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Electronic Supplementary Information for:

Room Temperature-processed Inverted Organic Solar Cells using High Working-Pressure-Sputtered ZnO films

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1. Experimental

Patterned ITO substrates (15 × 15 mm) with a sheet resistance of 9 Ω sq^{-1} (Techno Print Co., Ltd.) were used. The substrates were sonicated sequentially in cleaning surfactant (Semi Clean, M-Lo), water, acetone and 2-isopropanol for 15 min each. Before ZnO deposition, ITO substrates were exposed to UV/O_3 for 15 min. For ZnO sol-gel films, the method reported by Heegar and his collegues was used.

For the sputtered ZnO films, RF magnetron sputtering was used without any thermal process. ZnO_x ceramic (Kojundo Chemical Laboratory Co., Ltd.) was used as a target. The RF power applied to the target was 100 W. The thickness of ZnO layer varied according to the experimental purpose. The base pressure of the sputtering chamber was less than 1×10^{-4} Pa. The sputter deposition was conducted in Ar and O_2 gas mixture under a pressure in the range of 2.6×10^{-1} – 7.7×10^{-0} Pa. The O_2 partial pressure was also varied from 0% to 7% to the gas mixture pressure.

For the P3HT:PCBM photoactive layer deposition, a poly(3-hexylthiophene) (P3HT, regioregular, Sigma Aldrich Chemical Co., Inc.) and [6]-phenyl C61-butyric acid methyl ester and [6]-phenyl C71-butyric acid methyl ester in 16:3 ratio (mix-PCBM) (Frontier Carbon Co., Nanom spectra E124) solution with a donor:acceptor ratio of 5:3 and concentration of 40 mg ml^{-1} in ortho-dichlorobenzene (anhydrous, 99%, Sigma Aldrich Chemical Co., Inc.) was prepared. The solution was left stirring for 2 h at 65°C. The active solution was spin-coated on glass/ITO/ZnO substrates at 800 rpm for 45 s and kept inside a Petri dish for 40 mins. Poly(3,4-ethylenedioxythiophene)/poly(styrenesulfonate) dispersed in water (CleviosPVP, Heraeus Precious Metals) containing 0.5wt% poly[oxyethylene(6)tridecyl ether] (Sigma Aldrich) was spin-coated on top of the active layer to form a hole transport layer.

For the PTB7:$PC_{71}BM$ photoactive layer deposition, a solution of PTB7 and [6]-phenyl C71-butyric acid methyl ester ($PC_{71}BM$) was prepared in a mixed solvent of chlorobenzene (CB; 99%) and 1,8-diiodoctane (DIO) (97:3). PTB7 (10 mg) and $PC_{71}BM$ (15 mg) were initially dissolved in CB in a nitrogen glovebox

(0.97 mL). The solution was stirred overnight at 60°C. After 24 h, DIO (30 μL) was added and the solution was stirred for 1 h at 70°C. The PTB7:$PC_{71}BM$:DIO solution (80 nm thick) was spin coated at 1500 rpm for 60 s on a ZnO layer to give a film *ca.* 100 nm thick. For the hole-transporting layer, a 15-nm-thick MoO_3 layer was deposited on top, under vacuum via a thermal evaporator at a rate of 0.2 Å/s.

An approximately 100-nm-thick Au layer was thermally evaporated at a pressure of 2×10^{-3} Pa using a shadow mask followed by thermal annealing at 150 °C for 5 minutes for the P3HT:PCBM system. An approximately 100-nm-thick Ag layer was thermally evaporated at a pressure of 2×10^{-3} Pa and no annealing was necessary for the PTB7:$PC_{71}BM$ system.

