ZnO-PCBM bilayers as electron transport layers in low-temperature processed perovskite solar cells

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Abstract
We investigate an electron transport bilayer fabricated at \(<110^\circ C\) to form all low-temperature processed, thermally stable, efficient perovskite solar cells with negligible hysteresis. The components of the bilayer create a symbiosis that results in improved devices compared with either of the components being used in isolation. A sol-gel derived ZnO layer facilitates improved energy level alignment and enhanced charge carrier extraction and a [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) layer to reduce hysteresis and enhance perovskite thermal stability. The creation of a bilayer structure allows materials that are inherently unsuitable to be in contact with the perovskite active layer to be used in efficient devices through simple surface modification strategies.

1. Introduction

The emergence of perovskite solar cells has had a tremendous impact of the field of photovoltaics. Its low-temperature deposition route brings the possibility of large volume processing. The highest reported power conversion efficiency (PCE) at present exceeds 22% [1,2], which marks the rapid progress of this new class of hybrid materials [3]. Many properties of the hybrid perovskite make it suitable for photovoltaic applications, including high carrier mobilities, suitable and direct band gap, low trap densities, and etc. [4–8].

It is likely that perovskite photovoltaics will have impact in many emerging technical areas, such as wearable electronics and remote/isolated power generation systems. The fabrications of these devices benefit from low-cost, large-area routes such as roll-to-roll processing. However most roll-to-roll methods require flexible substrates, which often lack thermal and chemical stability, and therefore electronics should be prepared at low enough temperatures at all steps.

The device architecture of perovskite solar cells was emerged from dye sensitised solar cells (DSSCs), where the so-called regular structure, also known as the top-anode structure, was the most established. In such devices transition metal oxides (TMOs) have been well studied as electron transport layers (ETLs) owing to their suitable energy level alignment, visible transparency, air stability and the precision in electronic structure control, particularly when compared with the organic counterparts. To achieve the goal of low-temperature processing, colloidal nanoparticles (NPs) have been extensively used as ETLs [9,10]. However, the complexities of NPs processing, as well as the difficulties in achieving compact arrays hinder the applications of NPs. As an alternative, sol-gel processing is often preferable due to the ease in preparation, and long-term stability of precursors [11].

Here we incorporate sol-gel processed ZnO as an ETL in regular architecture perovskite solar cells, with a view to overcoming instabilities observed in nanoparticle derived ETLs [12]. Previously we have used similar chemistry to prepare sol-gel layers of ZnO that had a significant impact on the performance of organic solar cells [13,14]. For the use of sol-gel derived ZnO in perovskite devices, Kim et al. [15] reported ZnO deposited at 290 °C with CH3NH3PbI3 (MAPI) active layers. In this work, the ZnO/MAPI interface was modified with [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) to exploit the modulated ZnO electronic structure and reduce trap-assisted charge recombination. Reducing the processing temperature, Zuo et al. [16] annealed ZnO at 160 °C, but with its surface modified using a self-assembled monolayer (SAM), resulting in enhanced wetting and an improved energy level alignment to MAPI. Despite the progress towards reduced temperature of ZnO deposition, there remains the requirement to thoroughly investigate the stability of perovskite active layers when the ETL processing temperature is varied.

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In this manuscript, we investigate the influence of sol-gel ZnO processing temperature on the thermal stability of MAPI films processed in direct contact. PCBM was used as an interfacial modifier [17], which improves MAPI thermal stability and also significantly reduces current-voltage hysteresis. We highlight the importance of the interfacial modifier in stabilising devices prepared using ZnO processed at only 110 °C.

2. Experimental

2.1. Fabrication

Indium tin oxide (ITO, PsiOteC UK Ltd; 12–16 Ω/sq) coated glass substrates were cleaned using ultrasonics and sequential washing in acetone, isopropanol and distilled water followed by a 10 min UV-ozone treatment (UVOCs).

ZnO sol-gel solutions were prepared by dissolving equimolar zinc acetate dihydrate and 2-amino ethanol in 2-methoxyethanol followed by overnight stirring in dark and in air. Thin films were spin coated at 3,000 r/min for 30 s in air and then annealed on a hotplate at 110 °C for 30 min. PCBM was dissolved in chlorobenzene and heated at 60 °C with stirring overnight in a N2 filled glovebox. Spin coating of PCBM was in a glovebox at 1,000 r/min for 30 s and subsequently annealed on a hotplate at 70 °C for 3 min.

