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Effective Annealing of ZnO Thin Films Grown by Electrochemical Deposition Technique

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Abstract

Wide and direct band gap ZnO thin films have been grown on conductive indium-tin-oxide (ITO) substrates by electrochemical deposition (ECD) technique using different growth parameters. High quality films in terms of crystallographic and optical characteristics have been obtained under a cathodic potential of -0.9 V; a pH of 5.2, using 0.1 M $Zn(NO_3)_2$ solution. Oxygen gas flow through the solution increased the growth rate and the quality of samples. Subsequent heat treatments at various temperatures for 30 minutes under dry N_2 gas flow show that the most suitable annealing temperature is 300 °C for these electrochemically deposited thin films on ITO. X-ray diffraction (XRD) measurements show that the samples have preferably grown along the direction of (101) and that the annealing at 300 °C caused an increase in the peak intensity belonging the (101) surfaces. The Atomic Force Microscopy (AFM) measurements revealed that the annealing process improved the surface quality of the samples. It has also been observed from the absorption measurements that the band-gap is enhanced from 3.23 to 3.37 eV after this certain heat treatment.

Key Words: ZnO, electrochemical deposition, annealing effect.
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1. Introduction

ZnO is naturally grown as n-type and hexagonal wurtzite structure with a wide and direct band gap energy of 3.4 eV at room temperature (RT). ZnO has in the past found many applications, such as piezoelectric transducers, varistors [1] and phosphors [2]. Most of these applications require only polycrystalline material. However recent successes in producing large-area single crystals have opened up the possibility of producing blue and UV light emitters, and also high-temperature, high-power transistors [3]. As a light emitter, the

main advantages of ZnO over its chief competitor, GaN (3.5 eV at RT), of which both have many similarities [4], are its 3 times larger exciton binding energy of about 60 meV, and availability of well-developed bulk and epitaxial growth processes for electronic applications. Its attraction also lies in having high breakdown strength, high saturation energy [5], and high radiation tolerance. For example, Coşkun et al. [6] and Look et al. [7] have shown that ZnO is radiation hard because of rapid defect annihilations that take place at temperatures even below 150 K. This property could be advantageous for electronic and photonic applications in radiation environments.

Although ZnO semiconductor thin films are deposited by many conventional growth techniques such as metalorganic chemical vapour deposition (MOCVD), molecular beam epitaxy (MBE), hydryde vapour phase epitaxy (HVPE), the electrochemical deposition (ECD) technique used in this study has the following several advantages in comparison to these methods [8, 9]: (i) the thickness and surface morphology can be controlled by growth parameters; (ii) the deposition rate is relatively high; (iii) the experimental set-up is low-cost; and (iv) it is a low temperature process [10]. Gu et al. found that deposition rates depend strongly on substrate materials and that the growth rate of the film will decrease in time because of increasing electrical resistance of the growing semiconducting oxide layers [11]. Therefore, conductive ITO substrates are preferably used as in the case of present study. Dissolved oxygen was used for the synthesis of ZnO [12] which can also be produced in a two-step process: zinc metal is firstly produced cathodically, and then an anodic process produces ZnO [13].

Electrochemical deposition of ZnO has initially been introduced by Lincot et al. [13–15] and Izaki et al. [9, 16] using GaN and ITO substrates, respectively. Since then, several groups investigated the annealing effects on ECD-grown ZnO. For example, Pauporte et al. [15] found band gap values of 3.5 and 3.3 eV before and after annealing at 400 °C in air for 1 h, respectively, for the ZnO thin films on the transparent SnO_2/glass substrates, using PL and optical transmission measurements. In their another work [17], they have investigated the annealing effect at 500 °C in air for 1 h for ZnO films on GaN layers and found a decrease in the band gap energy. Gao et al. [18] have determined a direct band gap energy of 3.3 eV for as deposited ZnO films and investigated the annealing effects at 550 °C in N_2 and Ar atmosphere on PL characteristics of ZnO/ITO films. It has been observed that green emission is enhanced due to the generation of singly ionized oxygen related defects after annealing. Lin et al. [19] have also investigated the influence of different annealing conditions on UV and green PL characteristics of ZnO thin films grown by the dc reactive sputtering. They have found no effect on the near band edge UV emission but an increase in the intra band gap green PL emission, probably due to the production of O anti-site defects. It was also previously reported that the optical transparency and absorbency strongly depended on the surface roughness and defects such as pits and voids [16, 20]. This work is an attempt to investigate the effects of relatively low temperature annealing at 300 °C for 30 min under dry N_2 gas flow, on the structural and optical properties of ZnO thin films grown onto the transparent and conductive ITO substrates by the ECD technique.

