Supporting Information

Comparison of Thermal Annealing vs Hydrothermal Treatment Effects on the Detection Performances of ZnO Nanowires

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Supporting Information Text S1

After surface relaxation, the top and bottom surfaces were not equivalent and was needed to consider the unrelaxed surface energy (γ_u) to calculate the final surface energy of the relaxed surface. The unrelaxed surface energy is defined as the surface energy before any surface optimization and is calculated as:

$$\gamma_u = \frac{E_{slab,u} - nE_{bulk}}{2A} \qquad \text{(S1)}$$

where $E_{slab,u}$ - energy of the unrelaxed slab, nE_{bulk} - energy of an equal number of bulk atoms, and A - surface area of one side of the slab. Employing such a value, it is then calculated the relaxed surface energy (γ_r) out the total energy of the relaxed slab.

The relaxed surface energy, γ_r, is given by:

$$\gamma_r = E_{slab,r} - nE_{bulk} - \gamma_u \qquad \text{(S2)}$$

$E_{slab,r}$ - energy of the relaxed slab.

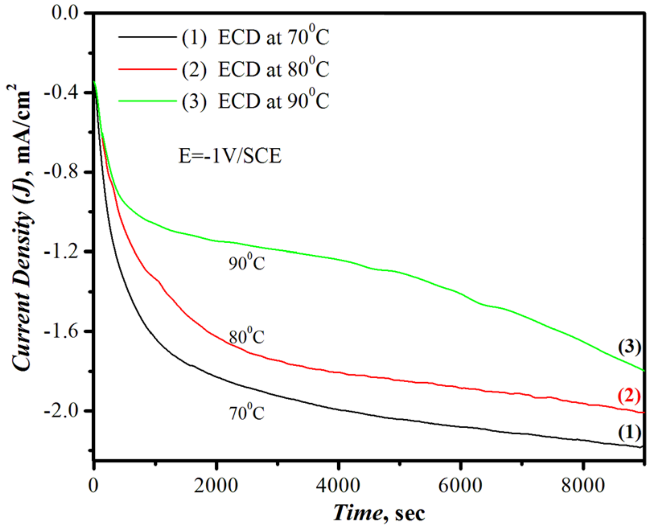

Figure S1. Dynamic dependence of current density versus the deposition time for electrochemical deposition of ZnO NWs/NRs on FTO substrate at 70 °C (see curve 1), 80 °C (see curve 2), and 90 °C (see curve 3) at E = – 1.0 V/SCE with rotating such a WE (ω = 301 rpm).

