

**Effect of Substrate Temperature on the Structural,
Surface Morphological and Optical Properties
of Nanostructured ZnO:As Films**

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Abstract

Nanocrystalline ZnO:As films prepared using RF-Magnetron sputtering with different substrate temperatures. Structural study has done using x-ray diffraction (XRD) and the lattice parameter is affected to the lattice mismatch of As with Zn and O. The scanning electron microscope (SEM) images of plane view and cross-sectional view shows the columnar growth is enhanced while increasing the substrate temperature. And the results showed that the solubility of As in ZnO lattices is low at temperature of below 200°C. The As percentage in ZnO:As film grown at a temperature of 200°C is estimated as 0.86 from x-ray photoemission spectroscopy (XPS). Photoluminescence (PL) spectrum showed the near band-edge (NBE) emission as well as defect level emission (DLE) and peak shift is found with the incorporation of As atoms.

Keywords: As:ZnO, XPS, PL, RF Sputtering

1. INTRODUCTION

Zinc oxide (ZnO) is a II–VI n-type semiconductor with wurtzite structure with ions connected with four counter ions in the tetrahedral bond of sp^3 hybridization [1]. It has been widely studied because of its unique properties such as wide bandgap of 3.3 eV and large excitonic binding energy of 60 meV at room temperature [2].

The undoped ZnO thin films show n-type and already good for the device applications due to the native defects such as zinc interstitials and oxygen vacancies. However, the growth of p-type ZnO is having few difficulties and it is hindered the developments of blue/UV p-n junction light emitting diodes and laser diodes. The most suitable dopants for p-type doping in ZnO are the group V elements (N, P & As) substituting for O, although the theory suggests the difficulty in achieving shallow acceptor levels. Preparation of p-type ZnO has been successfully made with monodoping with (N,P) [3-5] and codoping [6,7] of by a large number of groups. But in contrast, there are few reports on the fabrication of As doped p-type ZnO films. This is because of the As ionic radius is larger than the O ionic radius. Even though $As_{Zn}-2V_{Zn}$ defect complex produces the acceptors, it is achievable only at the super saturation of As atoms in the ZnO lattices. But As_{Zn} and $As_{Zn}-V_{Zn}$ are act as donors in the ZnO lattices.

And the researchers are giving more attention on the electrical properties of As doped ZnO for the fabrication of p-type ZnO. The structural, surface morphological and optical properties are also most important for the fabrication of high-quality optoelectronic devices. Nanocrystalline films are giving more attention

because the reduction of particle size novel electrical, mechanical and optical properties are introduced, which are largely believed to be the result of surface and quantum confinement effects.

For making the zinc rich environment in the preparation conditions for the possibility of substituting the As in O position because to avoid the bonding of As and O, we have tried ZnO nanocrystalline films in the absence of oxygen atmosphere on glass substrates prepared using RF magnetron sputtering technique. And we discussed the effects of substrate temperature on the growth of highly textured nanocrystalline ZnO:As thin films on glass substrates.

2. EXPERIMENTAL

Thin films were prepared by planar RF-magnetron sputtering from ZnO:As (3 Wt%) target. The target was prepared by mixing and grinding the powders of ZnO (99.99%, Merck) and As₂O₃ (99.99%, Merck) using the ball mill for 20 hours. Then the prepared target is palletized to a diameter of 50 mm and 5 mm thickness and sintered at a temperature of 950°C. The substrate was set at a distance of 6 cm above the target. Corning 7059 glass plates were used as substrate. Before deposition, the chamber was evacuated to an ultimate background pressure of 10⁻⁶ mbar for 1 h and pre-sputtering process employed for 10 min to clean the target surface. High purity Ar (99.999%) was used as sputtering gas. The Ar flow was introduced directly into dark space shields of the sputtering sources. The sputtering gas pressure was controlled by adjusting a needle valve and the deposition pressure in the chamber was maintained at 10⁻⁴ mbar. Substrate temperature was varied from room temperature (RT) 27 to 400°C, and the RF power was maintained at 200W.