2. Experiment

ZnO thin films were prepared by the ECD technique from an 0.1 M $Zn(NO_3)_2$ aqueous solution kept at a temperature of 65 °C. The deposition was performed on the conductive ITO coated glass slides with a sheet resistance of 15-25 Ω/□ bought from Aldrich, which were used as the working electrodes in a classical

electrochemical cell with three electrodes. Before deposition, the substrates were rinsed in the ultrasonic bath of acetone, methanol and deionized (DI) water. A zinc plate with 99.99% purity was used as the counter electrode. The reference electrode was an Ag/AgCl terminal in a KCl solution. The distance between counter electrode and ITO terminal was about 3 cm while the distance was maintained about 0.5 cm between the reference and working electrodes. Electrodeposition was carried out potentiostatically between -0.6 V and -1.2 V in 0.1 V intervals using a Perkin Elmer potentiostat/galvanostat without stirring. From try-test experiments, it was found that high quality films in terms of crystallographic and optical characteristics can be obtained under a potential of -0.9 V between the reference and ITO during 30 min. deposition time. The pH of the solution was initially adjusted to 5.2. It was determined that the ITO substrate remains stable under prolonged reaction conditions at this pH value. In order to increase the effect of dissolved oxygen, the electrolyte was bubbled with pure O_2 through the electrochemical cell during each growth. The possible reactions that take place in the cell, are written as the follows [21]:

$$NO_3^- + H_2O + 2e^- \rightarrow NO_2^- + 2OH^-$$
$$Zn^{2+} + 2OH^- \rightarrow Zn(OH)_2$$
$$Zn(OH)_2 \rightarrow ZnO + H_2O$$

The two samples, labelled as ZnONA (non-annealed) and ZnOA300 (annealed at 300 °C for 30 min under N_2 gas flow in a home-made furnace) were prepared to observe the influence of annealing on the ECD-grown ZnO thin films.

The same kinds of subsequent heat treatments at temperatures above 300 °C caused cracks and voids probably due to the decomposition of indium, tin and oxide in the substrate at temperatures above 350 °C, as will be discussed in the next section. All the samples were structurally characterised by X-ray diffraction (XRD) technique using Rigaku D/Max-IIIC diffractometer with, Cu Kα radiation of 1.54 Å, within the 2θ angle ranging from 5–60 with a resolution better than 0.2°. AFM imaging was performed in air using a Molecular Imaging model 2100 picoscan instrument. The images were taken in the contact mode using etched silicon probes (pointprobe) with a fundamental resonance frequency of 13 kHz. The 450 μm-long cantilevers were used to record topographic images at a scan rate of 2 Hz. Optical absorption measurements were taken via Perkin-Elmer UV-VS Lambda 2S spectroscope with a wavelength resolution better than 3 nm within the spectral range of 300–700 nm at the room temperature.

3. Results and Discussion

Figure 1 shows the X-ray diffraction results obtained for both non-annealed (as deposited) and annealed samples at 300 °C for 30 min. As seen in Figure 1, all of the lines are identified to be those from the ITO (substrate) and ZnO films grown by ECD. The normalized peak intensities and corresponding full width at half maximum (FWHM) values are tabulated in Table 1. The Joint Committee of Powder Diffraction Standards (JCPDS) file confirms that the peak at $2\theta = 30.53°$ belongs to the conductive ITO substrate and the others indicate ZnO with hexagonal wurtzite-type structure [22]. The width of the ZnO peaks is reasonably narrow which means that a good crystallization is occurred. The XRD data present that (101) direction is the preferred crystal orientation for both non-annealed ZnONA and annealed ZnOA300 samples. The peak intensity of this

dominant orientation of ZnO is increased and the line width is narrowed after annealing at 300 °C for 30 minutes. This result should suggest that the ZnOA300 sample contains more of ZnO grown with the (101) orientation. On the other hand, the annealing process improves the (100) and (110) peaks of ZnO in terms of line width and intensity while the other peaks remain almost the same as before annealing.

