

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

## Supporting Information

### High Performance Inverted Organic Solar Cells with Solution Processed Ga-Doped ZnO as Interfacial Electron Transport Layer

M.Thambidurai,<sup>\*a‡</sup> Jun Young Kim,<sup>a‡</sup> Jiyun Song,<sup>a</sup> Youngjun Ko,<sup>a</sup> Hyung-jun Song,<sup>a</sup> Chan-mo Kang,<sup>a</sup> N.Muthukumarasamy,<sup>b</sup> Dhayalan Velauthapillai,<sup>c</sup> and Changhee Lee<sup>\*a</sup>

<sup>a</sup> Department of Electrical and Computer Engineering, Global Frontier Center for Multiscale Energy Systems, Seoul National University, Seoul 151-744, Republic of Korea. Fax:+82-2877-6668; Tel:+82-2880-9093; E-mail: chlee7@snu.ac.kr (Changhee Lee), E-mail: phy\_thambi@rediffmail.com (M.Thambidurai)

<sup>b</sup> Department of Physics, Coimbatore Institute of Technology, Coimbatore 641 014, India. Fax: +91-0422-2575020; Tel: +91-94429-54202; E-mail: vishnukutty2002@yahoo.co.in

<sup>c</sup> Department of Engineering, University College of Bergen, Bergen, Norway. Fax: +4755587030; Tel: +4755587711; E-mail: Dhayalan.Velauthapillai@hib.no