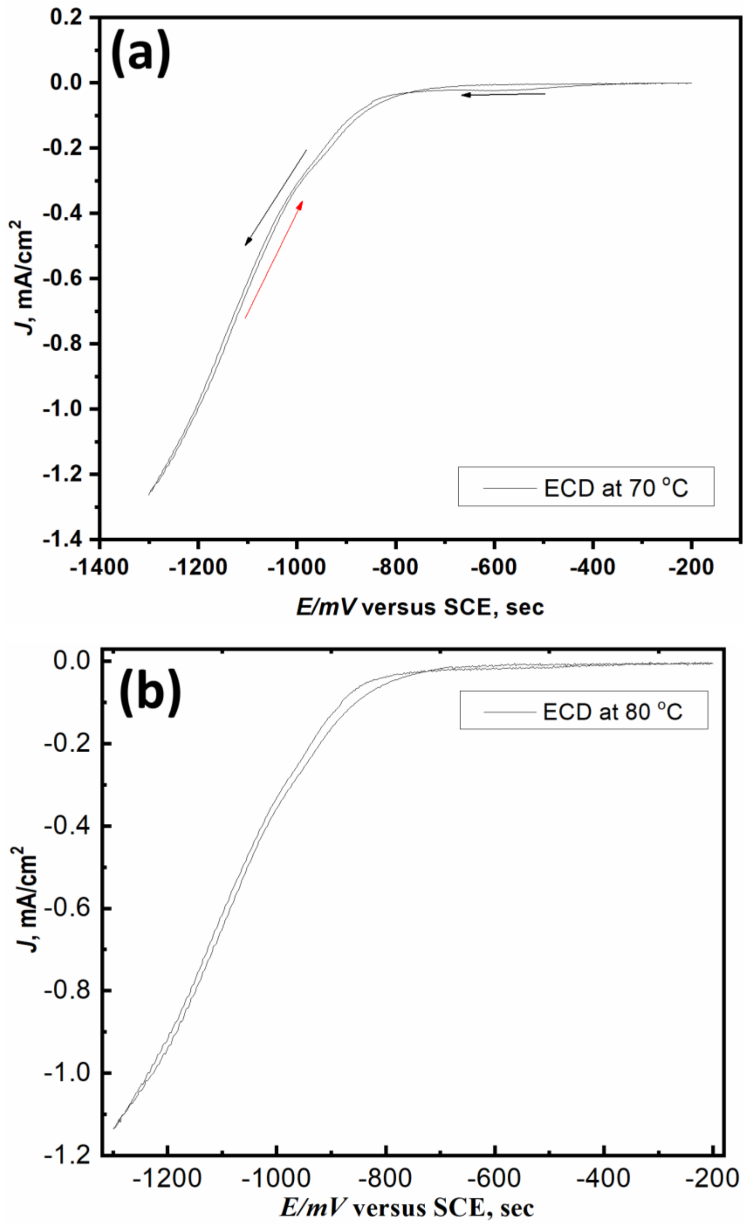

Figure S2. Cyclic voltammograms of ZnO electrodeposition on substrate covered with FTO. First scan in the electro-deposition bath containing 0.20 mmol·l^{-1} $ZnCl_2$ in 0.10 mol·l^{-1} KCl. Scan rate 11 mV·s^{-1}.

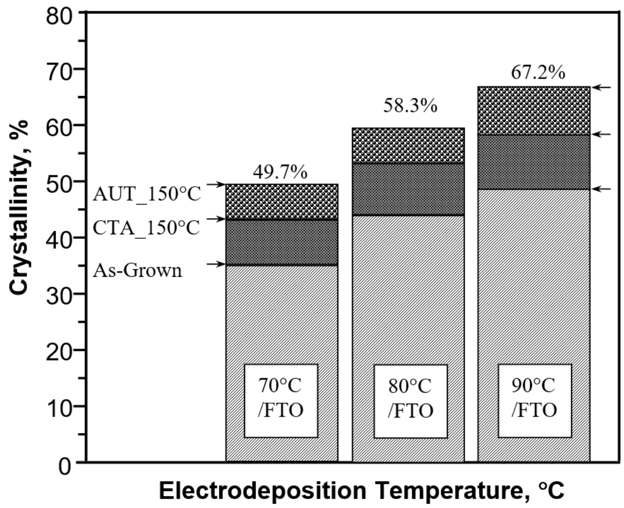

Figure S3. Crystallinity of ECD ZnO NWs before and after post growth-treatments.

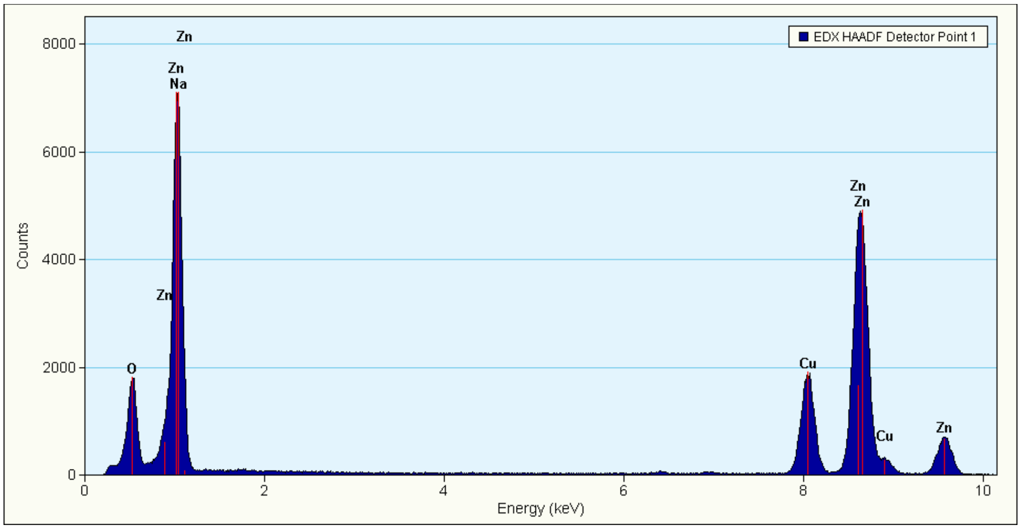

Figure S4. EDX spectrum performed from a single ZnO NW grown by electrodeposition method.

