Journal of
Materials Chemistry

Cite this: *J. Mater. Chem.*, 2012, **22**, 20896

www.rsc.org/materials

PAPER

ZnO layers for opto-electronic applications from solution-based and low-temperature processing of an organometallic precursor

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Received 16th July 2012, Accepted 16th August 2012
DOI: 10.1039/c2jm34656g

As printed and flexible plastic electronic gadgets become increasingly viable today, there is a need to develop materials that suit the fabrication processes involved. Two desirable requirements are *solution-processable active materials or precursors* and *low-temperature* processability. In this article, we describe a straightforward method of depositing ZnO films by simple spin coating of an organometallic diethylzinc precursor solution and annealing the resulting film at low temperatures (≤200 °C) without involving any synthetic steps. By controlling the humidity in which annealing is conducted, we are able to adjust the intrinsic doping level and carrier concentration in diethylzinc-derived ZnO. Doped or conducting transport layers are greatly preferable to undoped layers as they enable low-resistance contacts and minimize the potential drops. This ability to controllably realize doped ZnO is a key feature of the fabrication process that we describe in this article. We employ field-effect measurements as a diagnostic tool to measure doping levels and mobilities in ZnO and demonstrate that doped ZnO with high charge carrier concentration is ideal for solar cell applications. Respectable power conversion efficiencies (up to 4.5%) are achieved in *inverted* solar cells that incorporate diethylzinc-derived ZnO films as the electron transport layer and organic blends as the active material. Extensions of this approach to grow ternary and quaternary films with organometallic precursor chemicals will enable solution based growth of a number of semiconductor films as well as a method to dope them.

1. Introduction

Inorganic semiconductors such as transition metal oxides are generally known to be more robust and stable in ambient environment than their organic or polymeric counterparts. They are optically transparent, potentially confer higher charge carrier mobilities and can be doped. Metal oxide thin films are also increasingly being incorporated into conventional organic electronic devices as electrodes (*e.g.* indium-tin-oxide (ITO)- and fluorine-doped tin oxide (FTO)-coated glass), active semiconductor materials[1–4] and more recently, interfacial layers for *inverted* bulk-heterojunction solar cells.[5–7] Of the many oxides, ZnO is still intensively investigated for device applications due in part to the variety of ways it can be processed. Vapor-phase deposition techniques such as magnetron sputtering, atomic layer deposition (ALD) and metal organic chemical vapor deposition (MOCVD) permit low-temperature deposition of ZnO thin films on temperature-sensitive substrates and ensure better film thickness and morphology control. Solution-based deposition methods and procedures are more promising for higher throughput deposition. Some of such techniques involve depositing either (1) a precursor solution of ZnO (commonly zinc acetate ($Zn(CH_3COO)_2$) dissolved in 2-methoxyethanol)[8,9] or (2) a solution of colloidal ZnO,[10] and sintering at temperatures between 300 and 700 °C to decompose the organic constituents and densify the film. Such high sintering temperatures however limit the use of flexible and temperature-sensitive plastic substrates such as polyethylene napthalate (PEN) and polyethylene terephthalate (PET). The pursuit of solution or suspension based procedures that require no or low-temperature (<200 °C) post-deposition annealing is of immense importance to both research and the industry for they potentially enable low-cost and large-scale roll-to-roll printing of electronic devices.

There are currently only very few procedures that satisfy both liquid-phase and low-temperature requirements for ZnO deposition. Meyers *et al.* reacted aqueous $ZnNO_3$ and NaOH forming $Zn(OH)_2$ agglomerates that were dissolved in aqueous NH_3 producing a $[Zn(NH_3)_x](OH)_2$ solution. The solution was spin coated and the resulting film annealed at 150 °C for 4 hours producing ZnO films with an impressive field-effect mobility of