The prepared target was showing the powder particles were not tightly bonded. Even though the deposition lasted for 10 min, the prepared films show different thicknesses.

The structure and phase purity characterization of the films was carried out with a Rigaku X-ray diffractometer using CuK_α radiation. The optical transmittance of the films was studied using a UV-Vis-NIR spectrophotometer (Ocean-Optics Inc., HR2000 Model) with a cleaned corning glass in the reference beam.

3. RESULTS AND DISCUSSION

3.1 Film structure

Fig. 1 shows the XRD patterns of the As doped ZnO thin films deposited at 27, 100, 200, 300 and 400 °C substrate temperatures. All films show a pronounced (002) peak

around 34.32° for wurtzite structure of ZnO, indicative of preferential orientation with the c axis perpendicular to the substrate surface. The mean crystallite sizes (D_{XRD}) were calculated using the Scherrer formula, $D_{\text{XRD}}=0.94\lambda/(\beta \cos \theta_\beta)$, where λ , θ_β , and β are the x-ray wavelength, Bragg diffraction angle, and the line width at half maximum of the diffraction peak, respectively. The mean crystallite size values and lattice constant values are given in table 1.

When the substrate temperature is increased from 27 to 200°C , the 2θ peak position moved to lower angle side. It is due to the increase of lattice constant in c -axis. Atomic radius of As atom (1.20\AA) is higher than O (0.73\AA) and Zn (0.72\AA) and the solubility of As atom in ZnO crystallite is low at RT [8]. The ionic radius of As is greater than Zn and O ionic radius and it is reported that the diffusion behavior of Ag having the same ionic radius as As in ZnO thin film is restricted at low temperature on below 175°C [8]. At these temperatures it may formed interstitial defects or As_2O_3 precipitate in ZnO matrix. It is already reported that the As would preferably bind with O more strongly than themselves [9]. When further increasing of substrate temperature from 200°C , the peak position shift back to higher angle side and the c -axis lattice constant was get decreased. This is due to the formation the substitution of As in Zn position creates a two zinc vacancies near by ($\text{As}_{\text{Zn}}-2\text{V}_{\text{Zn}}$ defect complexes) so that it decreases the lattice constant.

It is noticed that the peak position of the film deposited at 400°C is showing asymmetry with the reduction in intensity and the peak was blewup at the low angle side indicates the poor orientation and crystallinity of the film.

3.2 Elemental Study

XPS spectra of ZnO films were analysed to investigate the chemical states of Zn, As and O in ZnO:As film. Figure 2 is the total XPS spectrum of ZnO:As grown at a substrate temperature of 200°C after 5 min Ar^+ sputter cleaning. From figures 3a, 3b & 3c, the peak positions of Zn($2p_{3/2}$), Zn ($2p_{1/2}$), O(1s), As(3d) are found and it is centered at 1024.21, 1047.36, 531.66 and 42.92 eV. The As(3d) peak is relatively weak because of the low concentrations and this peak is attributed corresponding to As-O bonding. The quantitative analysis were made and the relative percentage of As in ZnO:As film estimated as 0.86. The O(1s) peak shows asymmetry due to the defects formed under the incorporation of As elements.

3.3 Surface morphology

SEM micrographs of a surfaces and cross-section of ZnO:As layers which have been deposited at various temperatures are given in figure 4. All the films show the particles are closely bonded and no voids are observed.

Fig. 4a & 4b shows the cluster of particles with highly dense structure. As explained in the structural analysis, there may be As_2O_3 clusters or metallic clusters in the structure during the deposition below 200°C. Or the thermal energy was not enough to for the orientation of particles.

At a substrate temperature of about 200°C, the ZnO:As layer have the advanced surface and typical columnar structure with highly dense of grains and is shown in Fig. 4c. There are no voids observed in the structure. This means that the film is very dense structure with high packing density. There various models have proposed for the growth of columnar structure like Witten-Sanders model [10] and Thornton [11]. The columnar growth in our film is closely matched with Thornton model. In that, the increasing of substrate temperature at a low pressure there is a transition from a porous structure (tapered crystallites with voids) to a densely packed film (columnar structure).