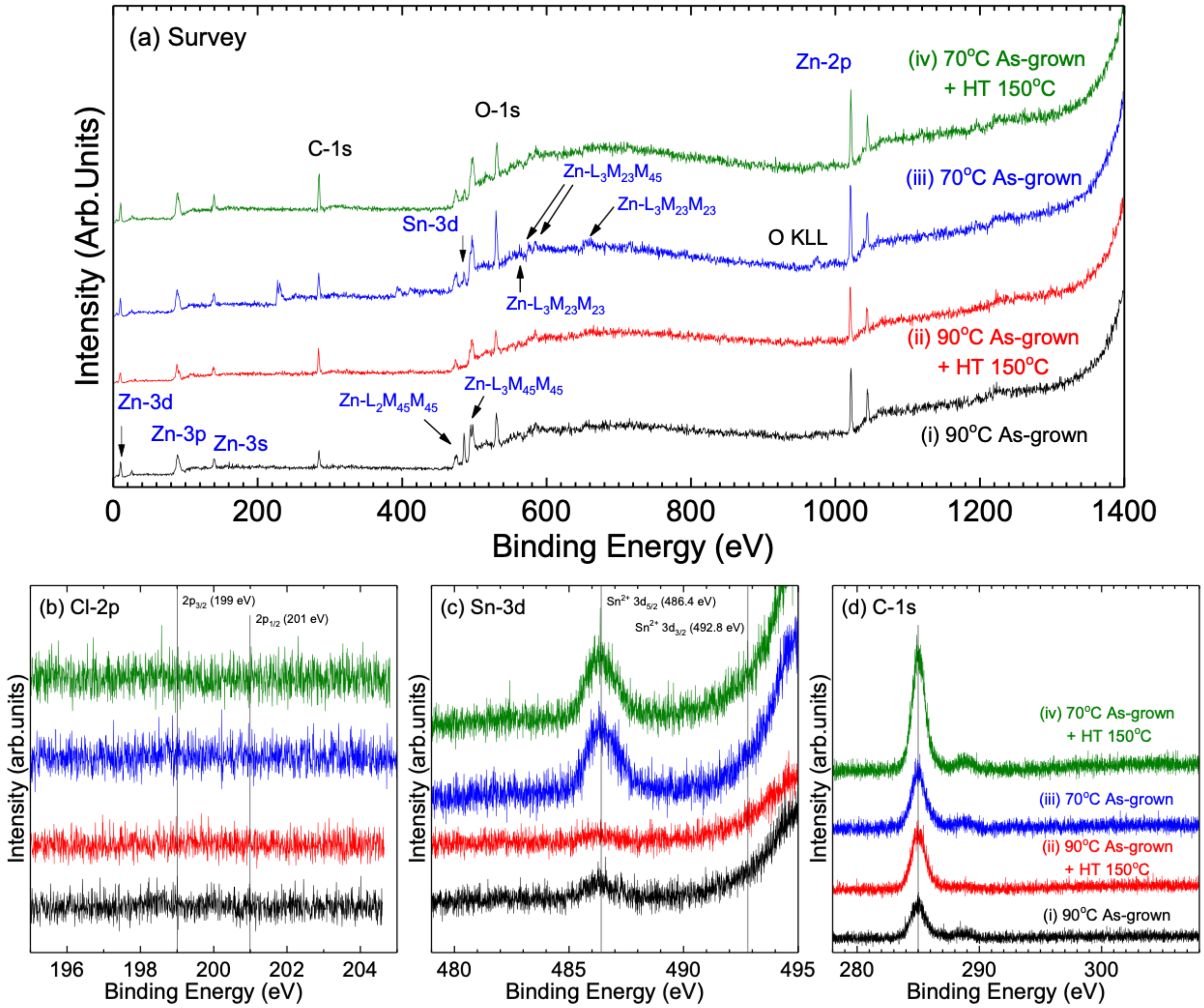

Figure S5. (a) XPS survey spectra corresponding to ZnO NRs/NWs synthesized on FTO/glass substrates. Only Zn, O and C related signals are detected within the sensitivity of the XPS system. The different photoelectron and Auger peaks are labeled in the graph. No detectable amounts of Cl were observed in our XPS measurements that is in accordance with EDX studies performed from a single ZnO NRs/NWs in TEM. High-resolution XPS spectra (Al-K_α = 1486.6 eV) of (b) Cl-2p; (c) Sn-3d and (b) C-1s core level regions of ZnO NWs synthesized on FTO/glass substrates as marked in (a). Cl signal was below the detection limits of our XPS system. Sn peaks are from the FTO substrate.

