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Influence of substrate type on morphology and photoluminescence properties of ZnO thin films prepared by ultrasonic spray pyrolysis method

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ABSTRACT In this study, ZnO thin films were grown on glass, n-Si (100), c axis textured graphite and indium tin oxide coated glass (ITO) substrates by ultrasonic spray pyrolysis method. X-ray diffraction studies showed that ZnO samples have hexagonal structure with (002) preferred direction. The preferred orientation of the sample prepared on ITO substrate changed from (002) to (101). Some diffraction peaks of graphite and ITO substrates were observed in X-ray diffraction pattern. Lattice parameters of ZnO samples grew on glass, graphite and ITO substrates were approximately equal to lattice parameters of bulk ZnO (a = 3.249 Å and c = 5.206 Å). Quasi-aligned hexagonal shaped ZnO microrods were obtained for glass and ITO substrates. Room temperature photoluminescence measurements indicated a sharp ultraviolet luminescence at ~380 nm. Band gap values were found from UV peak position between 3.25 – 3.28 eV. Relative intensity of defect related peaks between 400–700 nm in photoluminescence spectra decreased significantly for ITO substrate.

Keywords: ZnO; USP Method; Substrate; Format.

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1. INTRODUCTION

In recent years, micro- and nano-structured materials are becoming increasingly important in technology. These materials are intensively working for device applications such as field-effect transistors [1], single-electron transistors [2], photodiodes [3] and chemical sensor [4]. Among these materials ZnO has an important place due to its direct band gap of about 3.37 eV, its large exciton binding energy (60 meV) and its low cost. Therefore, fabrication of ZnO micro- and nano-structures in different morphologies is of critical importance for the development of novel device.

ZnO has various morphologies such as microsphere [5], microcomb [6], nanorod [7], nanotube [8] and nanowire [9]. Different methods such as chemical vapor deposition [10], thermal evaporation [11], spray pyrolysis [12] and chemical bath deposition [13] can be used for preparation of micro- and nano-structured ZnO samples. Spray pyrolysis method is simple and low cost for deposition of different materials [14]. Atomization of solution in spray method can be carry out by ultrasonic nebulizer, improved hydrolysis spraying, corona spraying, electrostatic spraying and pneumatic spraying [15]. Atomization type is important parameter due to better control over droplet size and its distribution on the substrate. Nowadays, spray by ultrasonic nebulizer has come into one of the most powerful methods for preparation of nanostructured materials [16]. Also, substrate type effects surface morphology of the thin films due to differences in the thermal conductivity and surface energy of the substrates [17].

In this study, undoped ZnO thin films were deposited on glass, Si, graphite and indium tin oxide coated glass substrates by ultrasonic spray pyrolysis (USP) method. Our aim is investigation of the correlation between structural and optical properties of ZnO thin films and substrates.

2. EXPERIMENTAL

ZnO thin films were prepared on different substrates (glass, n-Si (100), *c* axis textured graphite and indium tin oxide coated glass (ITO)) by ultrasonic spray pyrolysis in air atmosphere. First of all, substrates were cleaned ultrasonically with acetone, ethanol, and deionized water, respectively and then the substrates were dried by air flow. The initial solution was prepared from zinc chloride ($ZnCl_2$) at 0.15 M concentration in deionized water. Film growth was performed with a spray rate of about 2 ml/min. The substrate temperature was 400 °C and the process was carried out at atmospheric pressure. During growth, the substrates were rotated at 3.5 rpm in order to produce uniform and homogenous films. The crystal structure of ZnO thin films was examined by X-ray diffraction (XRD) using Rigaku Smartlab with CuK_α radiation (λ = 1.5408 Å) over the range 2θ = 30–60° at room temperature. Morphological information was obtained by JEOL JSM 6610 scanning electron microscope (SEM). Elemental analysis was studied by using Oxford Instruments Inca X-act energy dispersive X-ray spectroscopy (EDS) attached to the SEM. Room temperature photoluminescence (RTPL) spectra were measured using SpectraMax M5 spectrophotometer with a xenon flash lamp as light source operating at 280 nm and with an output power of 150 W.