The increase of substrate temperature further from 200°C to 400°C gives the reduction of the surface relief of ZnO:As layer and the disappearance of columnar structures (Fig. 3d & 3e). And the surface is smooth and flat with dense of grains.

In Fig. 4a & 4b, the surface of the film deposited at 27°C show the higher roughness than the film deposited at 100°C. When the substrate temperature is increased further, the surface becomes smooth and high dense of grains (Fig. 4c-4e). This is mainly due to the migration ability of atoms and molecules on the surface are increased during the growth at higher substrate temperature. This is an evidence of the film stress is decreased while increasing the substrate temperature.

The particle sizes were calculated from the SEM micrographs for the films deposited at 200, 300 and 400°C films. We could not attempt the particle size calculations to the films deposited at 27 and 100 °C because of the more cluster of particles and higher roughness. The measured particle sizes are given in table 1. The samples show the nanometer size grains. The average particle size of the film observed by SEM is larger than that calculated from XRD pattern. This is owing to the incorporation of defects such as twins, dislocations, etc., into the crystallites

during the growth [12]. But the particle size observed here is highly correlating with the particle size calculated from XRD pattern.

3.4 Photoluminescence

Fig.4 shows the photoluminescence spectrum of ZnO:As films measured at room temperature. The inset of fig.5 shows the NBE emission of ZnO:As films. The emission peak at the UV region of the ZnO:As film grown at a temperature of 27°C is inhomogeneous and relatively broad. This is due to the reduction in the particle size and inhomogeneous distribution of particles. And further increasing the substrate temperature to 100°C, the peak position get asymmetric and the intensity also decreases. The decreasing of intensity is an effect of lattice defects such as oxygen vacancy (V_O), zinc interstitials (Zn_i) or due to the segregation of As defect complex in the ZnO crystallites. The UV emission of the film deposited at 200°C showing almost homogeneous broadening and small blue-shift to (10 meV) is observed from the film deposited at RT. This shift is strongly believed as the effect of quantum confinement of free electrons. Further increases in the substrate temperature the peak again back to asymmetry with a small red shift in the peak and the intensity of the peak is too low. The red shift in peak position may be an effect of acceptor-bound exciton. It is known that, under Zn-rich conditions, oxygen vacancies dominate since the oxygen vacancies have lower formation energy than the zinc interstitials. The only possibility of As can engage the position in ZnO crystallite is oxygen sites rather than zinc sites. The first-principles total energy calculations show that arsenic-oxygen antisite (As_O) is deep about 930 meV above the valence band maximum [9]. This could be reason that the small red-shift (15 meV) has found related to the film deposited at RT. There is no UV emission is found at the film deposited at 400°C. With our experimental conditions (under zinc-rich environment) and also at higher substrate temperatures (~350°C) the oxygen deficiencies would occur due to the re-evaporation of oxygen atoms from the surface and insufficient oxygen atoms during the growth [13]. It explains the crystalline quality of the film is degraded due to the large lattice defects at 400°C.

Fig. 6 shows the intensity variation of the deep-level emission (DLE) with substrate temperature. When the substrate temperature is increased from 27 to 100°C, the intensity of the DLE is increasing. There is no DLE found on the film by increasing the substrate temperature to 200°C. This is already explained that the lattice defects due to the metallic cluster or As_2O_3 segregation. These lattice defects only decreasing the energy of free excitons due to the binding energy of excitons with defects. The reason of the DLE disappeared in the film is not understood fully. There may be a uniform distribution of the particles at that temperature with low formation

of defects. When the substrate temperature increased further from 200°C, the DLE is increased. It is obvious that the intensity of the NBE decreases while the intensity of the DLE increases.