Table 1. The FWHM, intensity and peak degrees of the planes observed in annealed and non-annealed samples.

ZnONA	FWHM	I/I_0	Peak Degrees	**ZnOA300**	FWHM	I/I_0	Peak Degrees
ITO	0.718	0.32	30.53	ITO	-	-	-
(100)	0.437	0.32	32.10	(100)	0.235	0.52	31.90
(002)	0.383	0.88	34.74	(002)	0.109	0.59	34.60
(101)	0.319	1	36.60	(101)	0.156	1	36.38
(102)	0.401	0.37	47.88	(102)	0.292	0.19	47.64
(110)	-	-	-	(110)	0.082	0.18	56.63

The data in Table 1 obviously show that the better crystal quality is obtained with 300 °C annealing under dry N_2 gas flow. This can be concluded from the fact that the FWHM value of the dominant (101) peak is improved approximately twice as much. The FWHM values before and after annealing process result in the crystalline sizes of about 31 and 63 nm obtained from the well known Scherrer equation [23], respectively. As can also be seen from Table 1, there exist deviations in the diffraction angles of the crystal planes before and after annealing. This may be due to the formation of different strain relief at the crystal grains [24].

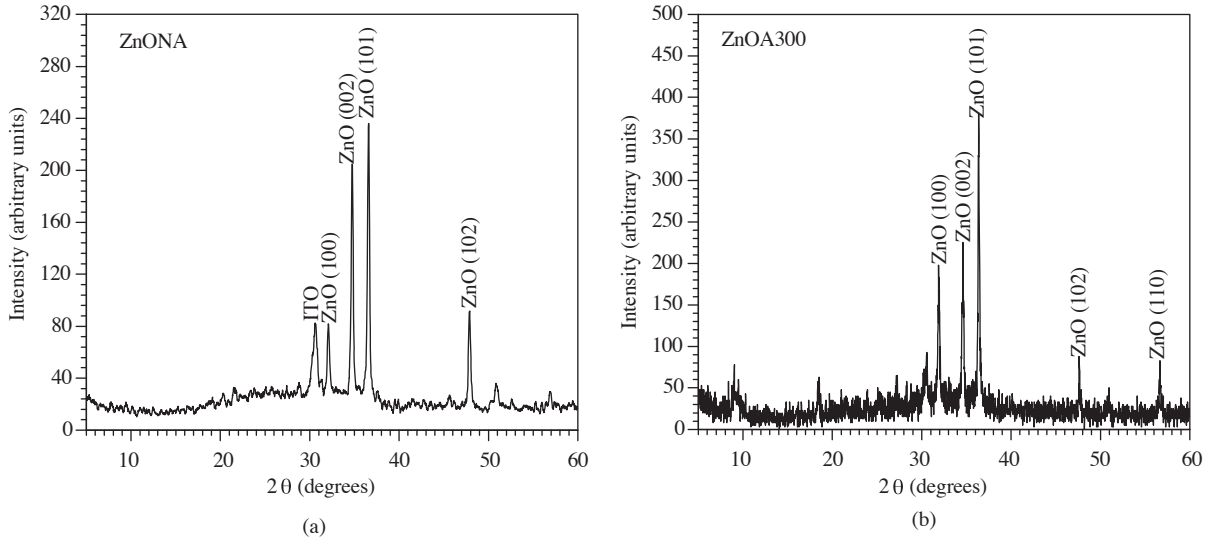
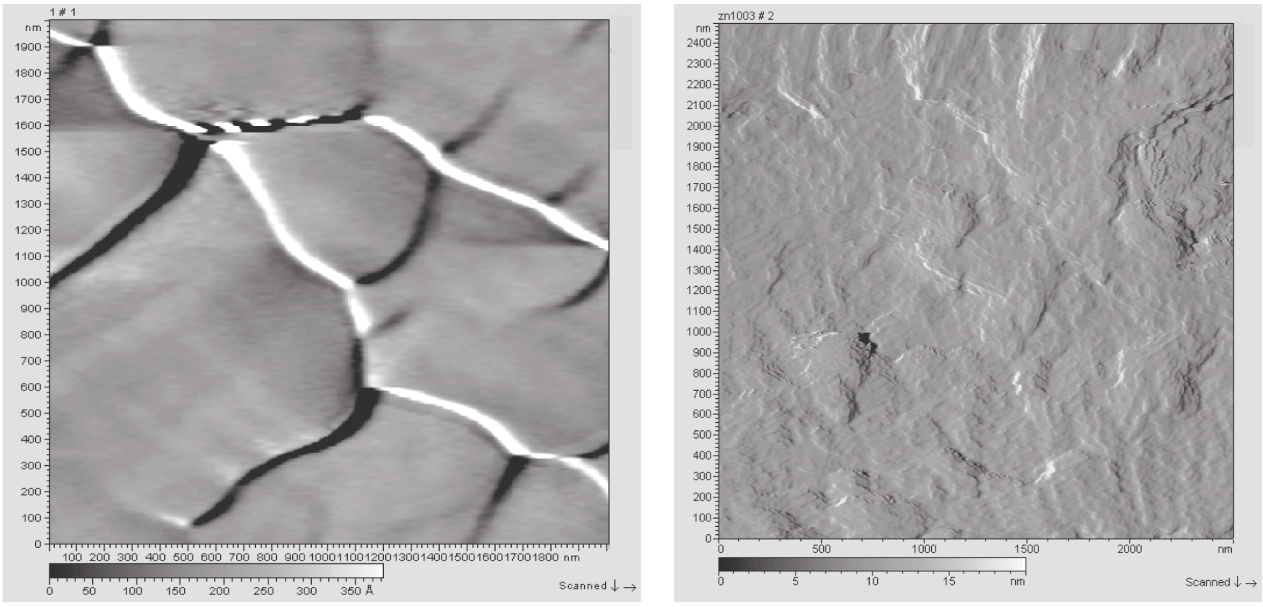