J–*V* characteristics were measured by using a software-controlled source meter (2400, Keithley) under dark conditions and 1 Sun AM 1.5 G simulated sunlight irradiation (100 mW cm^{-2}) with a solar simulator (EMS-35AAA, Ushio Spax Inc.), which was calibrated by using a silicon diode (BS-520BK, Bunkoukeiki). UV–vis absorption spectra were measured with a spectrometer (V-670, JASCO) at room temperature (298 K) on a 1.5 × 1.5 cm glass substrate. Atomic force microscopy (AFM; Multi-mode, Bruker) topography images were recorded in tapping mode. Silicon AFM probes, with a nominal frequency of 70 kHz. X-ray Diffraction (XRD; Rigaku Smartlab diffractometer) using Cu Kα radiation operating with a power of 9 kW (45 kV, 200 mA) was used. Core level photoemission measurements were performed by XPS (PerkinElmer, 5400MC) using monochromatic Al Kα radiation. The XPS resolution was estimated to be ≈1 eV and the energy offset was calibrated using the surface C 1s peak.

2. Sputtering schematic

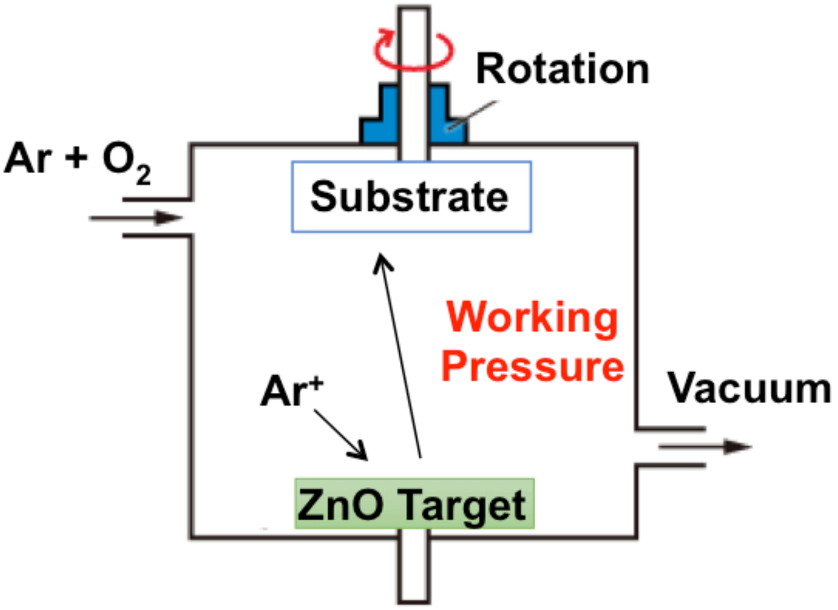
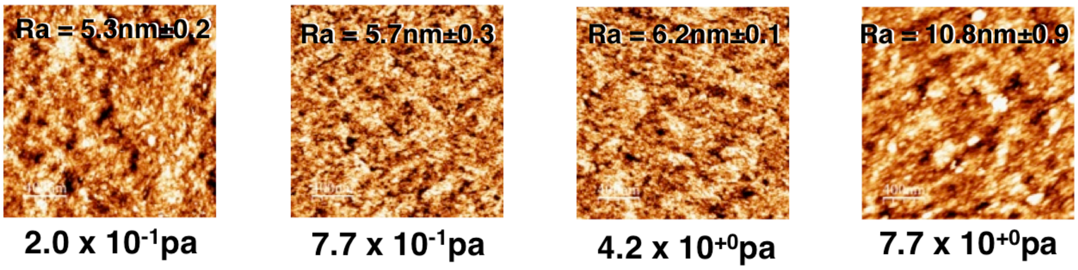


Figure S1. Sputter Schematic illustrating the location of working pressure and how pressure affect Ar^+ interaction with ZnO target.

3. Sputtered ZnO working-pressure splits

Table S1. Photovoltaic data of solar cell devices with different working-pressures and ZnO thicknesses under 1 sun (AM1.5G illumination, 100 mWcm^{-2}).