3. RESULTS

Fig. 1 shows the XRD spectra of the ZnO thin films prepared on different substrates. ZnO thin films had hexagonal structure. The preferred orientation was (002) plane and its intensity were same approximately for glass and n-Si. The preferred orientation and peak intensity decreased for graphite and ITO substrates. Also, the preferred orientation changed from (002) plane to (101) plane for ITO substrate. A small diffraction peak at approximately 43° (+) was observed in XRD pattern of the ZnO thin films prepared on glass and n-Si substrates. This peak can be attributed from (200) plane of cubic ZnO phase (PDF Card No.: 01-077-9353). However, the orthorhombic Zn_2SiO_4 (zinc silicate) phase has (004) diffraction peak at approximately 43° (PDF Card No.: 00-024-1469). Zn_2SiO_4 phase can be formed due to relatively high deposition temperature of ZnO thin films. Similar results were found by another researcher for ZnO samples [18, 19]. Diffraction peaks of ITO (*) and graphite (#) structures were formed in the samples prepared on ITO and graphite substrates.

The lattice parameters *a* and *c* were calculated according to the following relation:

$$\frac{1}{d^2} = \frac{4}{3}\left(\frac{h^2+hk+k^2}{a^2}\right) + \frac{l^2}{c^2} \quad (1)$$

where *d* is interplanar spacing of atomic planes and (*hkl*) is Miller indices. Calculated latttices parameters were listed Table 1. Lattice parameters of ZnO samples for glass, graphite and ITO substrates were approximately equal to lattice parameters of bulk ZnO (*a* = 3.249 Å and *c* = 5.206 Å). But, large amount change in *a* and *c* values (3.271 Å and 5.238 Å) of ZnO thin film for n-Si substrate was observed.

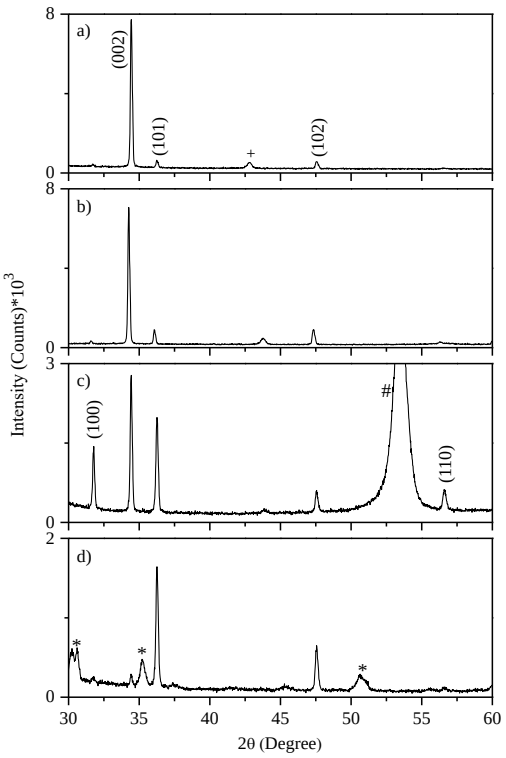

Figure 1. X-ray diffraction patterns of ZnO thin films for a) glass b) n-Si, c) graphite and d) ITO substrates.

Table 1. a and c attice parameters, compositional ratio, thickness (t) and band gap (Eg) of ZnO thin films.

