Aerosol assisted chemical vapour deposition of conformal ZnO compact layers for efficient electron transport in perovskite solar cells

*Shuqun Chen,[a] Jinshu Wang,[*a] Zhixin Zhang,[a] Joe Briscoe,[b] Michael E. A. Warwick,[c] Hongyi Li,[a] Peng Hu[a]*

[a] School of Materials Science and Engineering, Beijing University of Technology, Beijing, 100124, China. E-mail: wangjsh@bjut.edu.cn

[b] School of Engineering and Materials Science, Queen Mary University of London, Mile End Road, London, E1 4NS, UK

[c] Energy Safety Research Institute, Swansea University, Fabian Way, Swansea, SA1 8EN, UK

Abstract: Ultrathin and compact ZnO films were firstly deposited on textured fluorine-doped tin oxide (FTO) electrodes via aerosol assisted chemical vapour deposition (AACVD). Planar $CH_3NH_3PbI_3$ perovskite solar cells (PSCs) were fabricated under ambient conditions and a best power conversion efficiency (PCE) of 11.75% was achieved.

Keywords: Chemical vapour deposition; Thin films; Solar energy materials; Zinc oxide

1. Introduction

Transparent conductive oxide coatings are key in large scale thin film solar cell manufacture. FTO, for example, has been extensively utilised as front electrodes. [1] Growth of ultra-thin ZnO layer on surface-textured FTO has attracted a great deal of attention in recent years. This is due to substantial progress in developing planar-type PSCs, wherein ZnO can be employed as an efficient electron transport layer (ETL). [2] This metal oxide interlayer is required to be pin-hole free to eliminate the electrical shunts between the electrode and perovskite absorber and thin enough (normally 20-50 nm in thickness) to minimize the charge recombination within the oxide. Currently, sol-gel spin coating and atomic layer deposition (ALD) techniques have been reported to deposit ZnO compact layers on rough FTO for electron transporting in PSCs.[3,4] It is widely known that spin coating is not compatible with high-volume large area solar cell manufacturing,[5] and ALD on the other hand requires expensive precursors and facilities, hampering its large-scale application.[6] In this respect, new investigations on a better ZnO ETL deposition method are highly demanded.

Chemical vapour deposition at atmospheric pressure (APCVD) is one of the most promising approaches for producing large-are thin film materials. However, growth of ultra-thin ZnO by conventional APCVD remains a challenge due to high film growth rates (in the order of 10 nm s^{-1}) making the process hard to control.[7] To address this problem, here we propose an aerosol-assisted CVD technique to synthesis conformal ZnO coatings with thickness down to 20 nm onto textured FTO electrodes and serve as the ETL in planar PSCs. The resulting $CH_3NH_3PbI_3$ PSCs fabricated under ambient conditions achieves a maximum power conversion efficiency of 11.75%.

2. Experimental

AACVD of ZnO on pre-patterned FTO glass substrates was carried out in a tubular horizontal bed reactor. Precursor solutions were prepared by dissolving 25-75 mg zinc-acetate-dihydrate in 10 ml methanol (listed in Table 1). Precursor mist was generated using an ultrasonic humidifer and delivered to the reaction chamber by 80 L h^{-1} flow of nitrogen. The deposition temperature was set at 350 °C. After deposition, samples were annealed at 500 °C for 1 hour under argon atmosphere. $CH_3NH_3PbI_3$ perovskite active layer was deposited onto ZnO/FTO substrate by spin-coating process. 462 mg PbI_2 and 159 mg MAI were dissolved in 600 mg DMF and 78 mg DMOS at 70 °C. This perovskite solution was spun at 4000 rpm for 25 s, whereby 1 mL diethyl ether was rapidly poured onto the substrate after 8 s of spinning. The obtained films were annealed at 70 °C for 20 min. After that, spiro-OMeTAD solution consisting of 75 mg spiro-MeOTAD, 17.5 µL Li-TFSI solution (520 mg Li-TFSI in 1 ml of acetonitrile) and 28.5 µL TBP in 1 ml chlorobenzene was spin coated on the perovskite film at 4000 rpm for 30s. Finally, silver back electrode was thermally evaporated to finalize the devices. The active area of the solar cell is 0.046 cm^2.

X-ray diffraction (XRD) measurements were performed on a Rigaku Smartlab diffractometer in glancing angle mode. Surface morphologies of the samples were evaluated using a HITACHI S-4800 Field Emission scanning electron microscope (SEM). The thickness of the thin films was determined from their cross-section SEM images. The current density-voltage (J–V) curves of photovoltaic devices were measured on a Keithley 2420 Source Meter under simulated AM 1.5G sunlight (100 mW/cm^2) from a Newport solar simulator.