Conclusion:

In summary, high-quality ZnO:As films have been successfully grown on the glass substrate by the RF-Magnetron sputtering technique with different substrate temperatures. From XRD, SEM and PL measurements the solubility of As in ZnO lattice sites is low at a substrate temperature of below 200°C. The concentration of As in ZnO:As film grown at a substrate temperature of 200°C is estimated to be about 0.86%. The columnar growth of grains and the defect free UV emission is found in the film deposited at 200°C. From it we conclude that the substrate temperature of 200°C is the optimal temperature for the good solubility of As in ZnO lattices.

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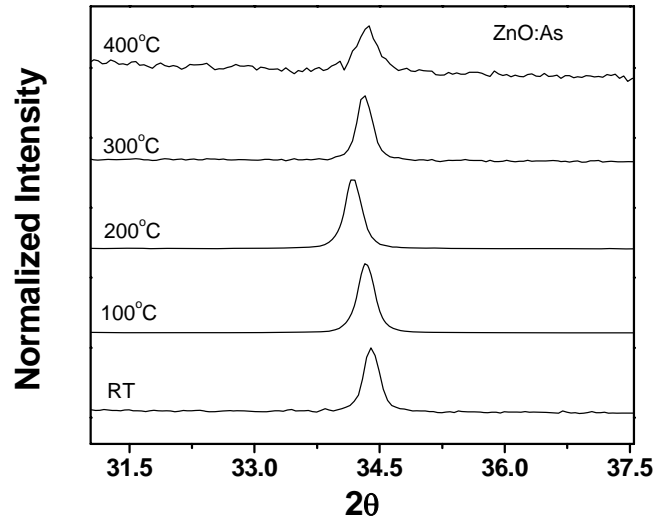


Fig. 1 XRD diffraction patterns of ZnO films grown on glass substrate for various temperatures

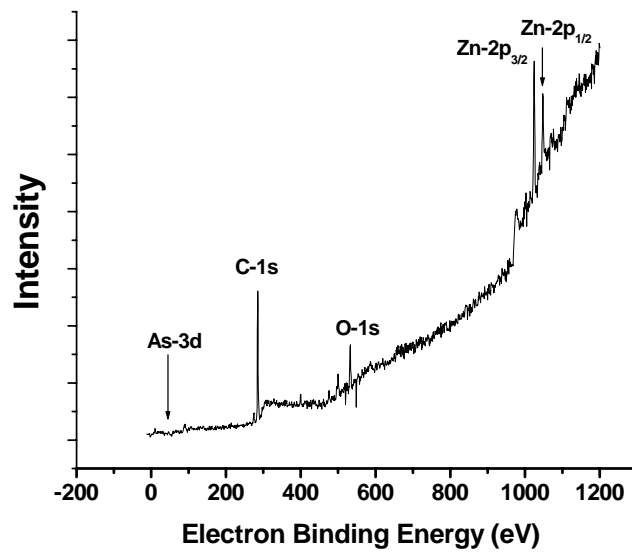


Fig. 2 Total XPS spectrum of ZnO:As grown at a substrate temperature of 200°C on glass substrate

