Electronic Supplementary Material (ESI) for Energy & Environmental Science.

Electronic Supplementary Information for: Stability of inverted organic solar cells that use sol-gel-deposited ZnO electron contact layers

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In the main text, zinc acetate (ZnAc) and diethylzinc (deZn) precursors are compared with annealing temperatures which have been commonly used in previous literatures, 300 °C and 120 °C, respectively. Sun *et al.* had previously reported device performance of inverted organic photovoltaic (OPV) devices that used ZnAc annealed at lower temperatures (130, 150, and 200 °C).[1] However, we found that these lower process temperatures did not produce devices which performed as well as those annealed at 300 °C, nor as well as those from using deZn annealed at 120 °C. Here we present data of the same experiments as in the main text of this paper, but which was not critical to the scope of the paper. These analyses show the many deficiencies of the ZnAc from low annealing temperatures, and provides some insight into the sol-gel conversion process of ZnAc precursor to ZnO. In this supplementary information, solar simulator current-voltage response is compared for devices containing both ZnAc and deZn layers, with all annealing temperatures mentioned above. The remaining supporting information compares just the ZnAc-ZnO films which were annealed at the various temperatures, by analyzing the data from grazing incidence X-ray diffraction (GIXRD), as well as UV-Vis, photoluminescence, X-ray photoelectron and UV photoelectron spectroscopies. Bandgap determination of all films (deZn and ZnAc at various temperatures) is presented together.

Devices with PCDTBT:PC$_{70}$BM active layers

Devices were formed from a blend of poly[[9-(1-octylnonyl)-9H-carbazole-2,7-diyl]-2,5-thiophenediyl-2,1,3-benzothiadiazole-4,7-diyl-2,5-thiophenediyl] (PCDTBT) and C$_{70}$- butyric acid methyl ester (PC$_{70}$BM), with materials processed as-received from the supplier, to form the structures ITO / ZnO / PCDTBT:PC$_{70}$BM / MoO$_3$ / Ag. The active layer solution was prepared in the same nitrogen glovebox as in the main paper, from a blend of 1 part PCDTBT (Konarka, batch 90809049) and 4 parts PC$_{70}$BM (Nano-C, batch TC120614) by weight with total solids concentration of 35 mg mL^{-1} in a solution comprised of 1 part anhydrous chlorobenzene and 3 parts 1,2-dichlorobenzene, with both solvents filtered through a 0.45 m pore size polytetrafluoroethylene membrane. The active layer solution dissolves readily when stirred at 60 °C, but was allowed to heat for several hours before use. The active layer solution was spincoated on the ZnO films within the glovebox at 60 °C, 4500 RPM for 40 s, at which point, the films appeared mostly dry. The film was further dried at 70 °C for 10 min by hotplate. The BHJ films were then transferred to a second nitrogen glovebox, as in the main paper, where molybdenum(VI) oxide (10 nm) and silver (100 nm) layers were sequentially thermally evaporated. Devices were stored in the evaporator nitrogen glovebox environment until testing. Table S1 gives the average and standard deviation of the devices measured at one-sun intensity on the Spectrolab XT-10 solar simulator, comparing devices with the series of ZnAc films to the deivce with the deZn film. It is apparent that the lower anneal temperatures do not sufficiently convert the ZnAc film into ZnO, having the largest consequence on the J_{SC}.

Table S1 Performance characteristics averaged over several devices with one standard deviation.

Electrode	Qty.	V_{OC} (V)	J_{SC} (mA cm^{-2})	*FF* (%)	*PCE* (%)
ZnAc, 130 °C	4	0.882 ± 0.001	9.9 ± 0.1	64.1± 0.2	5.59 ± 0.09
ZnAc, 150 °C	5	0.878 ± 0.005	10.0 ± 0.1	65.1 ± 1.1	5.69 ± 0.12
ZnAc, 200 °C	9	0.867 ± 0.006	10.6 ± 0.2	65.4 ± 1.3	6.02 ± 0.18
ZnAc, 300 °C	10	0.865 ± 0.004	11.0 ± 0.4	65.1 ± 0.8	6.19 ± 0.26
deZn, 120 °C	10	0.885 ± 0.033	10.6 ± 0.2	67.1 ± 0.7	6.20 ± 0.13