3. Results and discussion

Fig. S1 shows the XRD patterns of the studied coatings. Besides the intense peaks from the

SnO_2 substrate layer, formation of wurtzite ZnO phase (JCPDS 36-1451) can be indexed by the diffraction of (100) and (101) planes at 31.7˚ and 36.2˚, respectively. The surface morphology of the ZnO films on FTO substrates were then examined by SEM. As shown in Fig. 1a-c, the film topography clearly varies with the amount of zinc precursor added. Uncoated FTO displays a rough surface formed of connected triangular pyramid-like structures (Fig. S1a). The sub structure and morphology of the FTO layer is still visible in sample ZnO-1 (Fig. 1a) indicating a thin conformal over layer of ZnO. High magnification (Fig. S1b) revealed the ZnO layer to be highly compact and uniformly distributed onto FTO substrate. Conformal pin-hole free metal oxide coatings are usually only achieved through ALD, with CVD routes not reported to the best of the authors knowledge. The ZnO grains are observed to increase in size with increasing zinc concentration (Table 1), leading to a masking of the underlying FTO morphology (Fig. 1b-c). Fig. 1d-f depict the cross-section SEM figures of the studied coatings, in which the ZnO/FTO interface is indicated with red arrows. The average film thickness was then determined as ~20 nm, ~50 nm and ~80 nm for ZnO-1, ZnO-2 and ZnO-3, respectively.

To make a conformal coating onto rough substrate, the nucleation uniformity needs to be guaranteed at the first place. According to the theory of crystallization, the energy barrier for heterogeneous nucleation ΔG_c^* on uneven substrate can be defined as follows:

$$\Delta G_c^* = \frac{16\pi\gamma_{fv}^3}{3(\Delta G_v)^2} \quad \alpha$$

$$\alpha = \frac{2\sin\varphi - 2\sin\varphi\sin(\varphi+\theta) - \cos\theta\cos^2(\varphi+\theta)}{4\sin\varphi}$$

where γ_{fv} is the nucleus surface energy, ΔG_v is the difference between the chemical potential of the vapour and crystalline phase per unit volume, θ is the interfacial contact angle, ϕ is the semi angle of conical tip/pit related to the geometry location (see Fig. 2), and α is the surface factor.[8,9] Therefore, the nucleation energy varies at different sites on a rough surface, known as preferential nucleation, unless the nuclei diameter is much smaller than that of the surface roughness. The latter is because the surface factor becomes constant at most nucleation locations where ϕ was kept at 90°. Since the FTO topography is fixed, an effective way to avoid preferred nucleation in this work is therefore to reduce the ZnO nuclei size. This can be achieved by choosing an appropriate precursor, and zinc-acetate-dihydrate, for example, has been extensively utilized to produce ZnO nanoparticles.[10] Furthermore, a reduced deposition temperature would be favourable for uniform

nucleation because the adatoms arriving on the substrate surface have insufficient kinetic energy to migrate to the potentially-preferred nucleation sites.[11] After nucleation, the following film growth behaviour plays a crucial role in producing ultra-thin compact films. It has been reported that the decrease in precursor concentration effectively reduces the crystal growth rate, leading to stable crystal growth. [12] For this reason zinc-concentration in the precursor solution was carefully controlled.

As stated in the introduction, thin electron transport layers are beneficial for highly efficient PSCs, therefore ZnO-1 was selected as the ETL to assess its performance. A conventional PSCs structure of glass/FTO/ZnO/$CH_3NH_3PbI_3$/spiro-OMeTAD/Ag was constructed and the cross-section image is shown in Fig. 3a. The current density-voltage curve of the champion perovskite device is plotted in Fig. 3b. The detailed photovoltaic parameters of open-circuit voltage (Voc), short-circuit current density (Jsc), and fill factor (FF) were 1.03 V, 17.06 mA cm^{-2}, and 0.67, respectively, yielding the highest PCE of 11.75%. Since PSCs without ETL have been widely reported to be poor in Voc and FF due to the low shunt resistance by severe charge recombination,[2] the efficient electron transporting ability in our AACVD ZnO film therefore can be well demonstrated. The studied cells also showed good reproducibility of photovoltaic performance and exhibited minor hysteresis behaviour under different scanning directions, as illustrated in Fig. S3. Our device efficiency is only slightly lower than ALD-ZnO-based PSCs (13.1%) with identical configuration.[4] However, considering all our specimen were fabricated and tested under ambient air conditions, this result is still very encouraging.