The perovskite precursor was prepared by dissolving 1.25 mol/L methylammonium iodide and lead iodide in mixed solvent of dimethyl sulfoxide and gamma-butyrolactone (3:7 by volume). The solution was stirred at 60 °C for 2 h in air. The perovskite layer was fabricated via a so-called “toluene-dripping” method [18]. The precursor solution was first spin coated at 500 r/min for 5 s and then 2,000 r/min for 20 s. A 50 mL of toluene was rapidly dripped onto the film at the end of second stage of spinning, and followed by spun at 4,000 r/min for 20 s. The films were annealed on a 100 °C hotplate after spin coating. Both the spin coating and annealing processes were carried out in a N2 filled glovebox.

For the hole transport layers, the precursor solution was prepared by dissolving 82 mg 2,2',7,7'-tetraakis[N,N-di(4-methoxyphenyl)amino]-9,9'-spirobifluorene (spiro-OMeTAD) in 1 mL of chlorobenzene. 15.6 µL of bis(trifluoromethane)sulfonimide lithium salt (Li-TFSI) solution (450 mg in 1 mL of acenitride) and 24.4 µL of 4-tet- butylpyridine were added as additives. The solution was stirred at room temperature for 30 min and was filtered before use. Hole transport layer was prepared by spin coating the solution onto perovskite film at 3,500 r/min for 45 s in a N2 filled glovebox. The devices were put in dark prior to measurement and were measured in a nitrogen filled chamber.

2.2. Characterization

Film thicknesses were measured with a surface profilometer (Dektak 150). Optical transmission was accomplished using a custom single-beam UV–vis spectrometer (Agilent Technologies Cary 5000). Film morphology was studied using (1) a field emission scanning electron microscope (FESEM, LEO Gemini 1525) with the addition of a 5 nm chromium layer, and (2) an atomic force microscope (AFM, Bruker Multimode Nanoscope MMAFMLN) with image processing by the Gwyddion software suite. X-ray diffraction patterns were obtained using a diffractometer with Cu Kα as the source (XRD, Panalytical X'Pert Pro). Work functions were obtained from the measured chemical potentials using a Kelvin probe (KTechnology SKP5050) in air, with a highly ordered pyrolytic graphite reference for the calibration.

Transient absorption decays were investigated by exciting the sample film, under a N2 atmosphere, pumped with a Nd:YAG (YAG, Y3Al5O12) laser (Lambda Photometrics). The excitation wavelength of the laser was 500 nm, with a pump intensity of 8 µJ/cm² and a repetition frequency of 20 Hz. The probe light source is a 100 W quartz halogen lamp (Bentham, IL 1) with a stabilized power supply (Bentham, 605). A silicon photodiode (Hamamatsu Photonics, S1722-01) was used to detect the probe light passing through the sample film. The signal from the photodiode was pre-amplified and delivered to the main amplification system with an electronic band-pass filter (Costronics Electronics). A digital oscilloscope (Tektronics, TDS220) was used to collect the amplified signal, which was synchronized with a trigger signal of the pump laser pulse from a photodiode (Thorlabs Inc., DET210). To reduce scattered light, stray light and sample emission, a monochromator and appropriate optical cut-off filters were put before and after the sample.

2.3. Device testing

Current-voltage curves of perovskite solar cells were collected using a xenon lamp (1 Sun, AM 1.5 G, Oriel Instruments) with a Keithley 2400 source meter. The light intensity was adjusted to 1 Sun before use by adjusting the working current, which was calibrated using a standard silicon reference photodiode. All devices were stored in dark prior to measurement and were measured in a nitrogen filled chamber.