X-ray diffraction

From the same techniques described in the main paper, the series of ZnAc films were investigated by grazing incidence X-ray diffraction (GIXRD). Likewise, Figure S1 shows the GIXRD spectra with the hexagonal wurtzite ZnO peaks (JCPDS #361451). It is clear from the increase in sharpness of the three main hexagonal peaks that the films become more crystalline when the annealing temperature is increased.

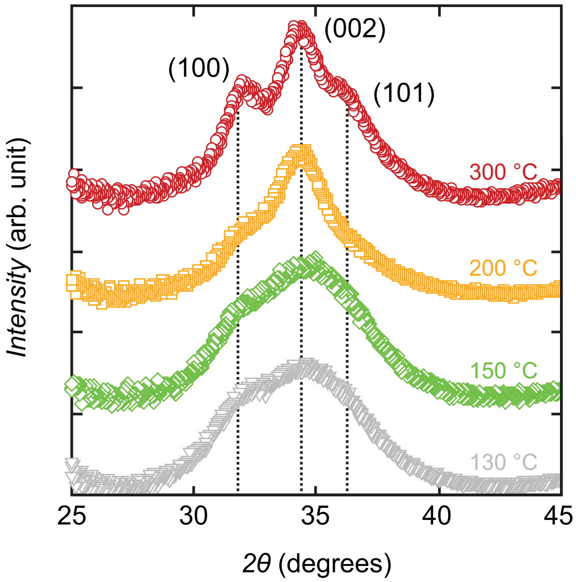

Fig. S1 GIXRD spectra of ZnAc-ZnO films annealed at 300 °C (red circles), 200 °C (orange squares), 150 °C (green diamonds), and 130 °C (grey triangles), with powder diffraction crystal peak references (dashed lines) for wurtzite ZnO.

Optical Bandgaps

Optical bandgaps for the ZnO films on fused silica (the same as were used for GIXRD) were determined from UV-Vis absorption spectroscopy, obtained using an UV/Vis-NIR spectrophotometer (Cary-6000i) with an integrating sphere attachment, and are given in the panes of Figure S2.

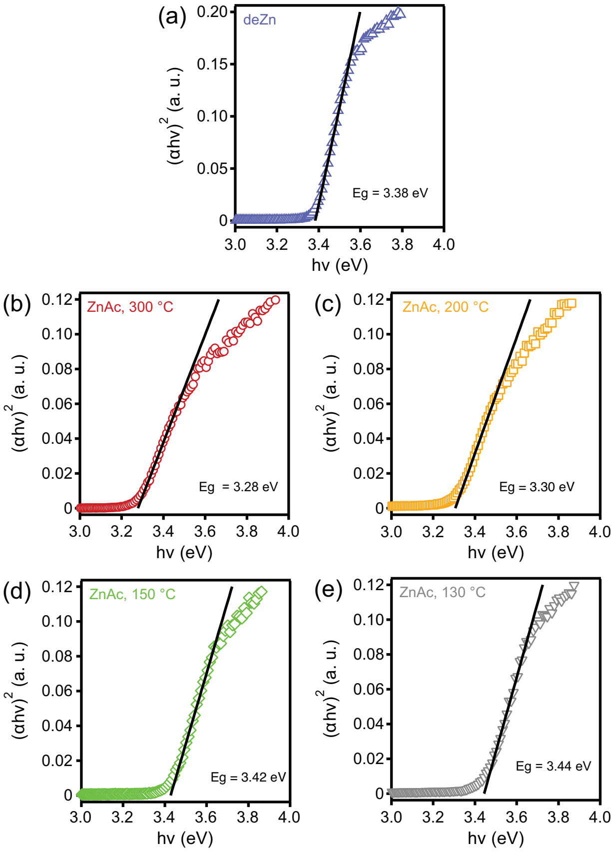

Fig. S2 Room-temperature optical absorption measurements of (a) deZn annealed at 120 °C (blue upward-facing triangles), and ZnAc annealed at (b) 300 °C (red circles), (c) 200 °C (orange squares), (d) 150 °C (green diamonds), and (e) 130 °C (grey triangles). Solid lines represent linear fits to the optical absorption edge, defined by the Tauc method.