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1.8 cm^2 V^{-1} s^{-1} (a bottom-gate field-effect transistor (FET) with an atypical aluminum oxide phosphate dielectric layer).[10] Fleischhaker *et al.*[11] improved on the above approach by dissolving pure commercial ZnO in aqueous NH_3 to form the same $[Zn(NH_3)_x](OH)_2$ precursor which they spin coated and then annealed at 150 °C. Such modification eliminated the need for repeated centrifugation to remove the Na contaminant. The resulting ZnO electron mobility was 1.2 cm^2 V^{-1} s^{-1} (FET fabricated on standard Si/SiO_2 substrates). More recently, Sun *et al.* produced ZnO films that functioned particularly well as the electron transport layer in *inverted* organic solar cells (power conversion efficiency (PCE) of 6% with a low band gap polymer) and fairly well as the channel material in FETs (μ_e up to 4×10^{-3} cm^2 V^{-1} s^{-1}).[12] Instead of fabricating ZnO by the common approach of decomposing $Zn(CH_3COO)_2$ deposited from 2-methoxyethanol at high temperatures of 300–700 °C, Sun *et al.* allowed the solution to stir vigorously in air for a prolonged duration to effect hydrolysis of $Zn(CH_3COO)_2$ to $Zn(OH)_2$. $Zn(OH)_2$ underwent condensation and crystallization to give crystalline ZnO at relatively low temperatures of 130–200 °C. Pacholski *et al.* showed that it is possible to catalyze the hydrolysis and condensation of $Zn(CH_3COO)_2$ (in methanol) by adding a small amount of KOH.[13] The reaction produced a colloidal ZnO suspension in methanol which Ajuria *et al.* spin coated and incorporated into 3.5% efficient *inverted* organic solar cells.[14]

In this work, we evaluate diethylzinc (an organometallic liquid reactant) for liquid-phase and low-temperature preparation of ZnO films that are primarily ideal as electron transport layers in organic solar cells. Diethylzinc is commonly used as a source material for depositing ZnO by vapor-phase techniques such as atomic layer deposition (ALD) and chemical vapor deposition (CVD)[15–17] but has not been thoroughly explored for liquid-phase deposition. Diethylzinc is by nature highly moisture sensitive and hydrolyzes spontaneously in air forming $Zn(OH)_2$, which undergoes condensation and crystallization during annealing producing ZnO. Low-temperature processing is made possible by the high reactivity of diethylzinc and low crystallization temperature of ZnO. Leveraging on such reactivity, several groups succeeded in fabricating hybrid polymer–ZnO bulk-heterojunction solar cells by spin coating a mixture of polymer and diethylzinc (dissolved in organic solvents) in air to effect the hydrolysis of diethylzinc and subsequently annealing the blends in an inert atmosphere to form ZnO and improve the ZnO–polymer blend network.[18–20] Moving forward, the key objectives of our work are to (1) establish a deeper understanding of the electrical characteristics of diethylzinc-derived ZnO films and where these films can be applied and (2) demonstrate the utility of organometallic precursors in achieving other solution- and low-temperature-processed metal oxide systems for more advanced applications. We discovered that the diethylzinc processing humidity has a pronounced effect on the charge carrier concentration of the resulting ZnO film. Doped and undoped ZnO can be controllably achieved by varying the humidity in which annealing is carried out. We used field-effect measurements to measure the carrier concentration in ZnO films processed at various humidity levels and further discovered that doped films with high charge carrier concentration perform much better than undoped films as electron transport layers in *inverted* solar cells. Power conversion efficiencies between 3.3 and 4.5% were achieved depending on the active materials employed. The abovementioned are key features of the diethylzinc approach that have not been reported in the literature. Extensions of the approach to synthesize films of ternary and quaternary oxides with organometallic precursors are being pursued.

2. Experimental

Preparation and spin coating of diethylzinc

Diethylzinc is commercially available from TCI Chemicals, dissolved in toluene at 1.0 M concentration. The diethylzinc solution for spin coating was prepared by diluting 1.8 ml of the 1.0 M source solution with 6.4 ml THF resulting in a 0.22 M precursor solution in mixed toluene and THF. THF stabilizes diethylzinc and reduces its reactivity towards moisture by coordinating with the Zn atom,[18–20] making the solution stable to handle in the ambient environment. Diethylzinc was spin coated on Si and ITO-glass substrates at 5000 rpm for 60 s in various environments (Tables 1 and 2), resulting in ZnO films that were *ca.* 35 nm thick after annealing. Humidity control was achieved as follows. The laboratory and clean room where the experiments were conducted have natural humidities of 75% RH and 55% RH respectively. We use an acrylic glove box with air supply fed in to achieve a humidity of 25% RH. The air supply (which comes from liquefied air tanks outside the lab) is at a constant humidity of 25% RH. The moisture-free environment (H_2O < 0.1 ppm) was provided by an MBraun glove box fitted with an inert gas purification system. A humidity gauge was used to monitor the environments in which the spin coating and annealing steps were conducted. Humidity fluctuations during experiments were no larger than ±5% RH.