3. Results and discussion

Our investigations employ low-temperature derived ZnO as the ETL, and MAPI as the perovskite active layer. We studied the influence of ZnO processing temperature on the thermal stability of MAPI films above. The thermal stability test was performed by annealing glass/ITO/ZnO/MAPI stacks at 100 °C in a N2 filled glovebox for 60 s. Significant variation in thermal stability is seen in the XRD patterns obtained from ZnO films processed between 110 and 450 °C, Fig. 1a, specifically the intensity variation between the (001) peak of PbI2 12.8° and the (110) peak of MAPI at 14.2° [19–22]. The presence of PbI2, a degradation product of MAPI, confirms thermal instability of the perovskite layer when deposited on top of the low temperature processed ETL films — only in the ZnO processed at 450 °C is stability observed. The surface morphology of perovskite films was investigated by SEM images, shown in Figs. S1 and S2 (online). In our previous work, we have shown that low temperature sol-gel ZnO films contains monoethanolamine and acetate species from the precursor [13,14]. Thus, the presence of surface hydroxyl groups and residual acetate ligands may be the reason for the perovskite thermal instability on our low temperature sol-gel ZnO films [12]. To overcome this limitation, we inserted a PCBM layer between ZnO and the MAPI active layer. We compared the thermal stability of MAPI on PCBM modified ZnO (110 °C), against on non-modified, high-temperature processed ZnO (450 °C) (Fig. 1b). After annealing, again at 100 °C in N2, however this time for 20 min, MAPI degradation is observed on the 450 °C ZnO ETL stack but not on the 110 °C ZnO. The origin of this instability may arise from the proton-transfer reaction at the ZnO/CH3NH3PbI3 interface due to the basic nature of the ZnO surface [12]. Hence the insertion of PCBM dramatically increases the thermal stability of the MAPI which allows the low-temperature processed ETLs to be used.

To compare the performance of modified and non-modified ETLs, devices were prepared with ZnO (110 °C, 30 nm) and ZnO...
The device structure (layer thicknesses in parenthesis) is glass/ITO (140 nm)/ETL/CH$_3$NH$_3$PbI$_3$ (300 nm)/spiro-OMeTAD (100 nm)/MoO$_x$ (10 nm)/Ag (100 nm). The ETL, perovskite and spiro-OMeTAD layers were solution processed, and the MoO$_x$ and Ag thermally evaporated. Representative current-voltage (J-V) curves are shown in Fig. 2a. It can be seen that device performance with ZnO (110 °C)/PCBM is much better than that with bare ZnO (110 °C). Poor device performance with bare ZnO (110 °C) is likely to originate in the inherent instability of the MAPI when in contact with the low-temperature processed ZnO. Devices with bare ZnO annealed at 450 °C (Fig. S3 online) show high performance compared to that with bare ZnO annealed at 110 °C, but still suffer from the J-V hysteresis issue. Notably, device with PCBM modified ZnO (110 °C) showed good performance with negligible J-V hysteresis at room temperature, as shown in Fig. 2b. The champion device without J-V hysteresis is with ZnO (110 °C, 30 nm)/PCBM (30 nm), showing 12.3% PCE with open-circuit voltage ($V_{OC}$) 1.1 V, short-circuit current density ($J_{SC}$) 19.1 mA/cm$^2$ and fill factor (FF) 58.8%. Thus PCBM can be inserted to significantly reduce J-V hysteresis when presents as a simple interface modifier and without the requirement of PCBM infiltrating the inter-grain structure of the perovskite, as has been reported in inverted architecture devices [23].

Fig. 2. J-V characterization. (a) Representative J-V characteristics for perovskite devices prepared using ZnO (110 °C) and ZnO (110 °C)/PCBM as electron transport layers (ETLs); (b) J-V characteristics for perovskite devices using ZnO (110 °C)/PCBM bilayer as ETLs measured by forward and reverse scans.

Given the good performance observed in the PCBM modified ZnO our curiosity focused on whether device processing can be simplified as to use only PCBM as an ETL. Representative J-V curves for devices prepared with a range of PCBM thicknesses are shown in Fig. 3. It is apparent that the absence of any ETLs result in large J-V hysteresis. As the PCBM thickness increased to 30 nm the J-V hysteresis reduces significantly, at 35 nm PCBM hysteresis reduced but an s-shaped curve emerges, due to increased series resistance that can be seen at $J = 0$. Further thickness increases result in devices with reduced performances. The high sensitivity of device series resistance to the PCBM film thickness may originate from the bulk resistance of PCBM films, caused by low electron mobility [24]. Thus, the co-existence of J-V hysteresis and s-curves for the 35 nm PCBM device indicates that PCBM is not suitable as an ETL in perovskite cells with conventional device structures.

To derive an understanding of the symbiotic relationship between the low-temperature sol-gel processed ZnO and PCBM, a range of complimentary measurements were carried out. Good optical transparency is observed across the visible spectral region of the PCBM modified ZnO as well as PCBM itself (Fig. S4 online). The crystallinity of MAPI on PCBM and PCBM modified ZnO are similar, Fig. S5 (online) indicates no detectable PbI$_2$ or precursor peaks – suggesting that the crystallisation of MAPI is not influ-
Fig. 3. J-V curves of device with PCBM as ETL. (a) 0 nm; (b) 30 nm; (c) 35 nm (d) 50 nm.

