilayer ZnO/TiO_x ETL on photovoltaic performance, PSCs were fabricated with a configuration of ITO/ZnO/TiO_x/$PC_{61}BM$/$MA_{1-y}FA_yPbI_{3-x}Cl_x$/spiro-OMeTAD/Ag. The detailed device statistical data were summarized in Table I, including open-circuit voltage (V_{oc}), short-circuit current density (J_{sc}), fill factor (FF) and PCE. The optimized ZnO and TiO_x annealing temperature was 250 °C.

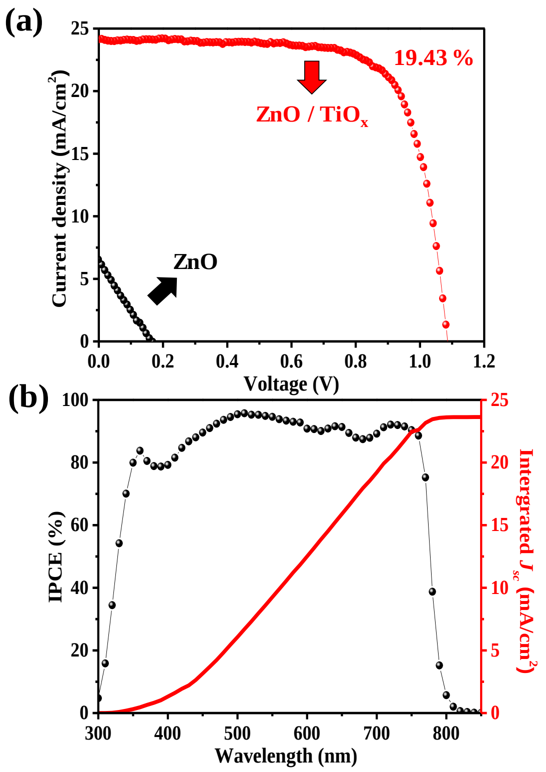

Fig. 1 (a) $J-V$ curves of devices deposited on ZnO and ZnO/TiO_x ETLs at 250 °C. (b) IPCE for PSC with ZnO/TiO_x ETL prepared at 250 °C.

The current density – voltage ($J-V$) curve of PSCs deposited on ZnO and ZnO/TiO_x ETLs at 250 °C was shown in Fig. 1(a). The device based on pristine ZnO with PCBM treatment only exhibited a much lower PCE. Nevertheless, after TiO_x treatment, the best cell (250 °C) exhibited a V_{oc} of 1.08 V, J_{sc} of 24.15 mA/cm^2, FF of 0.74 and PCE of 19.34 %, which demonstrated that TiO_x could efficiently passivate the ZnO surface and enhance the efficiency of PSCs. Fig. 1(b) demonstrated the incident photo-to-electron conversion efficiency (IPCE) spectrum of the PSC deposited on ZnO/TiO_x (250 °C) thin film. The integrated current density was 23.85

mA/cm^2 which closely matched with the measured J_{sc}.

Table I Average photovoltaic parameters of PSCs with ZnO/TiO_x ETL prepared at different temperatures, which were calculated by 15 individual devices.

Temperature (°C)	V_{oc} (V)	J_{sc} (mA/cm^2)	FF	PCE (%)
150	1.03	22.09	0.68	15.69
200	1.05	23.24	0.72	17.65
250	1.06	23.52	0.73	18.20

Top-view SEM images of perovskite films deposited on ZnO and ZnO/TiO_x ETLs at 250 °C were shown in Fig. 2. As reported before, crystalline perovskite grains based on ZnO films were decomposed into PbI_2 grains (film turned into yellow from black) with obvious boundary gaps above 90 °C. After TiO_x treatment, dense crystals were observed (film remained black), which indicated that TiO_x could efficiently passivate the ZnO surface and improve perovskite film quality.

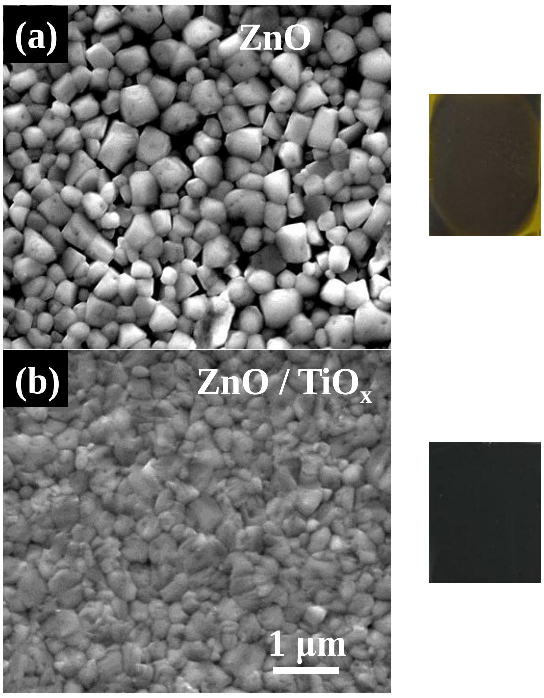

Fig. 2 The SEM images of perovskite films deposited on ZnO (a) and ZnO/TiO_x (b) annealed at 250 °C for 10 min. The real-time picture at the right of SEM images.

In order to characterize perovskite thin film crystallinity, XRD measurement was taken. Fig. 3 showed the XRD patterns of perovskites on ZnO and ZnO/TiO_x annealed at 250 °C. It is obviously observed that the perovskite based on ZnO films, the main peaks of PbI_2 became very strong, while after TiO_x passivation, the PbI_2 characteristic peaks of perovskite was removed with strong characteristic peak of <110>, which was consistent with SEM results.

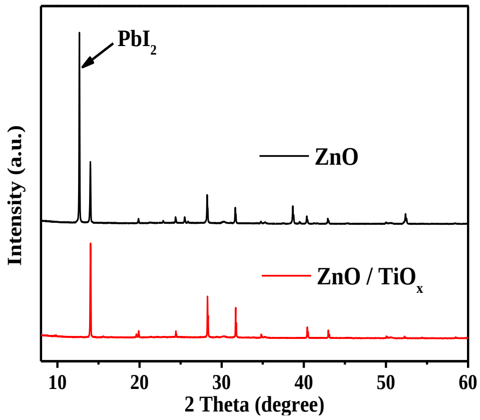

Fig. 3 XRD patterns of perovskite films prepared on ZnO and ZnO/TiO_x ETLs at 250 °C.

3. Conclusions

In conclusion, the quality of perovskite films deposited on low temperature aqueous solution-processed ZnO ETLs was significantly promoted by low temperature aqueous solution-processed TiO_x passivation, which could be confirmed by XRD and SEM results of perovskite. The ZnO/TiO_x annealing temperature was optimized and found 250 °C gave the best device performance. The process of surface passivation is simple and compatible with low temperature process, which can be applicable to flexible solar cells and other optoelectronic devices.

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