Substrate	***a* (Å)**	***c* (Å)**	**Zn (at.%)**	**O (at.%)**	**Zn/O**	***t* (μm)**	**E_g (eV)**
Glass	3.256	5.213	51.2	48.8	1.05	1.20	3.26
n-Si	3.271	5.238	52.9	47.1	1.12	0.88	3.25
Graphite	3.254	5.214	52.4	47.6	1.10	0.56	3.27
ITO	3.253	5.211	54.8	45.2	1.21	0.55	3.28

The thickness of the films was determined from the cross-sectional SEM micrographs (Fig. 2.) and was listed in Table 1. The thickness of the ZnO thin films prepared on glass, n-Si, graphite and ITO substrate was found as 1.20 μm, 0.88 μm, 0.56 μm and 0.55 μm, respectively. It was observed that substrate type had significant effect on the thickness of ZnO samples and ZnO sample grown with the largest thickness on glass substrate. The surface morphologies of ZnO thin films were studied by SEM and results were shown in Fig. 2.

As can be seen, substrate type affects significantly surface morphology of the samples. This result can be attributed to the differences in the thermal conductivity and surface energy of the substrates [17]. The thermal conductivity and the surface energy values of the substrates were listed in Table 2. It can be seen from Table 2 that glass and ITO substrates have the lowest thermal conductivity value, and glass and n-Si substrates have the largest surface energy value. Samples prepared on glass and ITO grew as quasi-