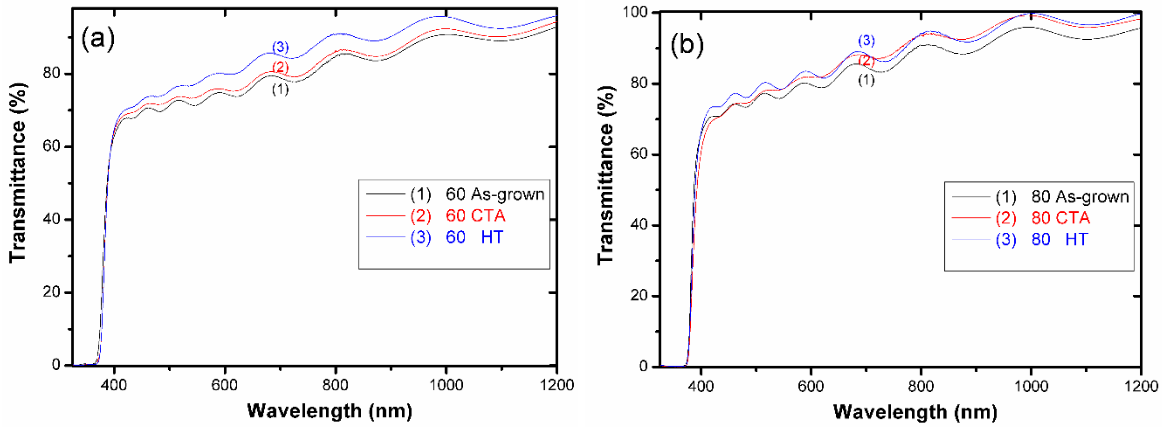

Figure S6. Transmission spectra of as-synthesized ZnO NRs/NWs electrochemically grown on FTO substrates at 60 °C (a), and 80 °C (b). These samples were compared with CTA and HT samples grown at the same temperatures of ECD.

The as-grown samples were compared with CTA and HT samples ECD at the same temperature. We can see a larger effect of CTA and HT o samples grown at lower temperature.