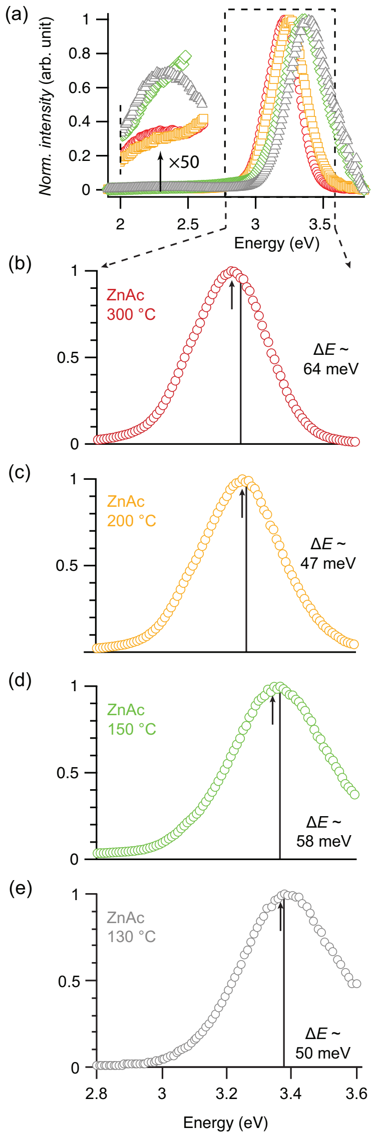

Fig. S3 (a) PL spectra for films annealed at 300 °C (red circles), 200 °C (orange squares), 150 °C (green diamonds), and 130 °C (gray triangles), normalized to the peak intensity in the NBE region, with the inset showing magnification of the midgap region by a factor of 50. The NBE region of each spectrum is shown in (b), (c), (d), and (e), with the solid vertical line showing the optical bandgap of each sample (see Figure S2).

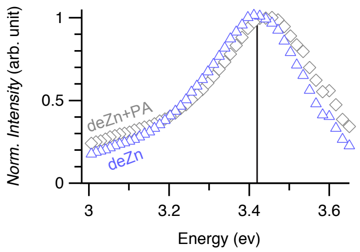

Fig. S4 Peak-normalized NBE region of deZn (blue triangles) and PA-modified deZn (gray diamonds) samples, showing a slight blueshift in the peak intensity upon modification. The solid vertical line represents the optical bandgap (3.42 eV).

Photoluminescence

Room-temperature PL measurements for the series of ZnAc films were investigated by photoluminescence (PL) spectroscopy. Figure S3a indicates that the green band emission is observed for lower annealing temperatures, but is diminished for the higher temperatures. The energetic spacing between the optical bandgap and the peak of the NBE PL is slightly larger for the sample annealed at 300 °C (red circles), but does not show a significant trend for the lower annealing temperatures. Although this energy difference is smaller for the lower annealing temperatures, the other characterization of these films suggest that they are not as much like stoichiometric ZnO, as we a lower degree of crystallinity GIXRD (Figure S1) and larger proportion of non-stoichiometric oxygen in the XPS O 1s spectral region (at left in Figure S6).

PA-modified deZn was not initially characterized by PL due to the poor stability observed in devices. In order to verify the blueshift of the NBE features upon PA-modification, a separate set of samples was prepared similar to as described in the main text: one deZn film and one PA-modified deZn film. With the PL normalized to the NBE peak, we observe a very slight blueshift (Figure S4) of the deZn sample ($\sim$9 meV) with a spincoated PA modifier, compared with the 16 meV shift observed for the same modification of the ZnAc film.