Thickness	Sputter Working Pressure (Pa)					
	2.0 X 10^{-1}	7.7 X 10^{-1}	2.6 X 10^{+0}	4.2 X 10^{+0}	5.5 X 10^{+0}	7.7 X 10^{+0}
4 nm	0.9	1.4	1.5	1.47	1.2	0
5 nm	0.7	2.2	2.9	3.71	2.0	0
6 nm	1.1	2.7	3.4	3.52	2.2	0.02
7 nm	1.4	2.9	2.5	3.16	2.4	0.05
10 nm	2.1	2.7	2.5	3.03	2.2	0
20 nm	2.4	1.8	3.5	3.41	1.9	0
50 nm	1.6	1.3	1.2	1.09	1.1	0



2.0 x 10^{-1}pa 7.7 x 10^{-1}pa 4.2 x 10^{+0}pa 7.7 x 10^{+0}pa

Figure S2. AFM images and *Ra* of sputtered ZnO on ITO under different working pressure (2 µm × 2 µm).

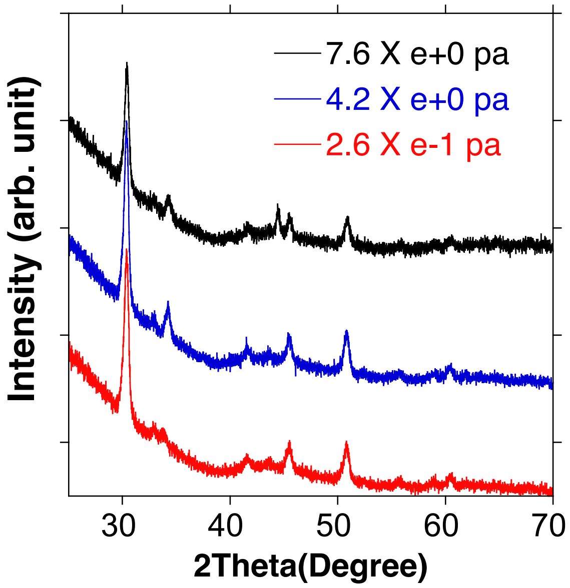


Figure S3. XRD spectra of sputtered ZnO on ITO under different working pressure.

4. Sputtered ZnO oxygen partial pressure splits

Table S2. Photovoltaic data of the solar cell devices fabricated using HWP-sputtered ZnO under different oxygen partial pressures under 1 sun (AM1.5G illumination, 100 mW cm^{-2}).

Oxygen partial pressure (%)	V_{OC} (V)	J_{SC} (mA cm^{-2})	FF	R_S (Ω)	R_{SH} (Ω)	PCE (%)
0%	0.02	0.1	0.1	800	2.1	0.00
1%	0.61	9.1	0.64	3	4.7×10^{2}	3.51
2%	0.60	8.2	0.53	3	3.8×10^{3}	2.60
4%	0.45	7.0	0.26	100	7.1×10^{3}	0.83
7%	0.44	6.8	0.23	70	5.2×10^{3}	0.69

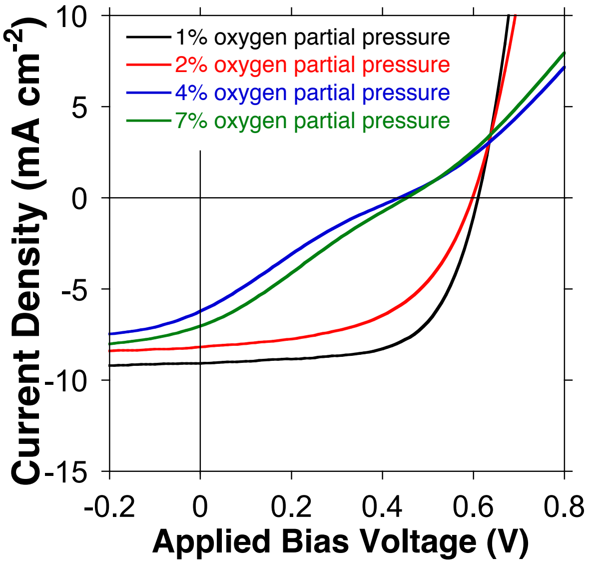
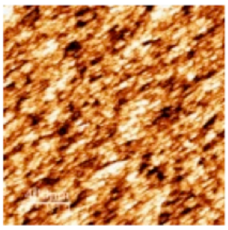
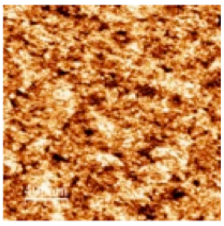