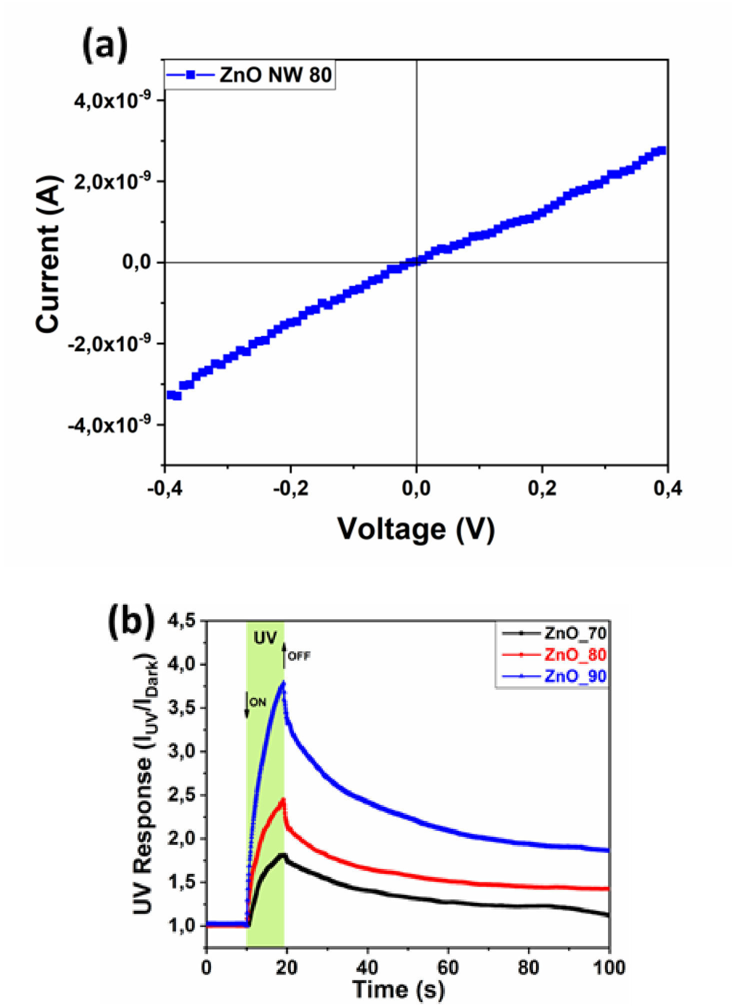

Figure S7. (a) Typical current-voltage characteristic of device based on individual ZnO NW grown at 80 °C. (b) UV response of individual ZnO NRs/NWs grown at 70 °C, 80 °C and 90 °C.

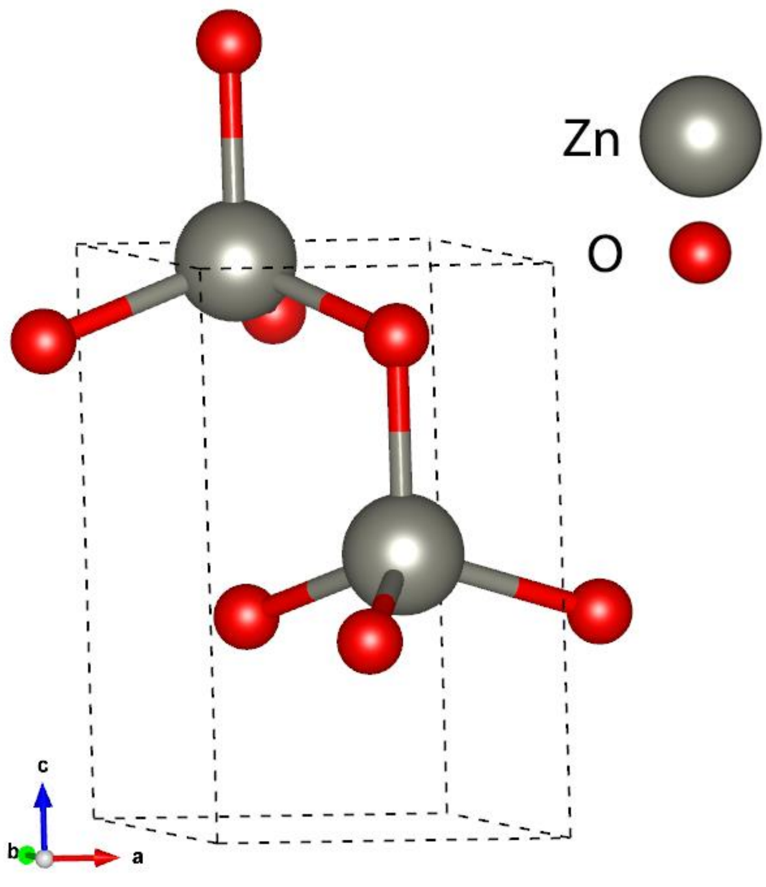

Figure S8. ZnO Bulk Structure.