Fig. 4. (Color online) Surface morphology of PCBM and MAPI films. Representative AFM images of PCBM (a) and ZnO (110 °C)/PCBM films (b) on ITO substrates, both indicating smooth and compact surface morphology. SEM images of CH₃NH₃PbI₃ on PCBM (c) and ZnO (110 °C)/PCBM films (d), both showing dense films without pin-holes.
ence by the ZnO. Good contact between ETLs and MAPI layers are also confirmed by cross-section SEM images, Fig. S6 (online). Atomic force microscopy (AFM) images of PCBM and ZnO (110 °C)/PCBM on ITO substrates are shown in Fig. 4a and b, indicating both smooth and compact surface morphologies, with root mean square (RMS) roughness 0.24 and 0.19 nm respectively. This is further confirmed from the SEM results, as shown in the Fig. S7 (online). The smooth surface of ZnO (110 °C)/PCBM bilayer hints at the fact that the layer contact between the PCBM and the perovskite is sufficient for PCBM to passivate the perovskite and to eliminate J-V hysteresis. The SEM images of MAPI films on top of PCBM and ZnO (110 °C)/PCBM are shown in Fig. 4c and d. We observe a dense-grained uniform surface morphology with grain sizes in the range 100–400 nm.

The work function (WF) of our ETLs and ITO substrates was calculated from the contact potential difference measured by Kelvin probe in ambient air (Fig. 5). Freshly cleaved highly oriented pyrolytic graphite was used as the reference (WF = 4.47 eV). The WF of PCBM (4.81 eV) is deeper than that of ITO substrates (4.47 eV), which may cause a charge extraction barrier towards the ITO cathode. One reason of J-V hysteresis in perovskite solar cells is the charge accumulation at the interfacial contact due to the inefficient charge transfer [25]. Hence, the hysteresis in devices containing only PCBM as an ETL may originate from the electron extraction barrier between ITO and PCBM. However, the WF is significantly reduced by inserting a ZnO (110 °C) layer between ITO and PCBM (Fig. 5). The low WF of ZnO (110 °C) films (4.34 eV) deposited by sol-gel method is ascribed to the interfacial dipole formed between the electron accepting ZnO and the electron donating amine group due of the MEA residues [13]. Schematic energy level of each layer in devices is shown in Fig. 5 [9,16,26–28], with measured ITO and ETL work functions. Lowered work function by insertion of ZnO (110 °C) enhances the energy level alignment, which increases the electron extraction speed and subsequently reduce the J-V hysteresis [16].

Fig. 6 shows μ-transient absorption (TA) kinetics of PCBM/MAPI with and without ZnO, excited selectively the CH3NH3PbI3 at 500 nm, and probing the MAPI ground state bleach signal at 750 nm (Fig. S8) (online) [29]. This bleach signal, which has a power law decay, is assigned to charge carriers remaining in the MAPI layer [26]. When a layer of ZnO is added next to the PCBM layer, the signal of these carriers diminishes within our instrument respond time (faster than 1 μs) suggesting the carriers are more efficiently extracted with the combination of ZnO/PCBM bilayer than that without the ZnO layer.

4. Conclusions

We investigate an electron transport bilayer processed at <110 °C to form all low-temperature fabricated efficient perovskite solar cells with negligible hysteresis and good thermal stability. The components of the bilayer create a symbiosis that results in improved devices compared with either of the components being used in isolation. A sol-gel derived ZnO layer facilitates improved energy level alignment and enhanced charge carrier extraction and a PCBM layer to reduce hysteresis and enhance perovskite thermal stability.

Using non-modified ZnO the thermal stability of the perovskite active layer improves as the ZnO processing temperature is increased, however some thermal instability is observed, even at moderate anneal durations, that may originate from the proton-transfer reaction at the ZnO/MAPI interface due to the basic nature of the ZnO surface. PCBM on its own shows poor energy level alignment with the surrounding layers in a conventional architecture device and the inherent low charge carrier mobility results in an increased series resistance in devices. However the combination of low-temperature processed, sol-gel-derived ZnO modified with PCBM allows both materials to work together to produce efficient devices, with enhanced thermal stability and significantly reduced J-V hysteresis.

Conflict of interests

The authors declare that they have no conflict of interest.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.scib.2018.02.004.