Electrical characterization of ZnO films

Bottom-gate top-contact field-effect transistor (FET) structures were fabricated by spin coating diethylzinc on pre-cleaned boron-doped p+ Si/SiO_2 (the gate) coated with a 200 nm SiO_2 dielectric layer (supplied by Addison Engineering). After annealing the films at various temperatures and humidities (Fig. 1A), Au source and drain contacts were evaporated through shadow masks forming devices with a channel width and length of 3 mm and 200 μm respectively. The FETs were evaluated on a standard probe station and a Keithley

Table 1 Effect of humidity on the electrical properties of diethylzinc-derived ZnO films

Spin coating humidity (%RH)	Annealing humidity (%RH)	Field effect
0[a]	0[a]	Insulating[b]
0[a]	0[a]	Weak FET[c]
55	0[a]	Insulating[b]
55	55	Conducting[c]
75	0	Insulating[b]
75	75	Conducting[c]

[a] <0.1 ppm H_2O in a N_2-filled glove box. [b] No annealing. [c] Annealed at 110 °C for 30 min.

Table 2 Effect of ZnO conductivity on inverted solar cells based on P3HT:$PC_{61}BM$ blends

Nature of ZnO	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF	PCE (%)
Insulating (as-spun)	0.50	5.0	0.20	0.53
Transistor with moderate mobility (10^{-3} cm^2 V^{-1} s^{-1}, 110 °C 25% RH)	0.50	8.5	0.35	1.50
Best transistor (0.05 cm^2 V^{-1} s^{-1}, 200 °C 25% RH)	0.52	8.2	0.30	1.38
Conducting (150 °C 75% RH)	0.51	9.1	0.40	1.90
Highly crystalline (350 °C 75% RH)	0.52	10.0	0.35	1.90

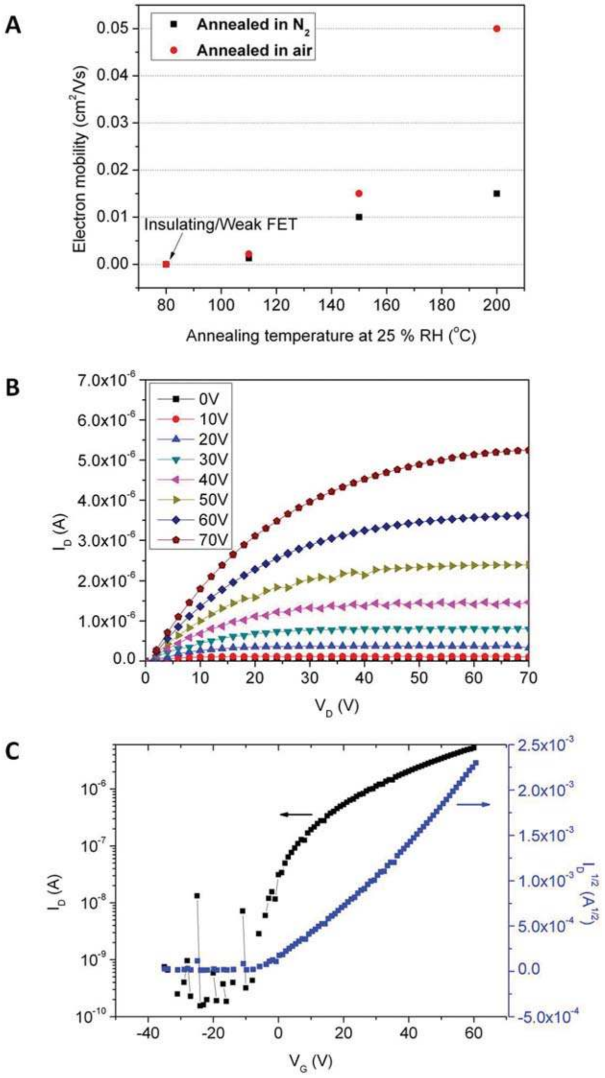

Fig. 1 (A) The electron mobility of diethylzinc-derived ZnO FETs increased as the annealing temperature at 25% RH was increased. A more pronounced mobility increase was observed for films that were annealed in air. The output and transfer characteristics of the best performing ZnO FETs that were produced by annealing the film at 200 °C are shown in (B) and (C) respectively.

4200 parameter analyzer in a N_2-filled glove box. The carrier mobility (μ) was calculated from the saturated regime of the output characteristics according to the equation $I_D = C_i\,\mu(W/2L)\,(V_G - V_T)^2$, where I_D is the drain current in the saturated regime, W and L the channel width and length respectively, C_i is the capacitance per unit area of the gate dielectric layer, and V_G and V_T, the gate and threshold voltages respectively. The residual carrier concentration is measured from the threshold voltage.