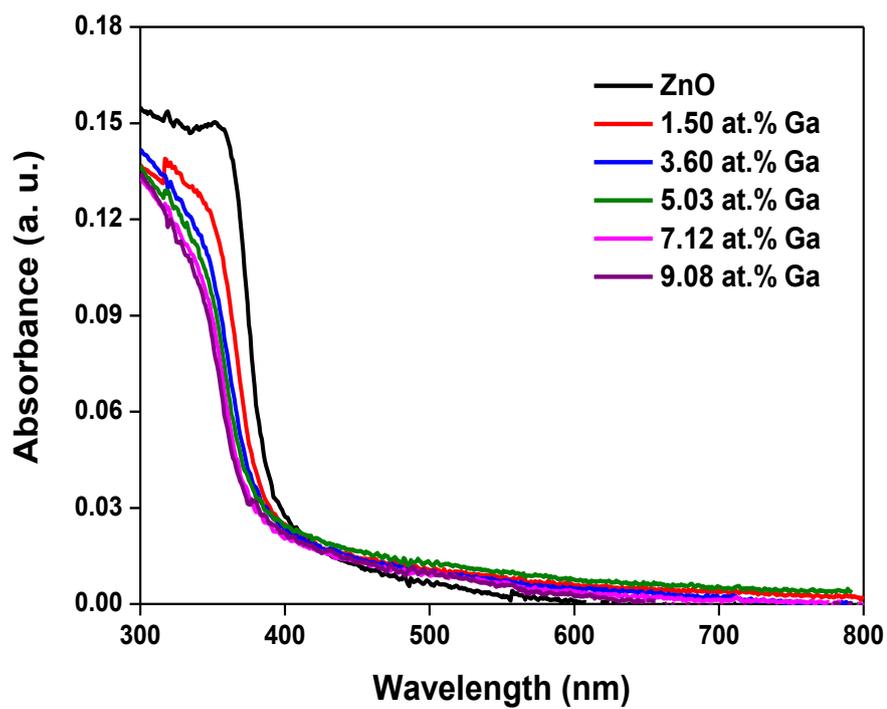


Figure S1. Absorption spectra of ZnO and GZO films

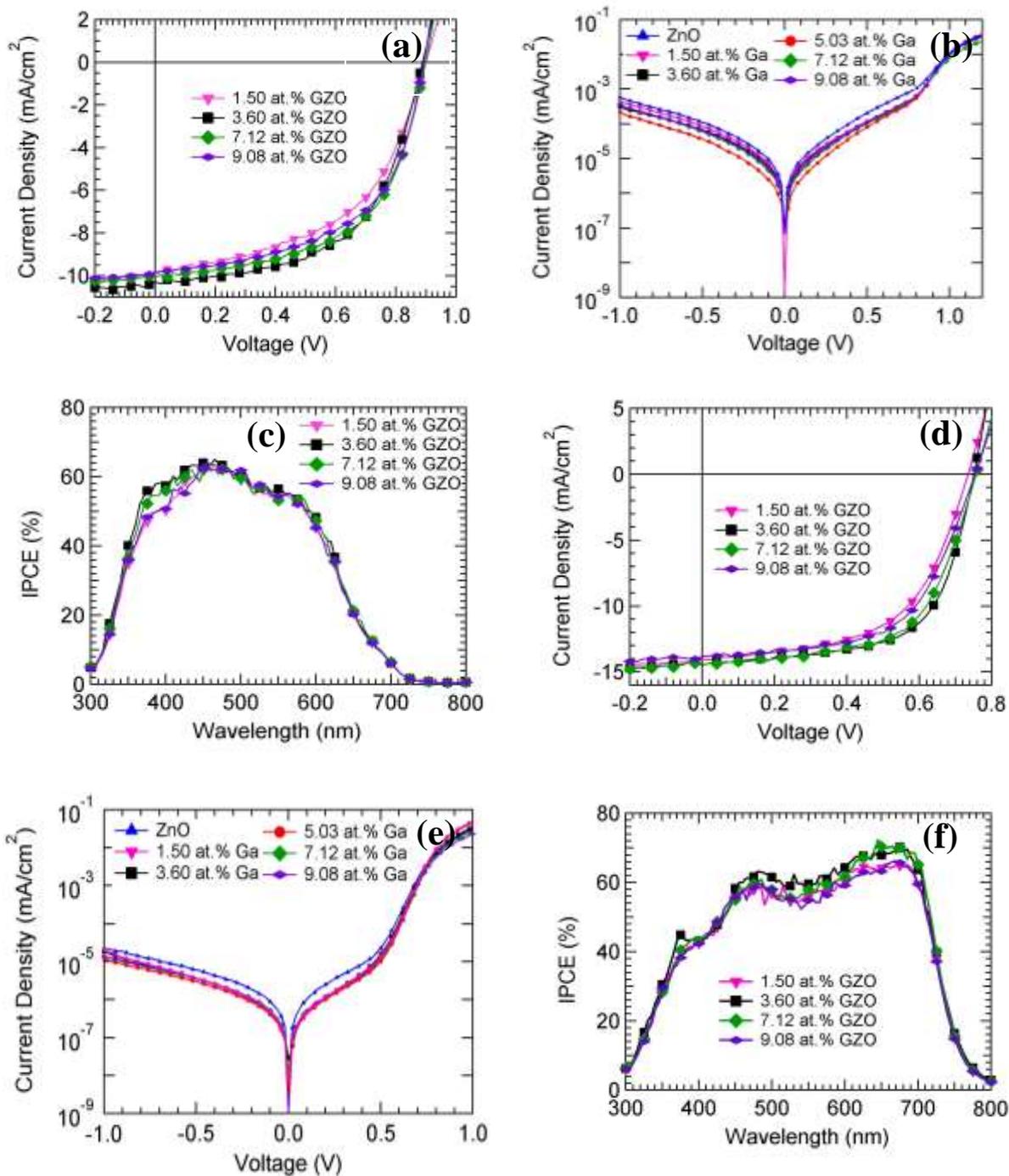


Figure S2. (a) J–V, (b) dark J–V characteristics and (c) IPCE spectra of PCDTBT:PC<sub>71</sub>BM based IOSCs. (d) J–V, (e) dark J–V characteristics and (f) IPCE spectra of PTB7:PC<sub>71</sub>BM based IOSCs with ETLs of ZnO and GZO.