4. Conclusion

In summary, we have reported the development of a facile AACVD method for the production of ultrathin conformal ZnO films on surface-textured FTO electrodes. The use of low concentration zinc-aceate solution and reduced reaction temperature result in an uniform film nucleation and stable grain growth. After incorporating the ZnO compact layers into perovskite solar cells, a high efficiency exceeding 11.7% has been achieved. These results demonstrate the possibility of using low-cost CVD technique to synthesis various metal oxide ETL for efficient perovskite devices.

Acknowledgements

This work was financially supported by the National Natural Science foundation of China (No.

52621003), Beijing Natural Science Foundation (No. 2151001), Beijing Municipal High Level Innovative Team Building Program (No. IDHT20170502), China Postdoctoral Science Foundation (No. 2017M610729) and Beijing Postdoctoral Research Foundation (No. 2017-ZZ-043). Michael E A Warwick has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No 663830.

References

[1] D.B. Potter, M.J. Powell, J.A. Darr, I.P. Parkin, C.J. Carmalt, Transparent conducting oxide thin films of Si-doped ZnO prepared by aerosol assisted CVD, RSC Adv. 7 (2017) 10806–10814.

[2] D. Liu, T.L. Kelly, Perovskite solar cells with a planar heterojunction structure prepared using room-temperature solution processing techniques, Nat. Photonics. 8 (2013) 133–138.

[3] X. Xu, H. Zhang, J. Shi, J. Dong, Y. Luo, D. Li, Q. Meng, Highly efficient planar perovskite solar cells with a TiO2/ZnO electron transport bilayer, J. Mater. Chem. A. 3 (2015) 19288–19293.

[4] X. Dong, H. Hu, B. Lin, J. Ding, N. Yuan, The effect of ALD-ZnO layer on the formation of CH3NH3PbI3 with different perovskite precursors and sintering temperatures, Chem. Commun. 50 (2014) 14405–8.

[5] J. Zheng, M. Zhang, C.F.J. Lau, X. Deng, J. Kim, Q. Ma, C. Chen, M.A. Green, S. Huang, A.W.Y. Ho-Baillie, Spin-coating free fabrication for highly efficient perovskite solar cells, Sol. Energy Mater. Sol. Cells. 168 (2017) 165–171.

[6] K. Mahmood, S. Sarwar, M.T. Mehran, Current status of electron transport layers in perovskite solar cells: materials and properties, RSC Adv. 7 (2017) 17044–17062.

[7] A. Illiberi, F. Grob, B. Kniknie, C. Frijters, J. van Deelen, P. Poodt, E.H.A. Beckers, P.J. Bolt, High-throughput Processes for Industrially Scalable Deposition of Zinc Oxide at Atmospheric Pressure, Energy Procedia. 44 (2014) 37–43.

[8] S. Nicolay, S. Faÿ, C. Ballif, Growth Model of MOCVD Polycrystalline ZnO, Cryst. Growth Des. 9 (2009) 4957–4962.

[9] C. Zhang, J. Lin, H. Sun, X. Shi, Influence of Characteristics and Roughness of Nucleation in Conical Pits on Surface Heterogeneous Nucleation, Procedia Eng. 121 (2015) 1281–1288.

[10] C. Biswas, Z. Ma, X. Zhu, T. Kawaharamura, K.L. Wang, Atmospheric growth of hybrid ZnO thin films for inverted polymer solar cells, Sol. Energy Mater. Sol. Cells. 157 (2016) 1048–1056.

[11] H. Chen, Y. Lu, W. Hwang, Characterization of sputtered NiO thin films, Surf. Coatings Technol. 198 (2005) 138–142.

[12] S. Wang, Y. Rong, Y. Fan, M. Pacios, H. Bhaskaran, K. He, J.H. Warner, Shape Evolution of Monolayer MoS2 Crystals Grown by Chemical Vapor Deposition, Chem. Mater. 26 (2014) 6371–6379.