Fabrication and characterization of *inverted* solar cells

Inverted solar cells were prepared by spin coating diethylzinc on pre-cleaned and pre-patterned ITO-glass substrates. After annealing the ZnO film at various temperatures and humidities (Table 2), the P3HT:$PC_{61}BM$ blend was spin coated on top of the ZnO layer at 500 rpm for 150 s in a N_2-filled glove box. The blend solution was prepared by dissolving poly(3-hexylthiophene) (P3HT) and phenyl-C61-butyric acid methyl ester ($PC_{61}BM$) in 1 : 0.8 weight ratio in 1,2-dichlorobenzene in 36 mg ml^{-1} concentration. The resulting films were dried at 60 °C for 10 min and used either as-is or annealed further at 120° and 150 °C for 10 min for annealing studies. A ~12 nm (optimized) MoO_3 hole transport layer and ~80 nm Ag or Al anodes were evaporated through shadow masks resulting in device areas of 3 × 3 mm. Devices based on blends of PDPP-TNT and $PC_{71}BM$ were fabricated on ITO-glass coated with diethyzinc-derived ZnO that was annealed at 150 °C in moist (75% RH) air. PDPP-TNT and $PC_{71}BM$ were dissolved in a 4 : 1 (volume ratio) chloroform : 1,2 dichlorobenzene solvent mixture at 1 : 2 weight ratio and 15 mg ml^{-1} concentration.[21] As-deposited blends were already optimized for OPV performance (*i.e.* no further improvements to device characteristics with annealing), therefore there was no need for further annealing. A ~5 nm MoO_3 layer (optimized) and ~80 nm Al electrode were evaporated to complete the device. IPCE measurements were made on a Stanford Research 830 lock-in amplifier with white light channeled from a Newport 150 W Xenon lamp through a 237 Hz mechanical chopper wheel and Cornerstone 130 1/8 m monochromator onto the device through an optic fibre. Current-voltage (I-V) characteristics were recorded on a Keithley 2400 Source Meter as the devices were subjected to AM 1.5G simulated illumination from a KH Steuernagel solar simulator. The intensity of the simulator was adjusted with an NREL AM 1.5G-calibrated Si photodiode to address any mismatch between the spectral output of the simulator and the true terrestrial AM 1.5G solar insolation.

XRD and AFM characterizations

X-ray diffraction (XRD) was performed on the Bruker General Area Detector Diffraction System (GADDs) that employs a Cu Kα target and a 2D detector. A voltage of 40 kV, current of 40 mA, 2θ angle range of 17° and a scanning duration of 15 min were used. AFM imaging was conducted on Bruker's Dimension Icon in tapping mode.

3. Results and discussions

Humidity and its effect on the electrical properties of diethylzinc-derived ZnO films

Given the sensitivity of diethylzinc to moisture, it was essential to investigate the effects of humidity (in which spin coating and annealing were conducted) on the resulting structure and electrical properties of ZnO films. We used field-effect transistor (FET) measurements to probe the electrical properties of ZnO. All as-spun films that did not undergo annealing were found to be insulating regardless of the humidity of the spin coating environment (Table 1). However, the humidity in which annealing (constant duration of 30 min) was carried out had a pronounced influence on the electrical characteristics of ZnO, with films annealed in moist (55 and 75% RH) environments being conducting and those annealed in dry atmosphere (<0.1 ppm H_2O) being almost insulating and exhibiting weak FET characteristics. The charge carrier mobility can be enhanced by annealing ZnO in a moderately moist environment (between 0 and 55% RH). Indeed, annealing the films in air at 25% RH resulted in better performing transistors. Annealing ZnO at higher temperatures at 25% RH led to higher electron mobilities (Fig. 1A). The best FET mobilities at 25% RH were achieved with a 200 °C anneal – $\mu_e = 0.05$ cm^2 V^{-1} s^{-1}, on–off ratio = 1.8×10^4 and threshold voltage (V_{th}) = 6.3 V (Fig. 1B and C) at a drain voltage of 70 V.

As-spun ZnO films were found to be insulating and amorphous (Fig. 2A). The corresponding atomic force microscopy (AFM) image in Fig. 2B shows a surface that is essentially smooth and featureless. The onset of crystallization occurred at about 80 °C where X-ray diffraction (XRD) shoulders and small ZnO particles started manifesting (Fig. 2A and C). Weak transistor characteristics were observed. Higher annealing temperatures increased the crystallinity and particle size of ZnO (Fig. 2A and D) and also the electron mobility of resulting FETs. Conducting films such as those annealed at 150 °C in humid air (75% RH) were strongly crystalline and had a grainier structure with particles (*ca.* 20 nm) that were more distinct (Fig. 2A and E). The ability to tune the charge carrier concentration of ZnO by adjusting the humidity and temperature of annealing is a unique feature of the diethylzinc system. Such flexibility is yet to be reported in other liquid-phase processes. In the following section, we analyze the performance of ZnO films of different conductivities (*i.e.* different charge carrier concentrations) and show that conducting ZnO is exceptionally useful as an electron transport layer in *inverted* organic solar cells.