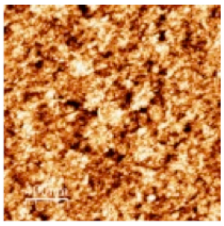
Figure S4. *J*-*V* curves of the solar cell devices fabricated using HWP-sputtered ZnO under different oxygen partial pressures under 1 sun (AM1.5G illumination, 100 mW cm^{-2}).



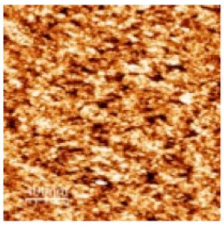
pO_2 0%



pO_2 1%



pO_2 4%



pO_2 7%

Figure S5. AFM images and *R*a of HWP-sputtered ZnO under different oxygen partial pressures (2 µm × 2 µm).

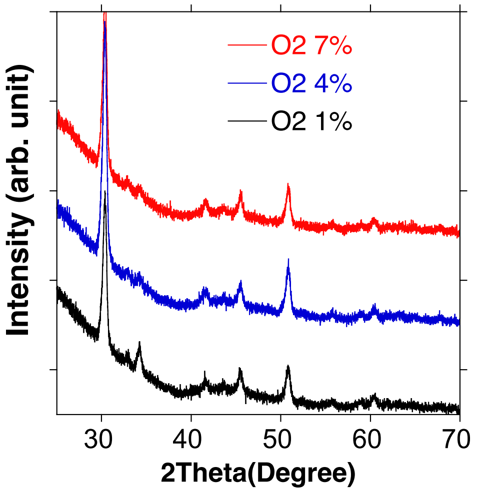


Figure S6. XRD spectra of HWP-sputtered ZnO under different oxygen partial pressures.