Figure 1. XRD data of (a) non-annealed and (b) annealed ZnO thin films grown by ECD technique.

The surface morphologies of the grown structures are observed by the AFM investigations and the images are shown in Figure 2. Some cracks and granular grains were seen between the single crystal columns having sizes ranging approximately from 500 to 1000 nm, for the as-deposited sample. However, a relatively smooth and compact surface was obtained for the film annealed at 300 °C for 30 min. The surface roughness of ZnOA300 is also less than ZnONA and the sharp grain boundaries seen in Figure 2a vanish in Figure 2b. This

difference between the non-annealed and annealed films suggests that the annealing process enlarged the grain sizes and reduced the surface roughness of the ZnO thin film grown by the ECD. Despite annealing at 300 °C, the annealing at higher temperatures caused even more severe cracks and voids as compared to the as-deposited samples and thus prevents to conduct the characterization measurements. This is probably due to the fact that indium, tin and oxygen in the ITO substrate start to decompose from each other at annealing temperatures above 300 °C. In fact, Giefers et al. [25] and Yıldırım et al. [26] have shown that stoichiometric disproportion of tin oxide samples is expected at substrate temperatures of above 300 °C due to the decomposition of tin from tin-oxide. It is possible that the same decomposition may occur in the ITO substrates at annealing temperatures above 300 °C. Bouhssira et al. have also shown that the stoichiometric ZnO can be obtained by the 300 °C annealing [27]. Therefore we conclude that the most effective annealing of the ZnO thin films on the ITO substrate is around 300 °C so that the crystallinity characteristics improve and the film may become more stoichiometric.

In order to get additional information about the effect of this particular heat treatment on the ECD-grown ZnO thin films, we have measured the optical absorption of the grown structures before and after annealing. Figure 3 shows the absorption spectra and band gap energies for these two samples. Highly sharp optical absorption edges of the materials indicate that there exists the high quality crystal formation of the ZnO films grown by the ECD. Original absorbency data were converted to absorption coefficient values using the conventional equations, details of which have been given in our previous work [28], considering the intensity losses of incident light due to the reflection from the surface of the material. Using the absorption values at a wavelength of 600 nm at which the intra-band gap absorption seems to be minimum, the reflectivity, R was found to be 32.7% for the ZnONA and 24.75% for the ZnOA300. The latter is much closer to the bulk reflectivity value 20% given in the literature [29], which shows the improving effect of annealing on the crystal quality.