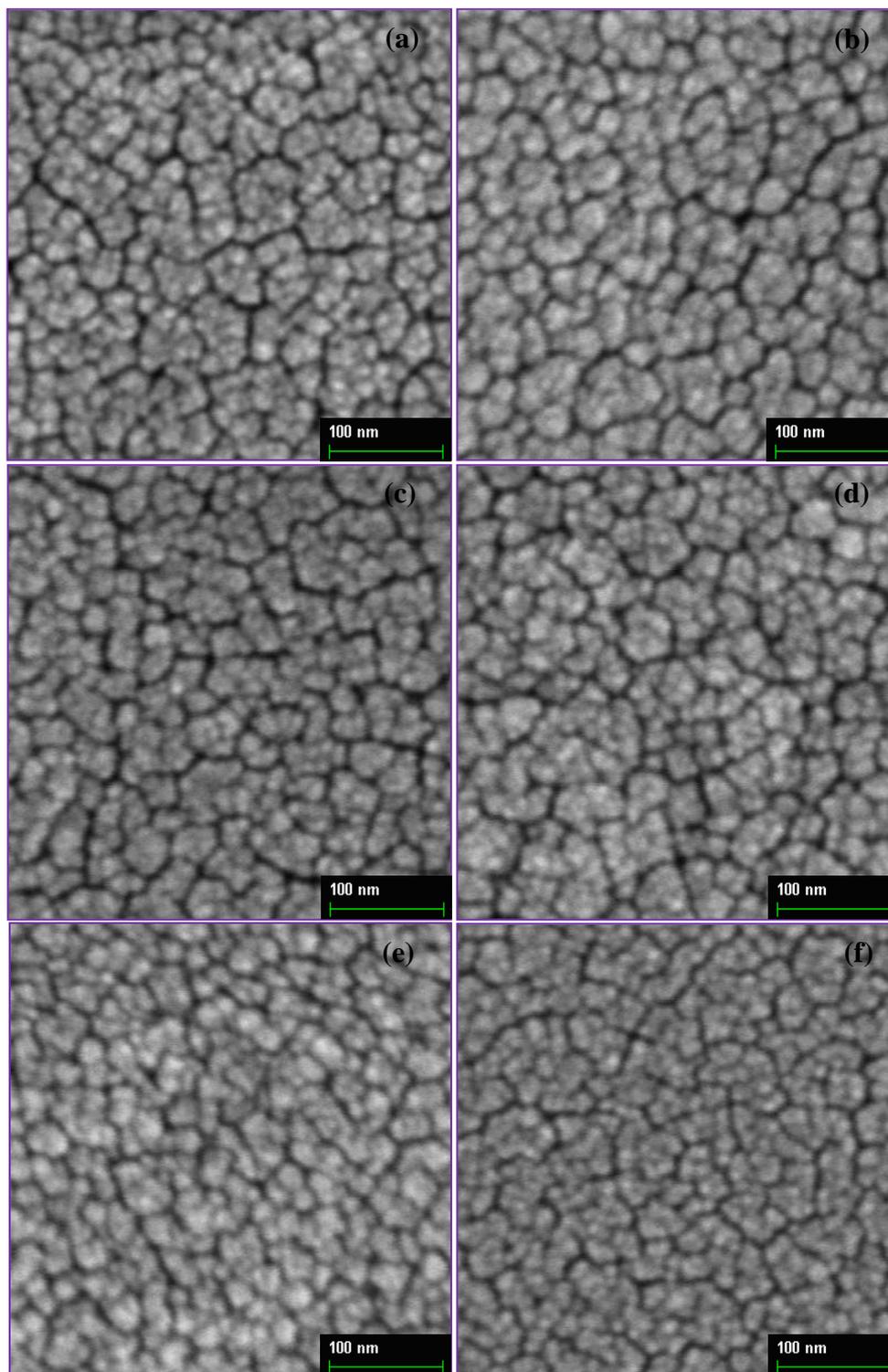


Figure S3. FESEM images of (a) ZnO and GZO, (b) 1.50 at.% Ga, (c) 3.60 at.% Ga, (d) 5.03 at.% Ga, (e) 7.12 at.% Ga, (f) 9.08 at.% Ga