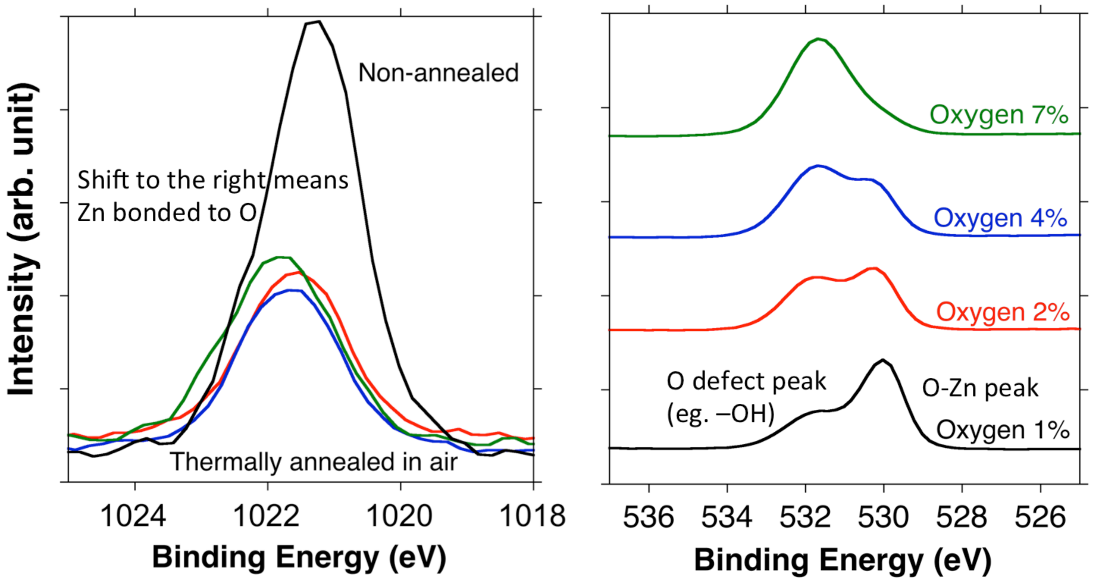
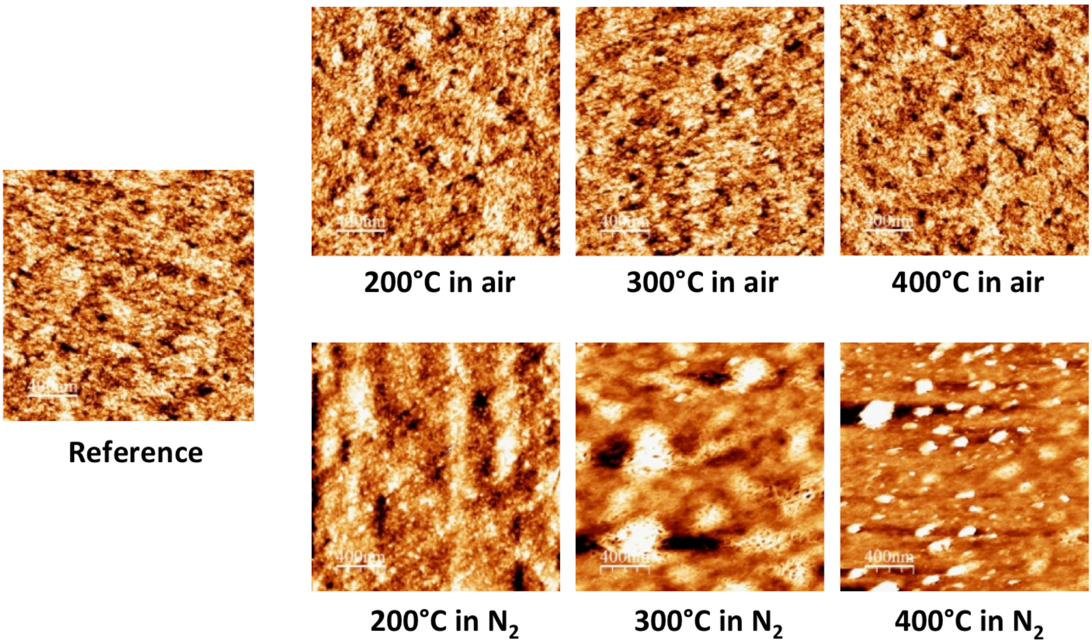


Figure S7. XPS spectra corresponding to Zn $2p_{3/2}$ (left) and O 1s (right) of HWP-sputtered ZnO under different oxygen partial pressures.

5. Sputtered ZnO thermal annealing

Table S3. Photovoltaic data of solar cell devices fabricated on HWP-sputtered ZnO with different annealing conditions under 1 sun (AM1.5G illumination, 100 mW cm^{-2}).

Annealing Temperature (°C)	Atmosphere	V_{OC} (V)	J_{SC} (mA cm^{-2})	FF	R_S (Ω)	R_{SH} (Ω)	PCE (%)
200	air	0.41	5.6	0.20	150	6.1×10^{3}	0.46
300		0.49	6.5	0.26	150	2.9×10^{3}	0.78
400		0.43	7.0	0.25	120	1.2×10^{3}	0.75
200	N_2	0.38	4.7	0.18	360	1.8×10^{3}	0.33
300		0.26	2.2	0.20	110	4.2×10^{2}	0.12
400		0.07	2.8	0.26	35	7.5×10^{1}	0.05



200°C in air

300°C in air

400°C in air

Reference

200°C in N_2

300°C in N_2

400°C in N_2

Figure S8. AFM images of HWP-sputtered ZnO films on ITO substrates after annealing at different temperatures in air and N_2.

