

## Electronic Supplementary Information

### THE ROLE OF SOL-GEL CHEMISTRY IN THE LOW-TEMPERATURE FORMATION OF ZnO BUFFER LAYERS FOR POLYMER SOLAR CELLS WITH IMPROVED PERFORMANCE

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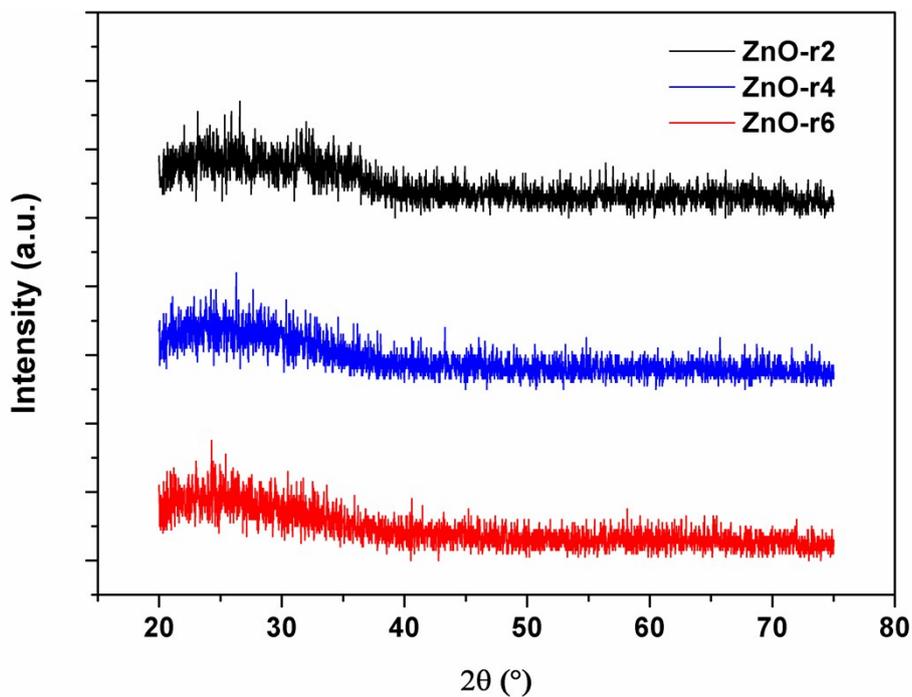
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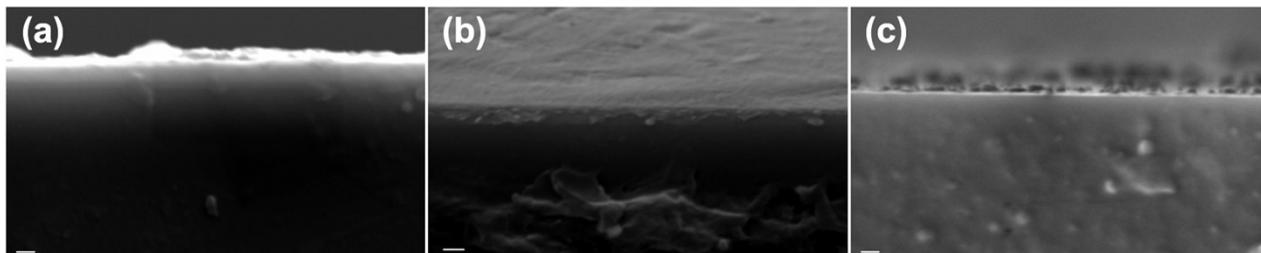
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The crystalline structures of the sol-gel based thin films was characterized by X-ray diffraction (XRD) using a D8 Advance (Bruker AXS) diffractometer with CuK $\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ). The range of  $2\theta$  scans was 20-75 $^\circ$ .



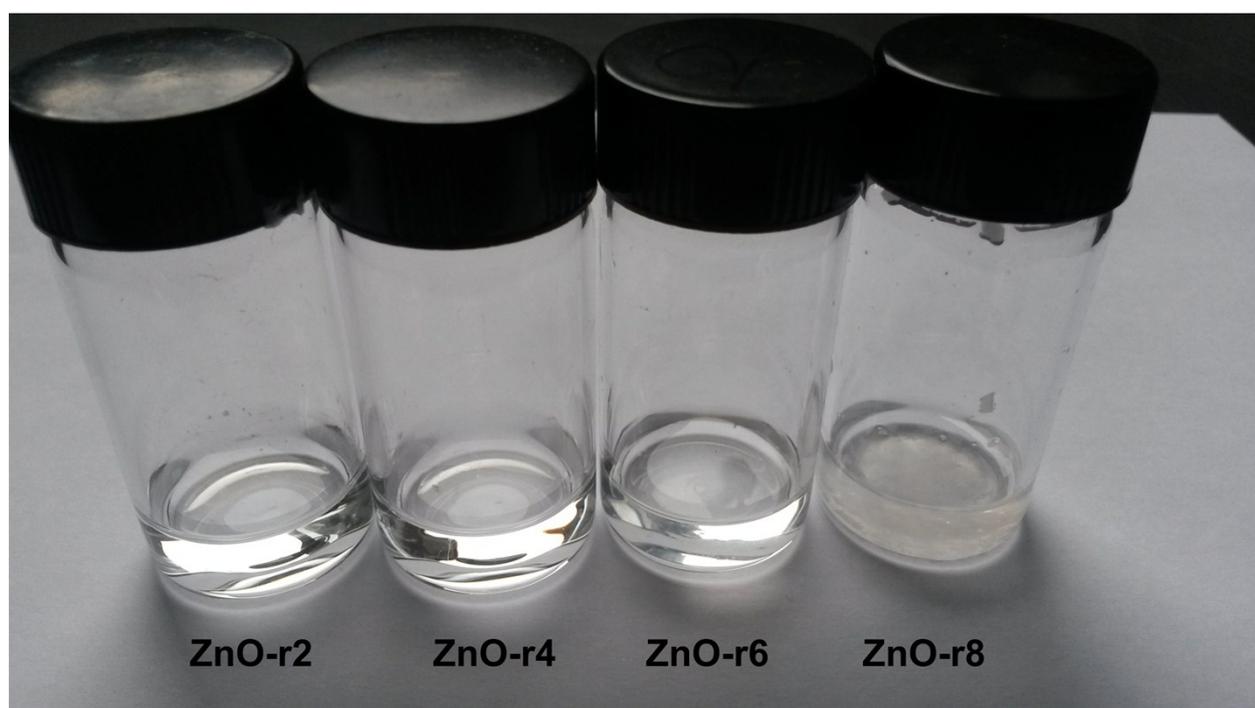
**Figure S1.** XRD patterns of ZnO-r2, ZnO-r4, and ZnO-r6 films.