Diethylzinc-derived ZnO electron transport layer in *inverted* solar cells

Inverted solar cells[5–7,12,22] are currently a subject of intense research given especially, the recent impressive power conversion efficiencies achieved (approaching 8% (ref. 22)). Key advantages of the *inverted* device structure over its conventional counterpart are the use of a high-work-function metal anode and avoidance of the standard poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) hole-transport layer (employed in the conventional structure) which is acidic and hygroscopic. Both modifications render the device more resilient to degradation by oxygen and moisture. Metal oxides that are integrated as charge transport layers further protect the active organic component from direct exposure to the environment. Coupled with deposition methods that are compatible with roll-to-roll fabrication on flexible plastic substrates, *inverted* solar cells make for an alternative cost-effective and environmentally robust energy-generating technology.

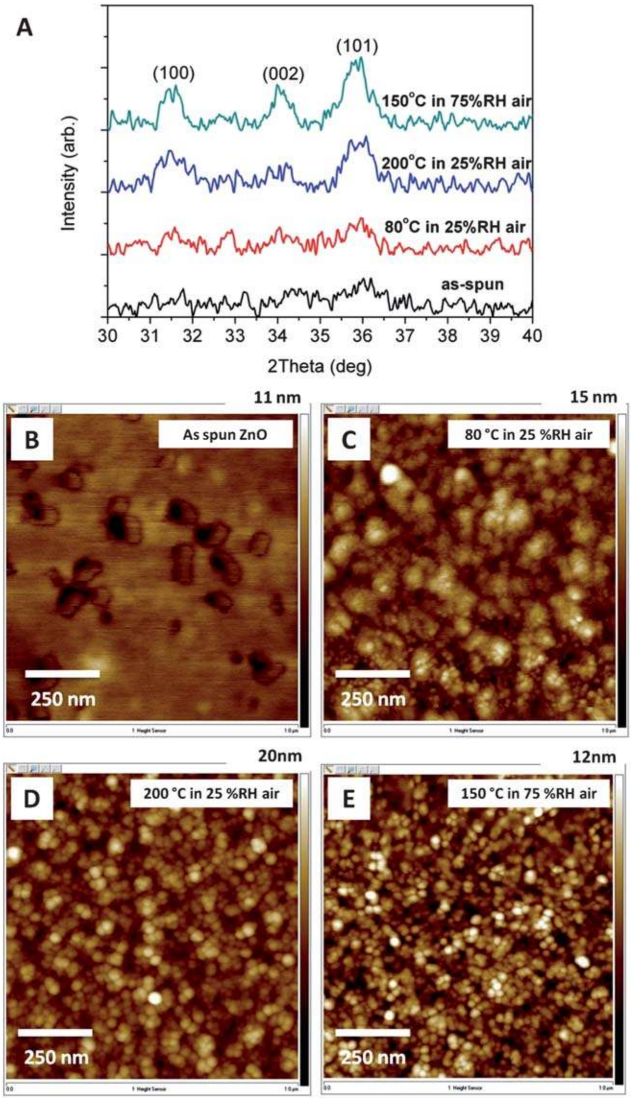

Fig. 2 (A) XRD crystal structure and (B–E) AFM morphology of as-spun ZnO and ZnO films that were annealed at various temperatures and humidity levels indicated.

We incorporated diethylzinc-derived ZnO electron transport layers into *inverted* solar cells composed of a blend of poly-(3-hexylthiophene) (P3HT) and phenyl-C61-butyric acid methyl ester ($PC_{61}BM$) as the active matrix with a MoO_3 hole transport layer and a Ag electrode evaporated to complete the device (Fig. 4A). P3HT:$PC_{61}BM$ blends are very often the choice of active material employed for exploring new device concepts due to their commercial availability as well as familiarity with the materials system stemming from past research.[5] In order to investigate *only* the effects of humidity and temperature and the resulting conductivity of ZnO on device characteristics, the

P3HT:PC$_{61}$BM blends were deposited without subsequent annealing (between 100 and 200 °C) usually applied to effect better molecular organization in the blends. Any annealing to reorder the blend could alter the crystallinity and conductivity of ZnO and distort the results of this study. ZnO films ranging from insulating to semiconducting and conducting were prepared. For comparison, highly crystalline and conducting ZnO obtained by annealing at 350 °C was also employed. Table 2 shows that the power conversion efficiency (PCE) of devices improved as the conductivity of the ZnO layer was increased, with particular improvements in the short circuit current density (J_{sc}). Notably, the performance of devices fabricated on conducting ZnO (annealed at 150 °C in humid 75% RH air) was similar to those prepared on the highly conducting benchmark (annealed at 350 °C). The fact that device efficiencies derived from milder plastics-compatible annealing temperatures matched up well to those derived from harsher temperatures was particularly encouraging and spurred further optimization of the diethylzinc system for application in solar cells.