Figures captions

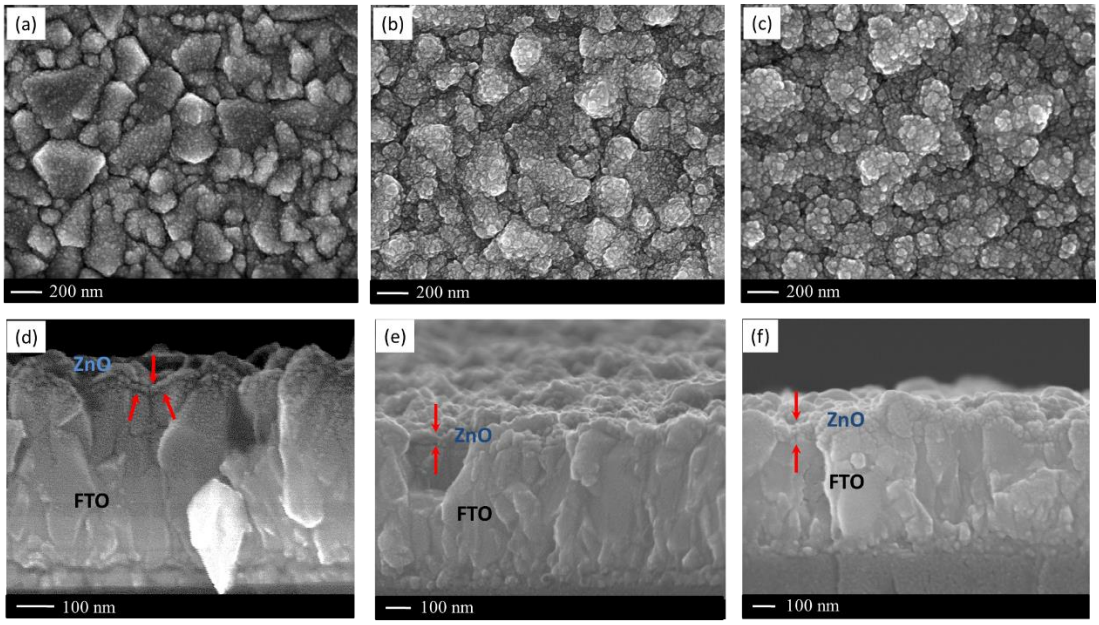

Figure 1 SEM images of the AACVD ZnO films on FTO substrates: (a, d) ZnO-1, (b, e) ZnO-2 and (c, f) ZnO-3.

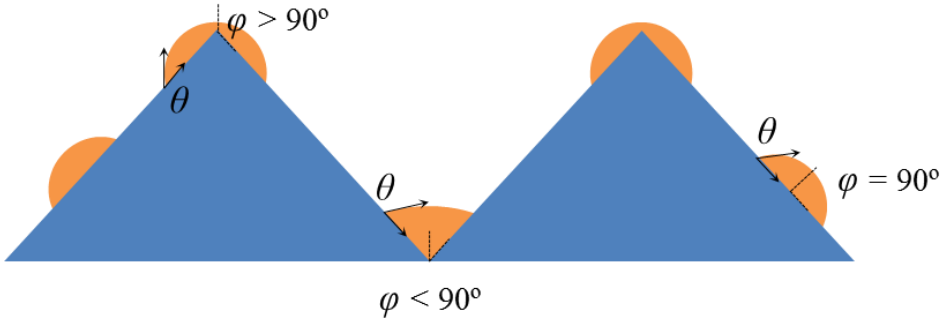

Figure 2 The schematic view of heterogeneous nucleation on uneven substrate.

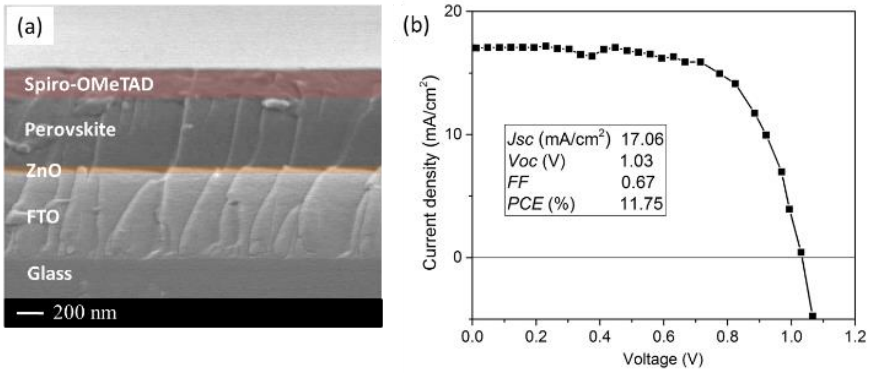

Figure 3 (a) Cross-sectional SEM image of the planar perovskite solar cell. (b) J-V curve of the best-performing device with reverse scan mode.

Tables captions

Table 1 Experimental, structural and optical parameters for the studied ZnO films.

Sample I.D.	Zinc-acetate-dihydrate content	Methanol content	Grain size	Film thickness	Transmittance
	[mg]	[mL]	[nm]	[nm]	[%]
ZnO-1	25	10	15	20	80.2
ZnO-2	50	10	20	50±10	80.3
ZnO-3	75	10	30	80±15	80.5