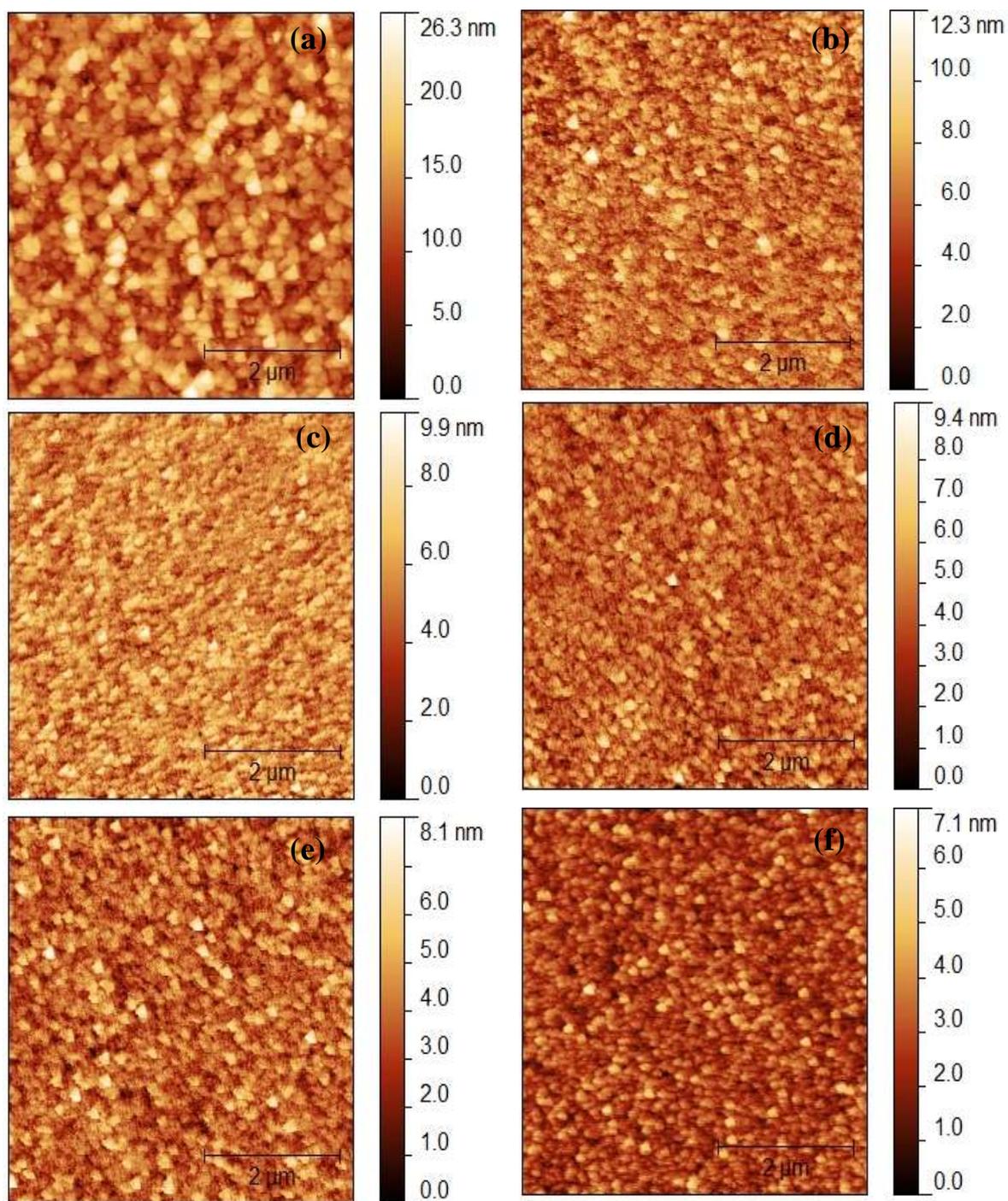


Figure S4. AFM images of (a) ZnO and GZO, (b) 1.50 at.% Ga, (c) 3.60 at.% Ga, (d) 5.03 at.% Ga, (e) 7.12 at.% Ga, (f) 9.08 at.% Ga

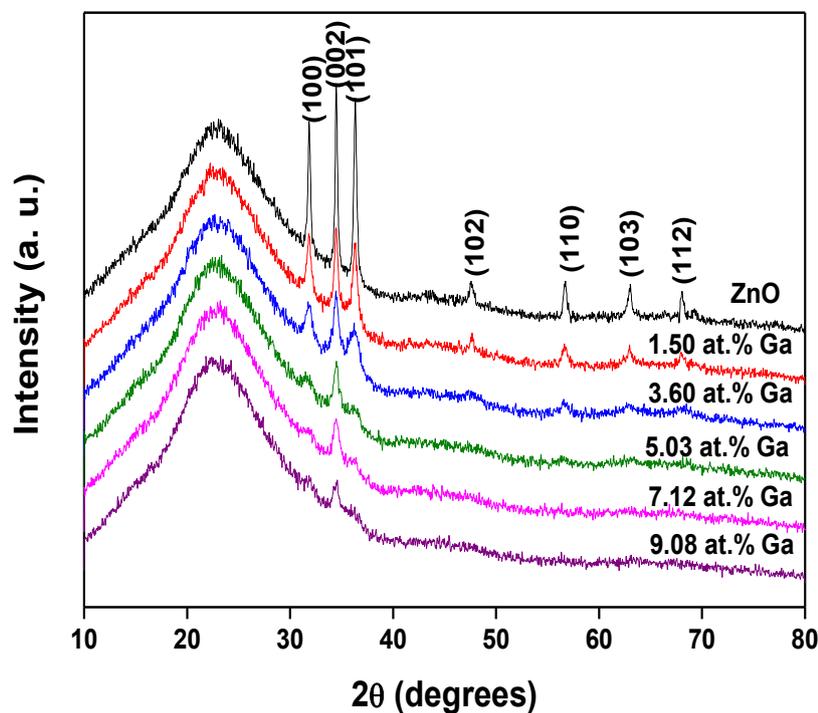


Figure S5. X-ray diffraction pattern of ZnO and GZO films

Figure S5 shows the x-ray diffraction pattern of ZnO and GZO nanocrystalline thin films. The diffraction peaks at  $2\theta$  (degrees) of  $31.77^\circ$ ,  $34.40^\circ$ ,  $36.26^\circ$ ,  $47.51^\circ$ ,  $56.55^\circ$ ,  $62.79^\circ$  and  $67.89^\circ$  are indexed as (100), (002), (101), (102), (110), (103) and (112) planes of ZnO. All the diffraction peaks can be indexed to the hexagonal phase of ZnO with lattice constants  $a = 3.248 \text{ \AA}$  and  $c = 5.207 \text{ \AA}$ , which are in good agreed with the reported standard values (JCPDS No.36-1451). It is observed that the diffraction peaks of the GZO show a small shift towards higher  $2\theta$  value when compared to that of ZnO. This shift may be due to occupation of Ga ions at Zn sites. The lattice constants have been calculated and are  $a = 3.245 \text{ \AA}$  and  $c = 5.200 \text{ \AA}$ . The diffraction pattern reveals that the GZO films also exhibits hexagonal wurtzite structure. It indicates the decrease of lattice constant, because the radius of  $\text{Ga}^{3+}$  ion ( $0.62 \text{ \AA}$ ) is smaller than that of  $\text{Zn}^{2+}$  ion ( $0.72 \text{ \AA}$ ). The decrease of lattice parameters could be