UV and X-ray photoelectron spectroscopies

Changes in the electronic properties of ZnAc-ZnO films upon varied precursor annealing temperature can directly be inferred from the photoelectron spectroscopy measurements. First of all, the work function measured by UV photoelectron spectroscopy (UPS) of the ZnAc-ZnO films annealed at 130 and 150 °C are the lowest in the series with a value of 3.3 eV (at left n Figure S5). The work function of the film increases with higher annealing temperatures to 3.5 eV for 200 °C and 3.7 eV for 300 °C. On the other side of the spectra the valence band maximum (VBM) experiences the same shift going from 3.7 eV to 3.3 eV measured with respect to the Fermi level (at right in Figure S5). Hence for all layers the ionization energy amounts to 7.0 eV leading to the conclusion that the work function shift is not related to a change in surface dipoles but a change in the band gap and the respective Fermi energy (E_F) level position. Note that both effects, change of

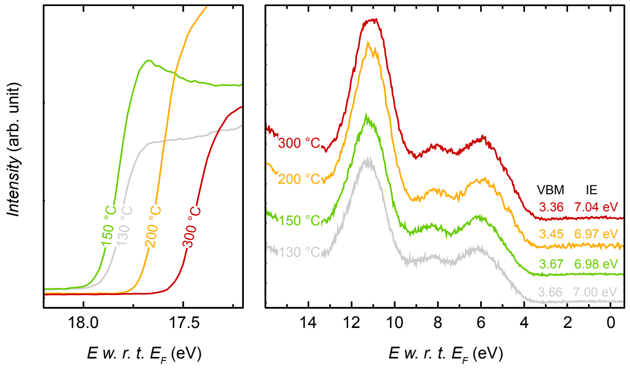

Fig. S5 The UV photoelectron spectra of the series of ZnAc-ZnO films in the (left) secondary electron cut-off and (right) valence band edge regions.

E_F in the gap and surface dipole modifications, are not mutually exclusive and can also partially compensate each other. However, the VBM shift is on the same order of magnitude as the decrease in the optical band gap as found in the PL measurements, which indicates that processing the films at higher annealing temperatures leads to a shift of the valence band effectively narrowing the band gap. Given the fact that the valence band is still very deep all films are expected to serve equally well the purpose of hole-blocking.

By analysis of X-ray photolectron spectroscopy (XPS) Zn 2p (at left in Figure S6) and O 1s (at right in Figure S6) core level region scans show that a rigid shift of the valence band (roughly 250 meV) occurs with annealing temperature. Moreover, a decomposition of the O1s core level informs on the degree of precursor conversion.[1] Going from low to high annealing temperatures the ratio of oxygen species in hydroxyl-environment to oxygen coordinated in the ZnO lattice continuously decreases from 1:1 to 1:2. This finding confirms that the film annealed at 300 °C shows the largest percentage of converted precursor and explains the comparably poor performance of the films treated at lower temperatures.

References

1 Y. Sun, J. H. Seo, C. J. Takacs, J. Seifter and A. J. Heeger, *Adv. Mater.*, 2011, **23**, 1679–1683.

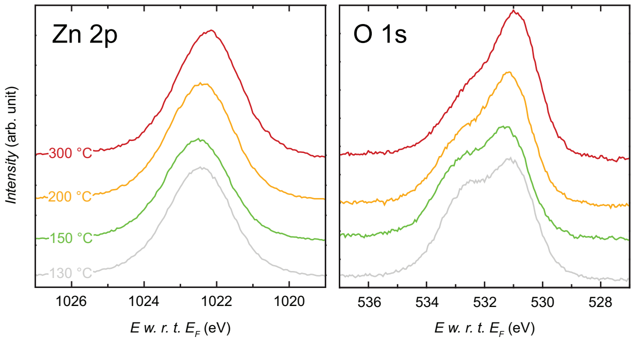

Fig. S6 The X-ray photolectron spectra of the series of ZnAc-ZnO films in the (left) Zn 2p and (right) O 1s regions.