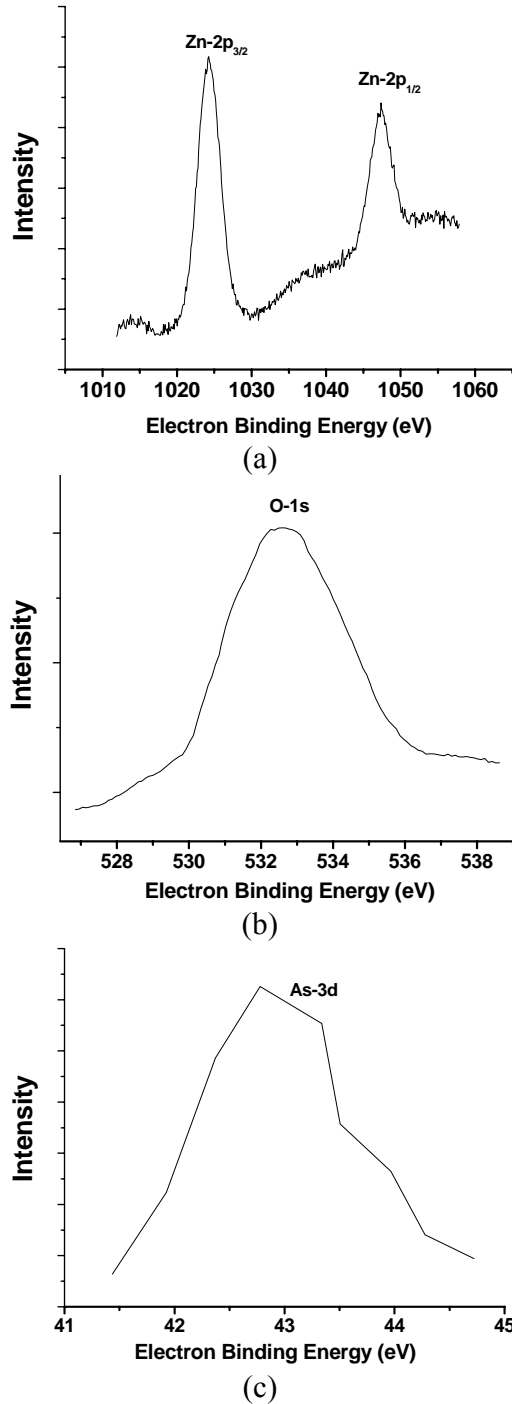


Fig. 3 XPS spectra of (a) Zn(2p), (b) O(1s) and (c) As(3d) of the nanocrystalline ZnO:As film deposited at a temperature of 200°C

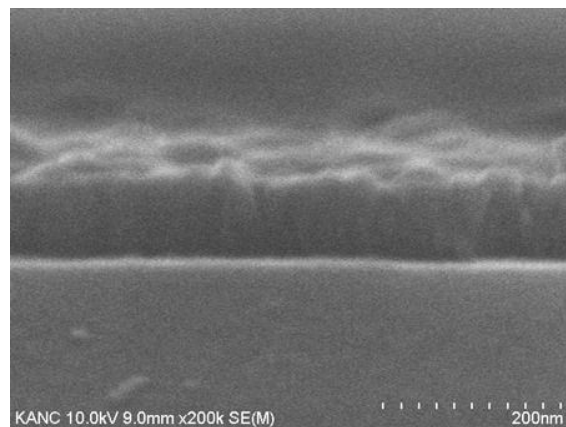
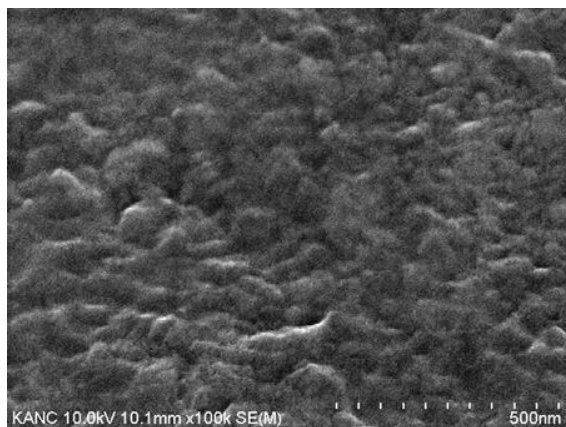