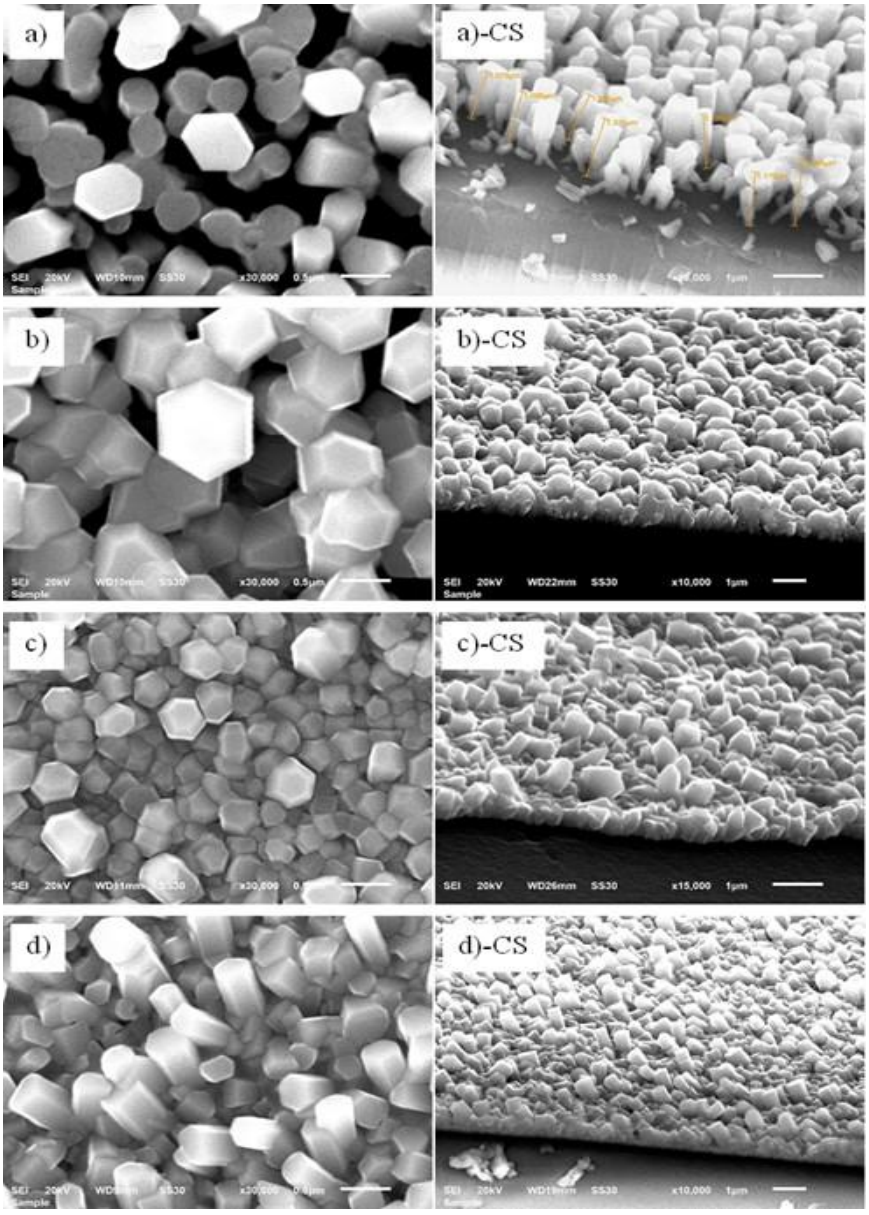

Figure 2. Surface and cross section (CS) scanning electron micrographs of ZnO thin films for a) glass b) n-Si, c) graphite and d) ITO substrates.

aligned hexagonal shaped microrods with diameters varying between 0.3 and 0.7 μm. It can be said according to these results that ZnO thin films prepared on substrates (glass and n-Si) with high surface energy have large thickness, and ZnO thin films prepared on substrates (glass and ITO) with low thermal conductivity have hexagonal shaped microrods. Different researchers were found similar hexagonal shaped microrods structure for ZnO thin films prepared with spray pyrolysis method [20-22]. However, while microrods for ZnO sample on glass substrate had c-axis orientation on substrate surface, microrods in ZnO thin film prepared on ITO had randomly orientation. The preferred orientation change seen in XRD data of the ZnO thin film prepared on ITO substrate confirms this result. The reason of randomly orientation in ZnO microrods prepared on ITO could be the lower surface energy of ITO than that of glass. The surface of the ZnO samples prepared on glass and n-Si had some voids. The larger grain size was obtained for n-Si substrate. Grain structure of ZnO thin film for graphite substrate was close packed, different size and shape. Zhang and co-worker in a similar study were obtained pyramidal-shaped nanosheets for ZnO prepared on graphite substrate [23]. The composition ratio of the films was determined by EDS analysis. Fig. 3 shows a typical EDS spectrum of the ZnO sample prepared on Si substrate. The atomic percent (at.%) of Zn and O in the films are listed in Table 1. It was observed that composition ratio of samples changed significantly depending on substrate type. All samples are Zn-rich because of Zn/O ratio is larger than 1. But ZnO sample prepared on glass substrate was more stoichiometric than the other samples.

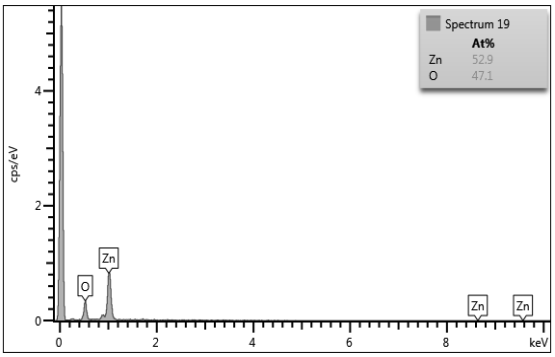

Figure 3. Energy dispersive X-ray spectroscopy of ZnO thin films for n-Si substrate.

Room temperature photoluminescence spectroscopy (RTPL) was performed for investigation of the optical properties and structural defects. Fig.4 shows RTPL spectra of the samples. The samples exhibited sharp and predominant UV luminescence at approximately 380 nm, which demonstrates high crystallinity. However, the intensity of UV peak for graphite and ITO substrate increased. The origin of near band edge UV emission is due to the free exciton recombination [24].