caused by the increase of the number of substitutional Ga<sup>2+</sup> ions into Zn<sup>2+</sup> sites. Doping of Ga in ZnO does not lead to any structural phase transformation but introduces a lattice contraction. No characteristic diffraction peak corresponding to Ga compound impurity phase is observed, indicating that all gallium ions come into the crystal lattice of ZnO to substitute for zinc ions. In addition, the full width at half maximum of diffraction peaks increases with an increase of Ga doping level, which means that the grain size decreases with the increase of Ga content. The grain size of ZnO and GZO are calculated using Scherrer's equation.

$$D = \frac{K\lambda}{\beta \cos \theta} \quad (1)$$

where, D is the grain size, K is a constant taken to be 0.94,  $\lambda$  is the wavelength of the x-ray radiation,  $\beta$  is the full width at half maximum and  $\theta$  is the angle of diffraction. The grain size has been calculated and is found to be 22.3, 18.3, 13.0, 12.0, 11.2 and 10.7 nm for ZnO, 1.50, 3.60, 5.03, 7.12 and 9.08 at.% GZO respectively. It is observed that the grain size of the ZnO thin films decreased with increase Ga dopant concentration.<sup>[1-4]</sup>

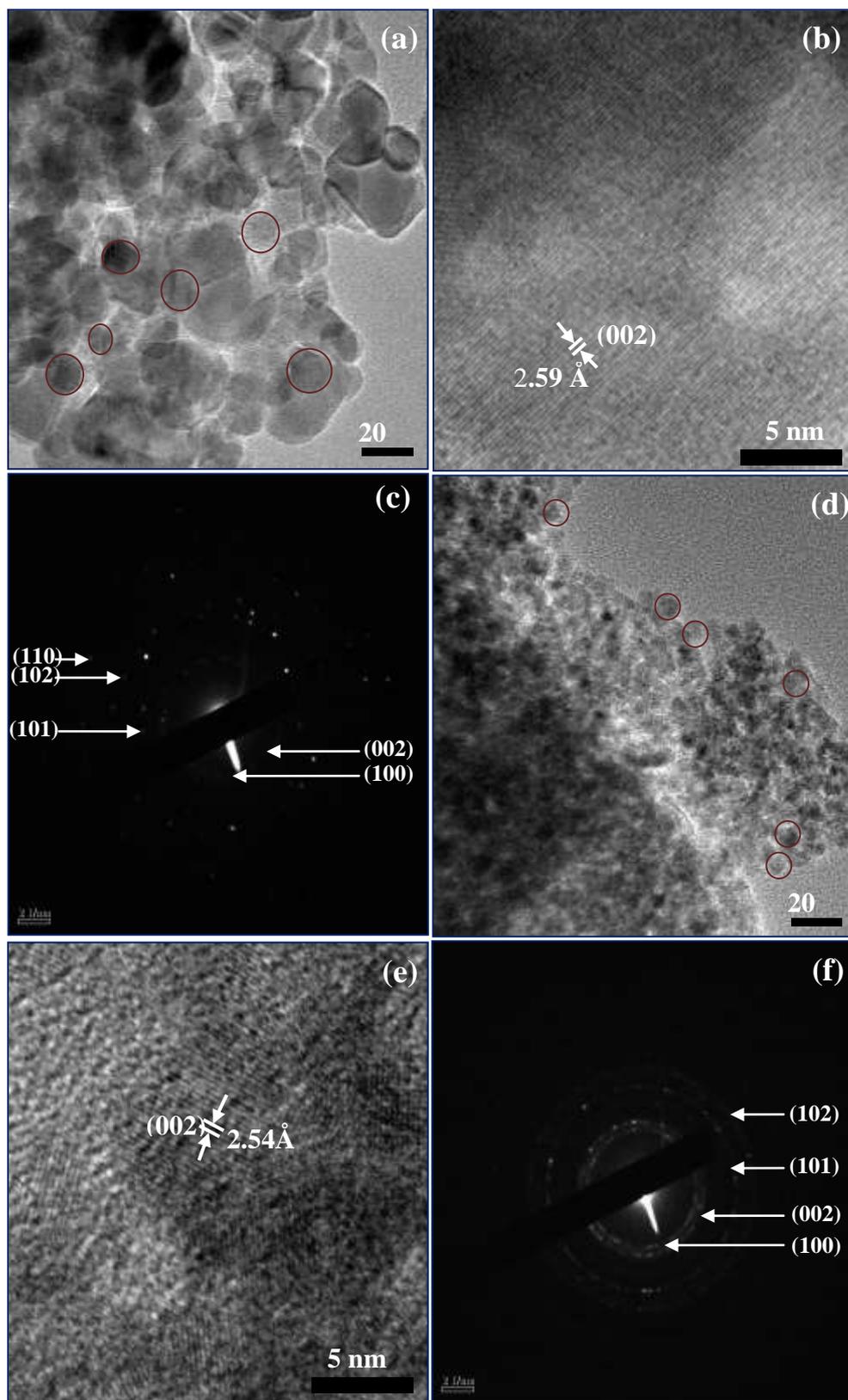


Figure S6. HRTEM, SAED images of (a, b, c) ZnO and (d,e,f) 5.03 at.% GZO