Fig. 4a

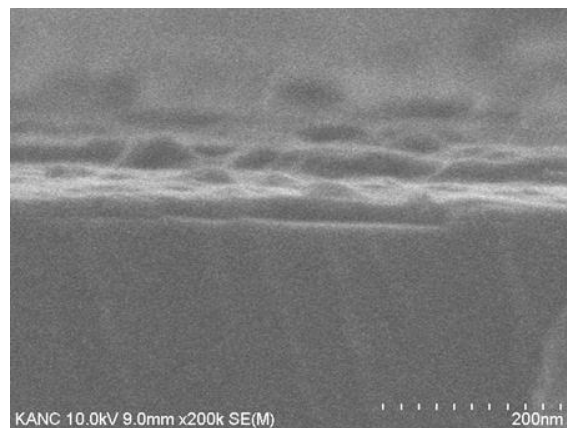
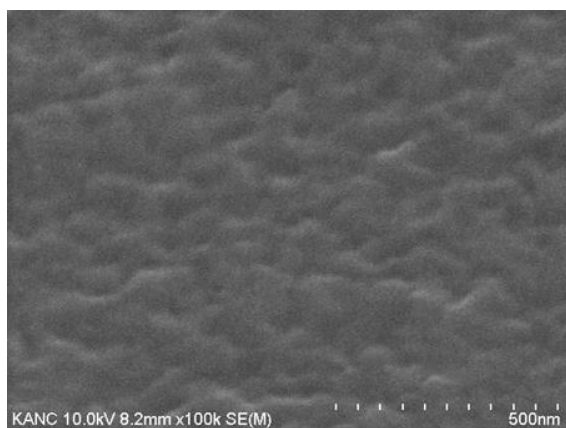