Thus far, we have determined that conducting (rather than insulating or semiconducting) ZnO electron transport layers result in better performing solar cells. We also showed that conducting ZnO can be obtained by annealing the films in humid air (55 and 75% humidities resulted in negligible differences in device characteristics). This control over the conductivity of ZnO films is a useful feature of our processing technique. All devices henceforth were fabricated on conducting ZnO that was spin coated and annealed in air at 75% RH. In addition, Al instead of Ag electrodes were employed because Ag atoms are heavier and occasionally produced leaky devices. We annealed ZnO at various temperatures in air at 75% RH and observed higher efficiencies in devices with ZnO annealed at higher temperatures (Fig. 3). Notably, devices with ZnO annealed at 150 and 200 °C were equally efficient, suggesting that a lower temperature of 150 °C was enough for processing decent solar cells. Further optimization was carried out on ZnO annealed at 150 °C and involved annealing the P3HT:PCBM blend at 120 and 150 °C respectively, to enhance molecular ordering in the blend. The blends were annealed prior to MoO$_3$ and Al evaporations to prevent possible oxidation of Al if post-evaporation annealing were conducted. The best-performing device derived from blends annealed at 120 °C was 3.3% efficient with an open circuit voltage (V_{oc}) of 0.56 V, a J_{sc} of 10.4 mA cm^{-2} and a fill factor (FF) of 0.57. The 3.3% PCE achieved is comparable to that of devices also fabricated with MoO$_3$ and Al layers[5] and is well in the range of published efficiency values (2.95–4.18%) of devices prepared using other types of hole transport layers (*e.g.* PEDOT:PSS, WO$_3$) and electrodes (*e.g.* Ag, Au).[5]

Two major limitations of the P3HT:PC$_{61}$BM system are the relatively large band gap (1.8 eV, Fig. 4A) and correspondingly narrow absorption wavelength range of P3HT as well as the relatively small energy offset between the HOMO of P3HT and LUMO of PC$_{61}$BM that collectively limit device V_{oc} to about 0.65 eV. In order to enhance the efficiency of our devices and further demonstrate that diethylzinc-derived ZnO can be a general platform electron transport layer for the *inverted* device structure, we explored devices comprising a blend of a lower

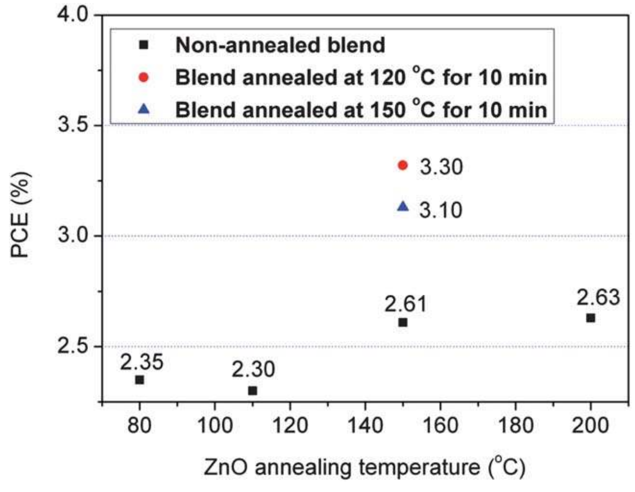

Fig. 3 The effect of ZnO annealing temperature (in air at 75% RH) on the PCE of *inverted* solar cells based on blends of P3HT and PC$_{61}$BM. The blends of 150 °C annealed ZnO underwent annealing at 120 °C and 150 °C to further optimize their morphology for better device performance.