The size of the ZnO and GZO have been studied using high resolution transmission electron microscope (HRTEM). It can be seen from figure S6 (a and d) that the grains are of nearly spherical shape with little agglomeration. The grain size of ZnO and 5.03 at.% GZO are found to be 22 and 12 nm. The figure S6 (b and e) exhibit lattice fringes and the lattice spacing has been determined using these fringes. The HRTEM images of ZnO and 5.03 at.% GZO shows the lattice spacing of the (002) plane to be 2.59 Å for ZnO and 2.54 Å for 5.03 at.% GZO. The lattice spacing of 5.03 at.% GZO is slightly less than that of ZnO and this is because of the small ionic radius of Ga<sup>3+</sup> when compared to that of Zn<sup>2+</sup> ( $r_{\text{Ga}^{3+}}^{3+}=0.62 \text{ \AA}$ ,  $r_{\text{Zn}^{2+}}^{2+}=0.72 \text{ \AA}$ ). Selected area electron diffraction (SAED) was performed to identify the crystallite structure of ZnO. Figure S6 (c and f) shows the SAED pattern of ZnO and 5.03 at.% GZO films. The d spacing values calculated from these images are in close agreement with the values obtained from x-ray diffraction studies.

Figure S7 (a, b, c, d, e, f) shows the energy dispersive x-ray spectroscopy (EDS) spectra of the ZnO and GZO films. The EDS analysis reveals that Zn, O and Ga are present in the sample.