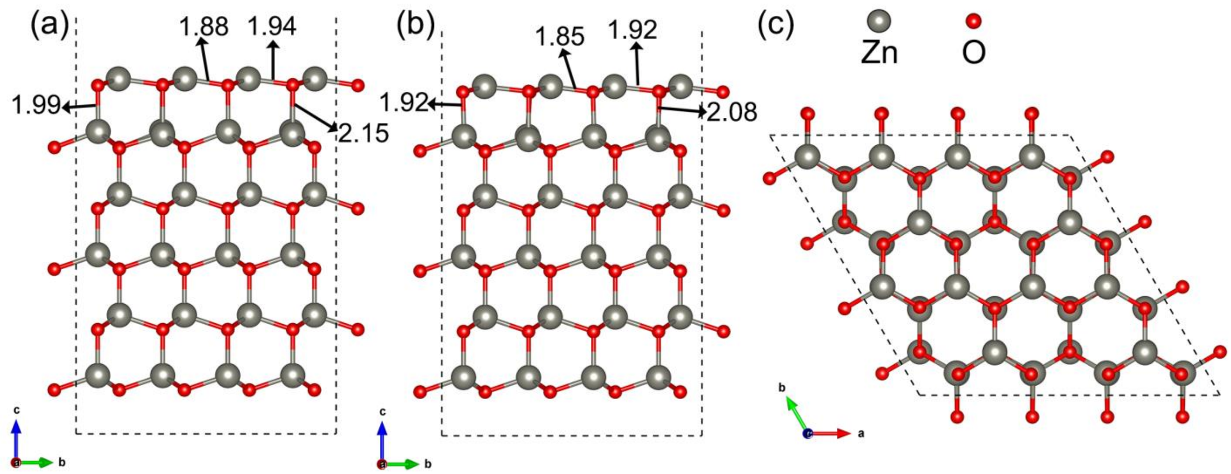

Figure S9. 2*2 supercell of the ZnO (0001) surface. (a): side view of un-relaxed structure, (b): side view of relaxed structure, and (c) top view of relaxed structure.

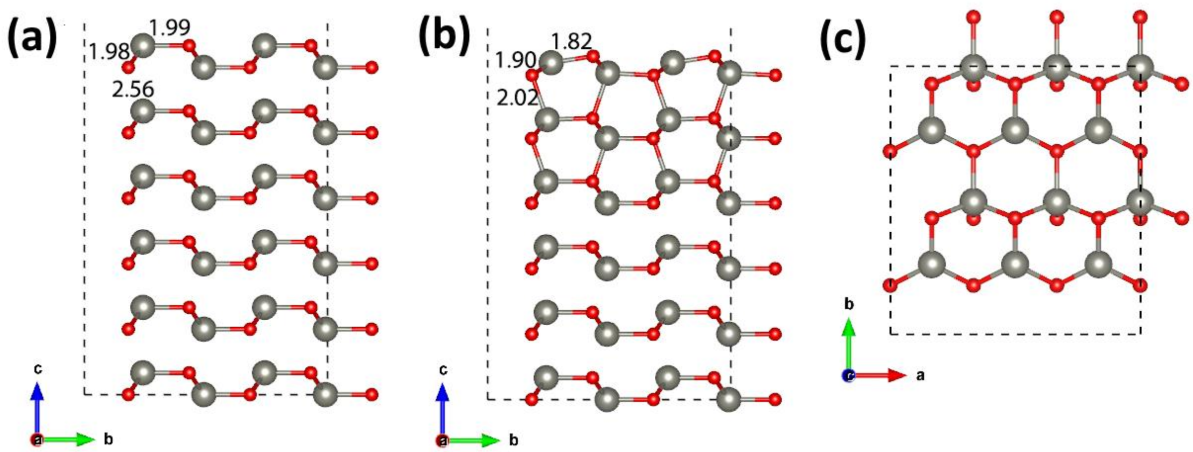

Figure S10. 2*2 supercell of the ZnO $(10\bar{1}0)$ surface. (a): side view of un-relaxed structure, (b): side view of relaxed structure, and (c) top view of relaxed structure.

Table S1. Comparison of different sensors H_2 sensors based on single NW/NR of metal oxides.

Individual structure	H_2 conc. (ppm)	Gas response (Sensitivity) (R_{gas}/R_{air}) or (R_{air}/R_{gas})	Operating temperature (°C)	Response time (s)	Recovery time (s)	Stability
ZnO:NR[1]	200	~ 0.04	RT	~ 50	~ 100	-
ZnO:NR[2]	2000	~ 0.429	RT	~ 60	~ 49	-
ZnO:AgN[3]	100	~ 0.6	RT	~ 22	~ 11	-
ZnO:Ni[4]	100	~ 0.4	RT	~ 100	~ 25	-
ZnO-[5]	40	~ 59	400	~ 102	-	-
ZnO:NWs-[6]	2500	~ 0.9	RT	~ 130	>150	-
ZnO:Al-[7]	100	~ 5	250	~ 19.6	~ 14.7	-
ZnO:Eu-[8]	100	~ 120	250	~ 22	~ 12	-
ZnO:NW(this work)	50	~ 61.5	150	~ 4.22	~ 2.1	-
	100	~ 136	150	~ 6.86	~ 3.2	-
	200	~ 180	150	~ 5.19	~ 7.6	-

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