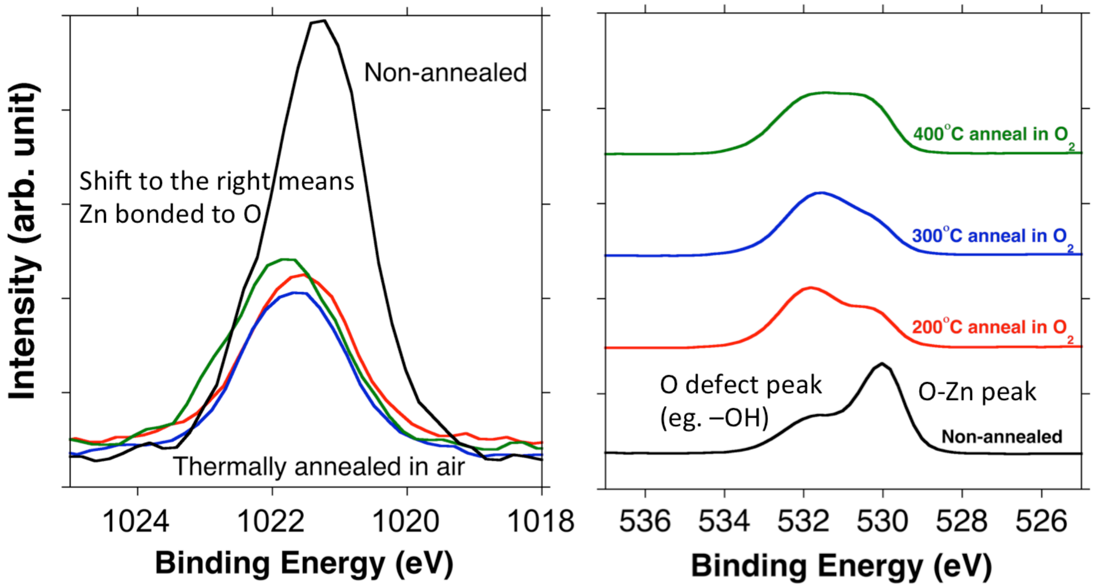


Figure S9. XPS spectra corresponding to Zn $2p_{3/2}$ (left) and O 1s (right) of HWP-sputtered ZnO films after annealing at different temperatures in air.