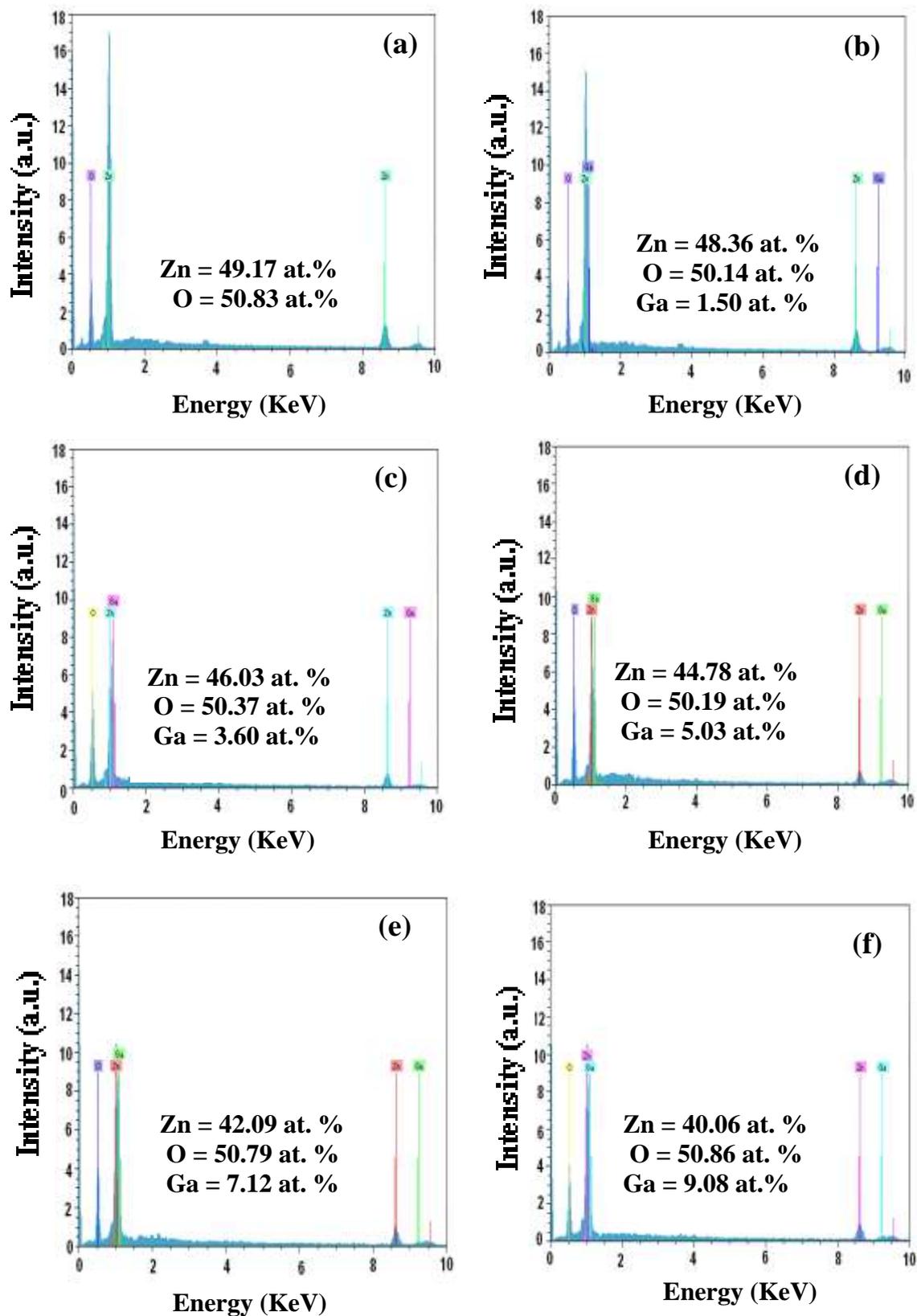


Figure S7. EDS spectra of ZnO and GZO films

## References

- 1 Yuan-Qing Li, Kang Yong, Hong-Mei Xiao, Wang-Jing Ma, Guang-Lei Zhang and Shao-Yun Fu, *Mater. Lett.*, 2010, **64**, 1735.
- 2 Hao Wei , Meng Li, Zichao Ye, Zhi Yang and Yafei Zhang, *Mater. Lett.*, 2011, **65**, 427.
- 3 V. Khranovskyy, U. Grossner, O. Nilsen, V. Lazorenko, G.V. Lashkarev, B.G. Svensson and R. Yakimova, *Thin Solid Films*, 2006, **515**, 472.
- 4 Chien-Yie Tsay, Chun-Wei Wu, Chien-Ming Lei, Fan-Shiong Chen and Chung-Kwei Lin, *Thin Solid Films*, 2010, **519**, 1516.