**Figure S2.** SEM micrographs of (a) ZnO-r2, (b) ZnO-r4, and (c) ZnO-r6 films (bar indicates 300 nm). The thickness is found to be approximately 60 nm for all ZnO thin films.

**Table S1.** Peak heights of functional group associated with acetate residuals (carboxylate  $\text{C}=\text{O}_{\text{asym str}}$  and  $\text{C}=\text{O}_{\text{sym str}}$ ) extrapolated from the FTIR spectra of ZnO-r2, ZnO-r4, and ZnO-r6.

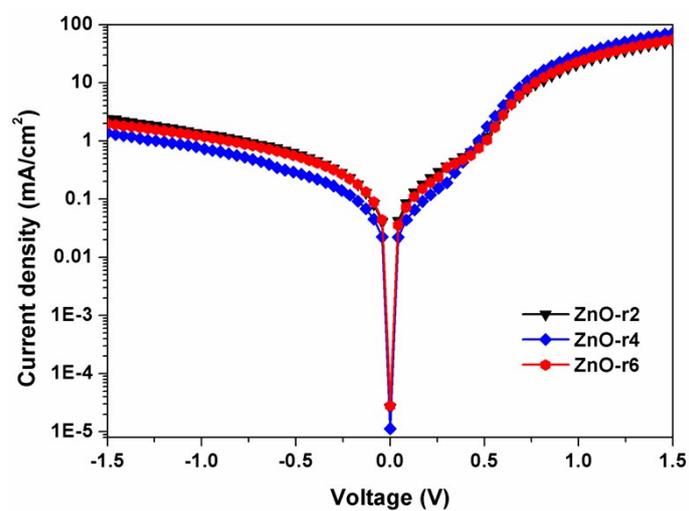
Sample	Peak Height	Peak Height
	$\text{C}=\text{O}_{\text{asym str}}$ (1575 $\text{cm}^{-1}$ ) Absorbance	$\text{C}=\text{O}_{\text{sym str}}$ (1403 $\text{cm}^{-1}$ ) Absorbance
ZnO-r2	0.056	0.033
ZnO-r4	0.041	0.027
ZnO-r6	0.056	0.034



**Figure S3.** Photograph showing ZnO sol-gel precursor solutions prepared with increasing water-to-zinc molar ratios ( $r = [\text{H}_2\text{O}] / [\text{Zn}^{2+}]$ ).

**Table S2.** Root mean square roughness ( $\sigma_{\text{RMS}}$ ) of ZnO-r2, ZnO-r4, and ZnO-r6.

Sample	$\sigma_{\text{RMS}}$
ZnO-r2	27.1
ZnO-r4	25.2
ZnO-r6	25.8



**Figure S4.** *J-V* characteristics in the dark of inverted PSCs incorporating sol-gel based ZnO-r2, ZnO-r4, and ZnO-r6 ETLs

An experimental campaign was carried out in order to evaluate the electrical properties of sol-gel based ZnO thin films with increasing water-to-zinc molar ratios by measuring the electrical conductivity using the four-point probe method. The results evidenced the impracticality of such characterization due to the very thin thicknesses (60 nm) of all spin-coated ZnO films, resulting in inevitable failure contact with the electrical connections of the equipment used for the measurements. The thickness of ZnO films could be increased by increasing the number of spin coating depositions. Nevertheless, we did not opt for this approach since the electrical properties of the thicker ZnO films produced with multiple spin coating depositions are not representative of that of the thinner ZnO films incorporated as ETL in the PSC devices. For an analogous reasons, we did not performed electron mobility measurements in electron-only devices using the space-charge-limited-current (SCLC) model, as in this case thicknesses of at least 250 nm are required to confirm the space-charge region<sup>1</sup>. Other estimates of the electrical properties of the ZnO films, including hole mobility measurements in field-effect transistors (FETs), were not taken into account as they do not correctly reproduce the charge transport processes taking place in ZnO ETLs in PSC devices<sup>2-4</sup>.

## References

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