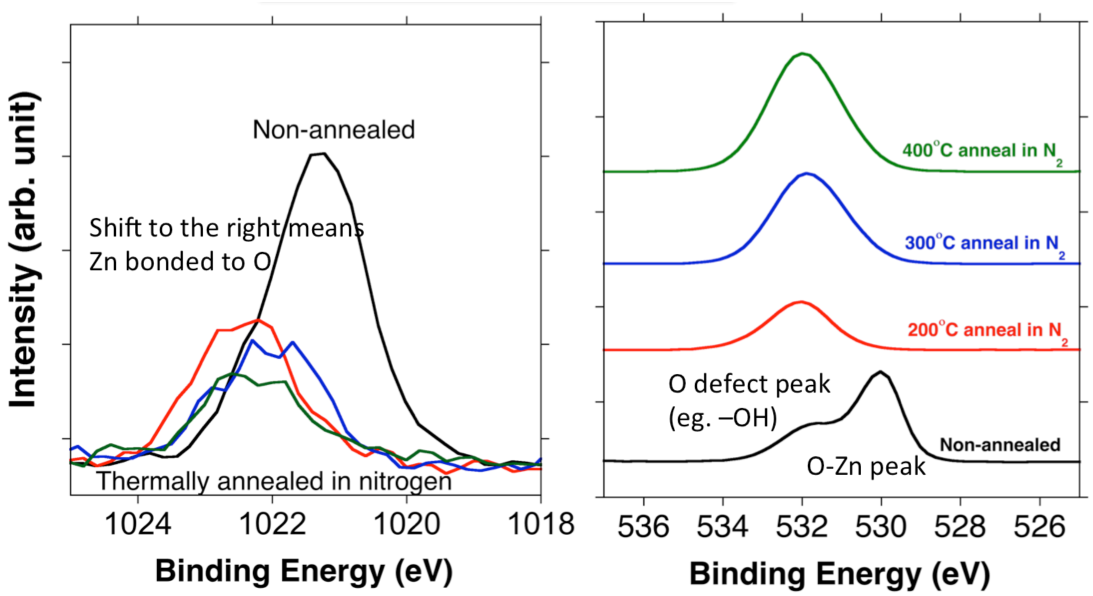


Figure S10. XPS spectra corresponding to Zn $2p_{3/2}$ (left) and O 1s (right) of HWP-sputtered ZnO films after annealing at different temperatures in N_2.

6. Sputtered ZnO Optical Analysis

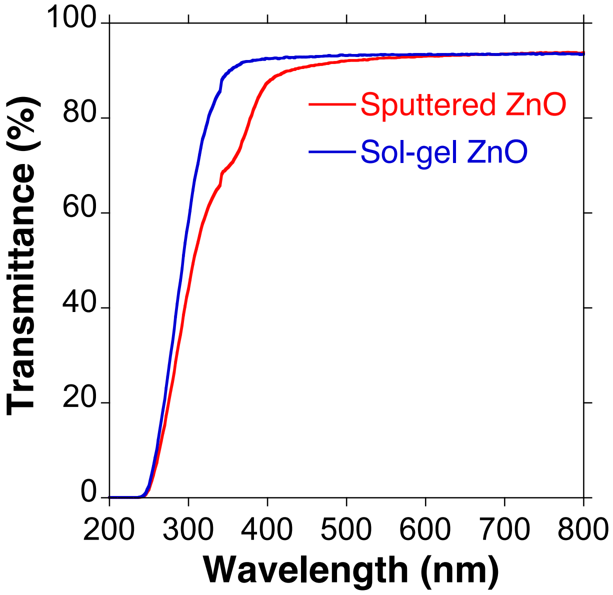


Figure S11. Transmittance spectra of HWP-sputtered ZnO and sol-gel ZnO films on glass/ITO substrates.

7. Literature Comparisons

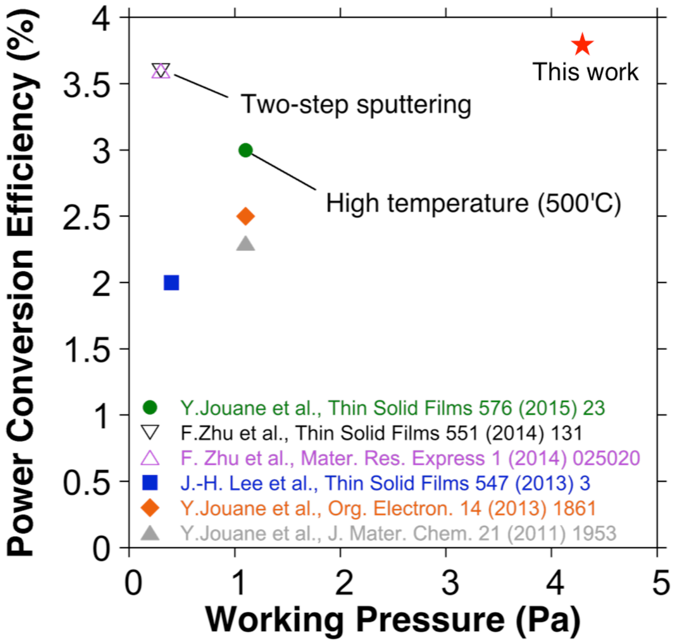


Figure S12. PCEs of previously reported sputtered ZnO-based OSCs with their working pressure values during the sputtering.