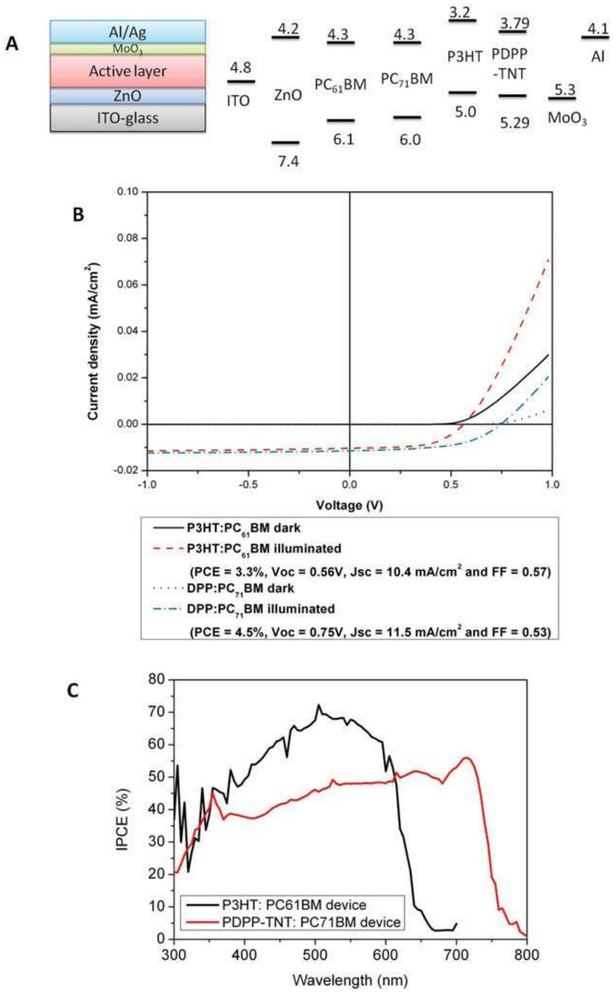

Fig. 4 (A) The *inverted* device configuration and energy levels of the components. The (B) *I–V* and (C) IPCE characteristics of best performing P3HT:PC$_{61}$BM and PDPP-TNT:PC$_{71}$BM devices.

band gap donor–acceptor diketopyrrolopyrrole (DPP)-based alternating copolymer (PDPP-TNT, Fig. 4A) and phenyl-C71-butyric acid methyl ester ($PC_{71}BM$) as the active matrix. The condensed DPP acceptor moiety combined with a fused naphthalene donor building block in the polymer backbone supports better charge transport in the polymer. PDPP-TNT exhibits a low band gap of 1.50 eV which effects better photon harvesting than P3HT and also covers a wide absorption wavelength from 350 to 900 nm. Additionally, its lower HOMO of 5.29 eV compared to that of P3HT (4.7–5.1 eV) favors an enhancement in device V_{oc}. In earlier work, PDPP-TNT had proven an excellent material for both FET and OPV applications, having resulted in a hole mobility of 0.98 $cm^2 V^{-1} s^{-1}$ and optimized PCE of 4.7% ($V_{oc} = 0.76$ V, $J_{sc} = 11.8$ mA cm^{-2} and FF = 0.52) in conventional *non-inverted* OPVs with a $PC_{71}BM$ acceptor.[21]

Inverted OPVs composed of PDPP-TNT:$PC_{71}CM$ were comparatively much more efficient than those composed of P3HT:$PC_{61}CM$ due mainly to the large improvement in V_{oc} resulting from the larger energy offset between the HOMO of DPP and LUMO of $PC_{71}BM$ (Fig. 4A and B). Furthermore, the smaller band gap of PDPP-TNT (1.5 eV) extended the spectral response of the DPP blend further to ~800 nm (about 150 nm more than that of the P3HT system, Fig. 4C). The wider response resulted in a higher J_{sc}, which also improved the PCE. The highest PCE garnered thus far on the DPP:$PC_{71}BM$ system was 4.5% (Fig. 4B, $V_{oc} = 0.75$ V, $J_{sc} = 11.5$ mA cm^{-2}, FF = 0.53) with an optimized MoO_3 layer thickness of 5 nm, comparable to that of the conventional *non-inverted* device (4.7%).[21]

4. Conclusions

To summarize, we described a simple technique for forming ZnO films by spin coating an organometallic diethylzinc precursor solution and annealing the films in air at relatively low temperatures (≤200 °C). We demonstrated the unique ability to adjust the charge carrier concentration of ZnO by controlling the humidity in which the annealing step was carried out. ZnO films annealed in dry air were intrinsically un-doped and showed field-effect transistor characteristics (μ_e of 0.05 $cm^2 V^{-1} s^{-1}$ by annealing at 200 °C in air at 25% RH). Intrinsically doped and highly conductive ZnO films were obtained by annealing the films in moist air (55 or 75% RH). The highly conductive films were exceptionally promising as electron transport layers for *inverted* solar cells. The 3.3% PCE of *inverted* OPVs based on P3HT:$PC_{61}BM$ blends was comparable to literature values as well as our benchmark devices produced on highly crystalline ZnO (annealed at 350 °C). This shows that a relatively low annealing temperature of 150 °C was sufficient for achieving decent device efficiencies. We further incorporated a donor polymer (PDPP-TNT) that has a wider absorption wavelength range and larger theoretical V_{oc} (with $PC_{71}BM$) than P3HT and achieved a much higher PCE of 4.5%. Because of its simplicity, plastic-substrate-compatibility and effectiveness in FET and OPV applications, diethylzinc-derived ZnO is a promising platform electron transport material for printable and flexible electronics. Extensions of this approach to form ternary and quaternary oxide films from organometallic precursors are being pursued. We have provided proof-of-concept on traditional ITO-glass and Si substrates and are progressing to flexible substrates for future work.