Fig. 4b

Plan View

Cross-sectional view

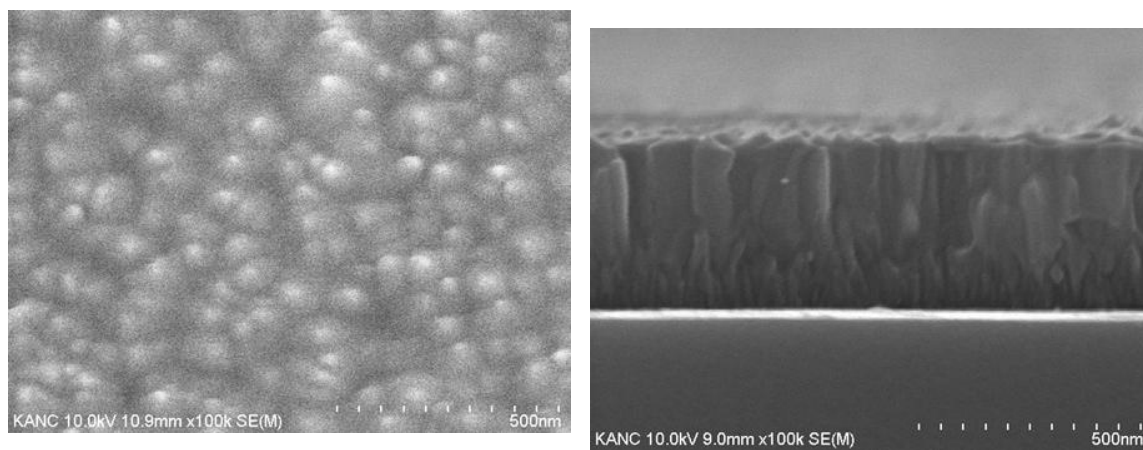


Fig. 4c

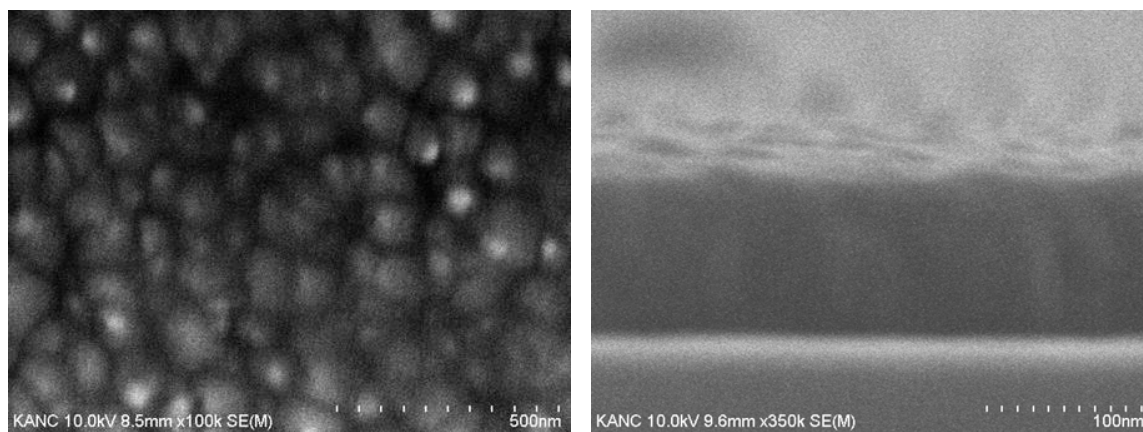


Fig. 4d

Plan View

Cross-sectional view

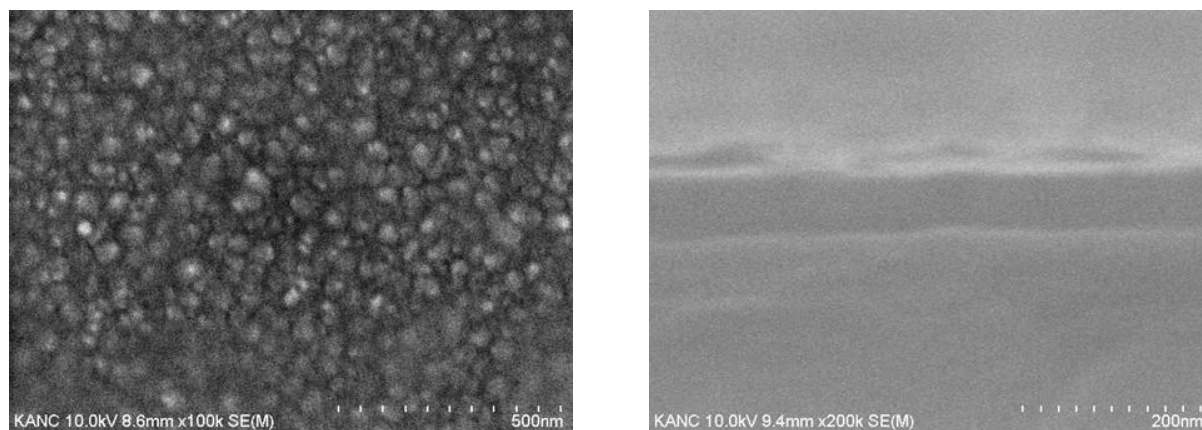


Fig. 4e

Plan View

Cross-sectional view

Fig. 4. SEM micrographs of ZnO:As films prepared at (a) 27, (b)100, (c) 200, (d) 300 and (e) 400 °C.