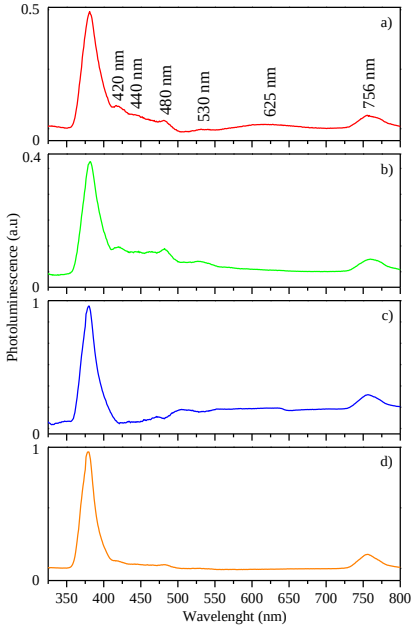

Figure 4. Room temperature photoluminescence spectra of the ZnO thin films for a) glass b) n-Si, c) graphite and d) ITO substrates.

The peak at 756 nm is related to second-order properties of the UV peak [25]. The position of UV peak was used for determining of band gap (E_g) of the samples. Obtained band gap values listed Table 1, which were between 3.25 – 3.28 eV. Five defect related peaks were observed at 420, 440, 480, 530 and 625 nm for RTPL spectra of ZnO samples on glass substrate. The peak at 420 nm attributes to interstitial zinc atoms (Zn_i) [21]. The peaks at 440 nm and 480 nm are related to transitions of interstitial Zn levels to vacancy Zn levels and transitions of interstitial O levels to vacancy O levels, respectively [26]. The peak at 530 nm can be related to vacancy Zn, interstitial Zn, vacancy O, interstitial O and anti-sites defects [25, 27]. The broad peak at 625 nm can be explain with to O and Zn anti-sites [28]. The defect peak at 625 nm for n-Si substrate and defects peaks between 400 – 500 nm for graphite substrate disappeared. In addition, the region between 400 – 700 nm in RTPL spectrum of ZnO on ITO substrate had become more flattened, which shows that defects concentrations decrease. We found that although ZnO thin films prepared on ITO and graphite substrate had lower XRD intensity, lower thickness and lower stoichiometry (higher Zn/O ratio), they had higher UV intensity, which is reverse in the expected situation. This result can be explained with surface properties of ZnO thin films. As can be seen from Fig. 2 ZnO thin films prepared on glass and n-Si substrates had more voids on their surface. Higher voids density increase surface defects and so UV intensity of ZnO thin films decrease. It is known that the effect of the surface becomes important when dealing with samples having high surface to volume ratio and so the presence of surface states must be considered as potential influencers on the material's optical properties [29].

Thus, substrate type affects significantly luminescence properties of the ZnO films by defect type and their concentration.

Table 2. Thermal conductivity and surface energy of glass, Si (100), graphite and ITO coated glass substrates [17, 30-33].

Substrate	Thermal conductivity (W/cmK)	Surface Energy (ergs/cm$^{2)}$
Glass	1.13×10^{-2}	2.0×10^{3}
n-Si	1.48	2.1×10^{3}
Graphite	16–20	70–80
ITO	3.20×10^{-2}	28–31

4. CONCLUSION

Structural and optical properties of ZnO thin films grown by ultrasonic spray pyrolysis on different substrates were investigated. It was determined from XRD result that ZnO samples have hexagonal structure. The preferred orientation of sample prepared on glass, n-Si and graphite substrates was (002) plane. But the preferred orientation for ITO substrate changed from (002) to (101). Also peak intensity decreased significantly for ITO and graphite substrates. The lattice parameters of *a* and *c* (3.271 Å and 5.238 Å) for ZnO thin film grown on n-Si substrate changed significantly compared to the bulk values (a = 3.249 Å and c = 5.206 Å). ZnO sample with the largest thickness was obtained on glass substrate. According to the SEM results, ZnO thin films prepared on glass and ITO substrates had a hexagonal rod morphology. But, ZnO microrods for ITO had randomly orientation on substrate surface. A sharp ultraviolet luminescence at 380 nm and some defects peaks at 420, 440, 480, 530 and 625 nm for all samples were observed from photoluminescence spectra. However, the maximum UV peak intensity was observed for ITO and graphite substrates.

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