Acknowledgements

We gratefully acknowledge the Institute of Materials Research and Engineering (IMRE), the Agency for Science, Technology and Research (A*STAR) and the Visiting Investigator Program (VIP) for financial support.

Notes and references

1 Z. E. Ooi, T. R. B. Foong, S. P. Singh, K. L. Chan and A. Dodabalapur, *Appl. Phys. Lett.*, 2012, **100**, 93302.

2 M. G. Kim, M. G. Kanatzidis, A. Facchetti and T. J. Marks, *Nat. Mater.*, 2011, **10**, 382.

3 K. Banger, Y. Yamashita, K. Mori, R. Peterson, T. Leedham, J. Rickard and H. Sirringhaus, *Nat. Mater.*, 2011, **10**, 45.

4 C. G. Lee and A. Dodabalapur, *Appl. Phys. Lett.*, 2010, **96**, 243501.

5 J. Huang, Z. Yin and Q. Zheng, *Energy Environ. Sci.*, 2011, **4**, 3861.

6 S. K. Hau, H. L. Yip and A. K. Jen, *Polym. Rev.*, 2010, **50**, 474.

7 M. White, D. Olson, S. Shaheen, N. Kopidakis and D. Ginley, *Appl. Phys. Lett.*, 2006, **89**, 143517.

8 C. S. Li, Y. N. Li, Y. L. Wu, B. S. Ong and R. O. Loutfy, *J. Phys. D: Appl. Phys.*, 2008, **41**, 125102.

9 D. C. Olson, J. Piris, R. T. Collins, S. E. Shaheen and D. S. Ginley, *Thin Solid Films*, 2006, **496**, 26.

10 S. T. Meyers, J. T. Anderson, C. M. Hung, J. Thompson, J. F. Wager and D. A. Keszler, *J. Am. Chem. Soc.*, 2008, **130**, 17603.

11 F. Fleischhaker, V. Wloka and I. Hennig, *J. Mater. Chem.*, 2010, **20**, 6622.

12 Y. Sun, J. H. Seo, C. J. Takacs, J. S. eifter and A. J. Heeger, *Adv. Mater.*, 2011, **23**, 1679.

13 C. Pacholski, A. Kornowski and H. Weller, *Angew. Chem., Int. Ed.*, 2002, **41**, 1188.

14 J. Ajuria, I. Etxebarria, W. Cambarau, U. Munecas, R. Tena-Zaera, J. Carlos Jimeno and R. Pacios, *Energy Environ. Sci.*, 2011, **4**, 453.

15 S. Y. Pung, K. L. Choy, X. Hou and C. Shan, *Nanotechnology*, 2008, **19**, 435609.

16 D. Kim, I. Yun and H. Kim, *Curr. Appl. Phys.*, 2010, **10**, S459.

17 D. A. Lamb and S. J. C. Irvine, *J. Cryst. Growth*, 2004, **273**, 111.

18 W. J. E. Beek and R. A. J. Janssen, Hybrid Polymer-Inorganic Photovoltaic Cells, in *Hybrid Nanocomposites for Nanotechnology – Eletronic, Optical, Magnetic and Biomedical Applications*, ed. Merher L., Springer, 2009.

19 S. D. Oosterhout, M. M. Wienk, S. S. van Bavel, R. Thiedmann, L. Koster, J. Gilot, J. Loos, V. Schmidt and R. A. Janssen, *Nat. Mater.*, 2009, **8**, 818.

20 D. J. Moet, L. Koster, B. de Boer and P. W. Blom, *Chem. Mater.*, 2007, **19**, 5856.

21 P. Sonar, S. P. Singh, Y. Li, Z. E. Ooi, T. J. Ha, I. Wong, M. S. Soh and A. Dodabalapur, *Energy Environ. Sci.*, 2011, **4**, 2288.

22 C. E. Small, S. Chen, J. Subbiah, C. M. Amb, S. W. Tsang, T. H. Lai, J. R. Reynolds and F. So, *Nat. Photonics*, 2012, **6**, 115.