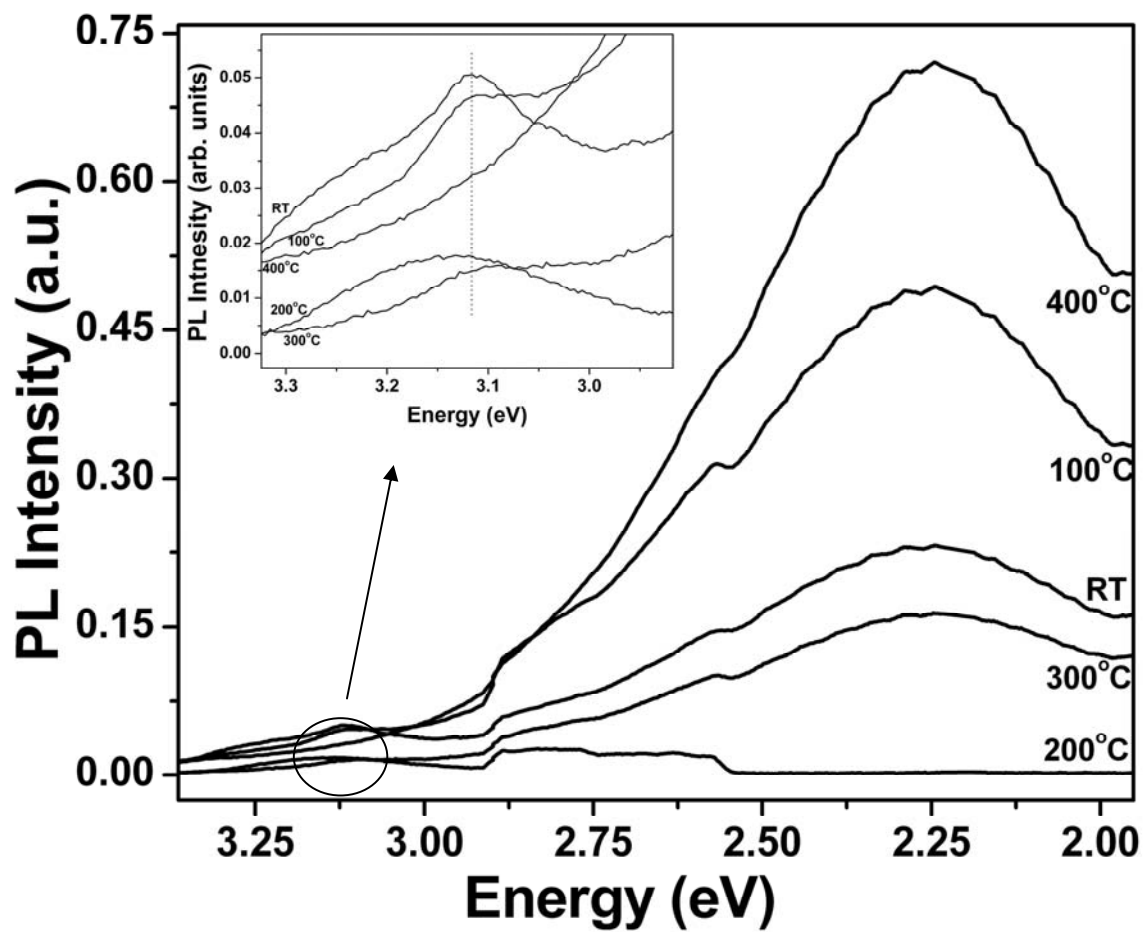


Fig. 5 Photoluminescence spectrum of ZnO:As films

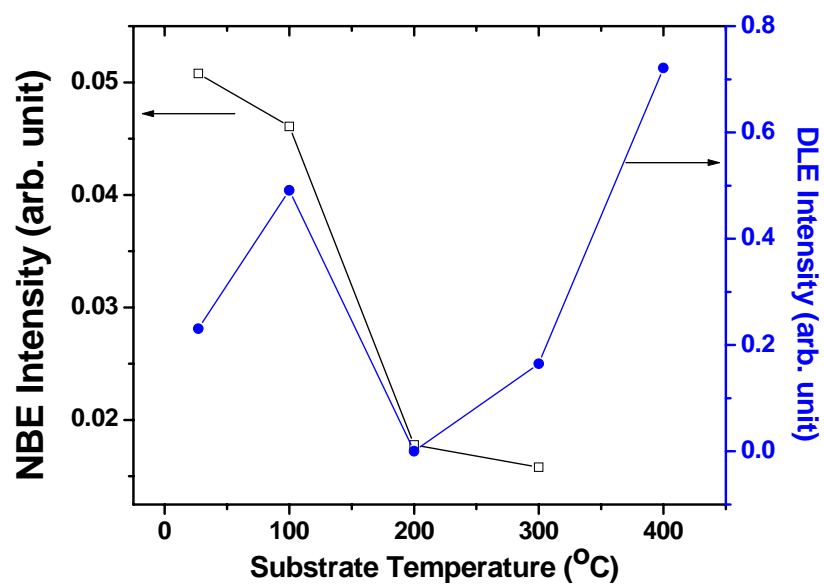


Fig. 6 Variation of NBE and DLE Intensity with substrate temperature

Table 1
Structural and surface morphological properties of ZnO:As films

Substrate temperature	27°C	100°C	200°C	300°C	400°C
D _{XRD} (nm)	38.87	35.86	35.86	38.87	29.17
Lattice constant c (Å)	5.21	5.22	5.24	5.23	5.22
D _{SEM} (nm)	-	-	49.41	84	37.8
Thickness (nm)	92.10	231.57	385.42	104.92	68.42

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