(a) (b)

Figure 2. AFM images, (a) sample ZnONA and (b) ZnOA300 taken by Molecular Imaging 2100 Picoscan STM/AFM microscope.

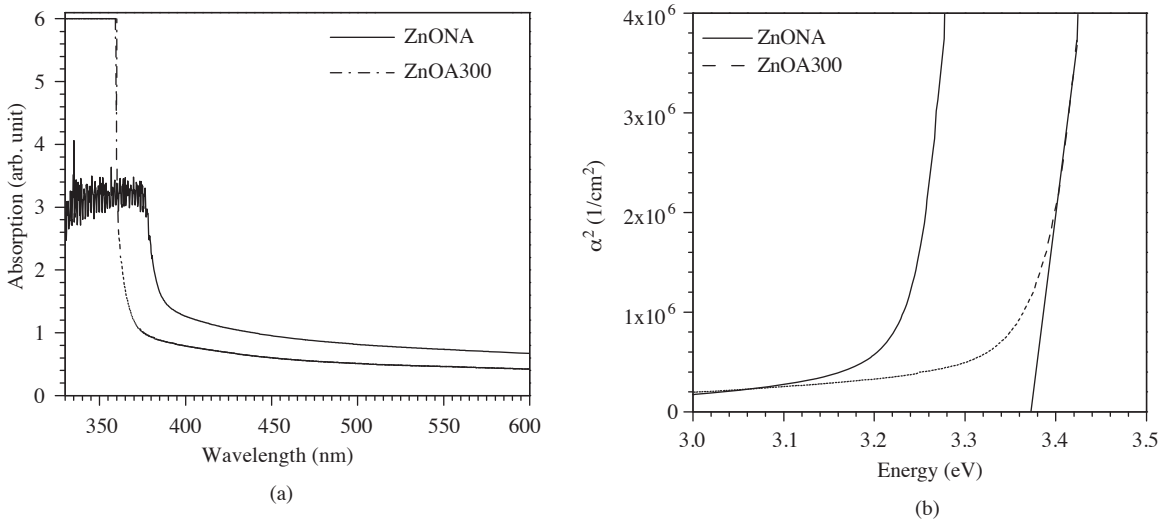


Figure 3. Optical absorption spectra (a) and band gap energies (b) of ZnO thin films prepared on ITO, for both samples.

The band gap energy of the grown thin films can be determined by extrapolation of the linear part of the plot of α^2 versus the incident radiation energy, $h\nu$, as shown in Figure 3b; which indicates that the near band edge optical absorption coefficient has spectral dependence of only the joint density of states in both samples. The optical absorption edge has been observed at a wavelength of about 385 nm corresponding to band gap energy of about 3.23 eV for non-annealed sample. This value is quite consistent with the literature for as-deposited ZnO films grown by the ECD [1, 10, 30]. However, the real band gap energy of a single crystal ZnO is 3.4 eV [5, 31]. The observed band gap energy of the annealed sample is about 3.37 eV corresponding to a wavelength of 368 nm, which is much closer to that of single crystal. These results show that the band gap energy of ZnO thin film shifts to higher energy values after annealing. The increase of the band gap energy after annealing is quite consistent with some of the following studies in the literature. For example, Bouhssira et al. have shown that the band gap energy increases from 3.3 eV in as-grown up to 3.7 eV after systematic annealing experiments at temperatures from 100 to 600 °C [27]. Xue et al. have observed almost no change, a little 10 meV increase in the band gap energy up to 750 °C annealing temperature and a decrease of about 10 meV at annealing temperatures between 750–950 °C [32]. They attribute the blue shift of the optical absorption edge to the increasing crystallinity quality of the ZnO films. Furthermore Zou et al. showed the increase in the band gap energy from 3.18 eV to 3.20 eV after annealing of the electrodeposited samples as well [33]. Most of these films are on much larger substrates in terms of melting point such as sapphire so that they can anneal at higher temperatures. Although our sample is grown on the ITO substrate, we can get much more enhancement in the band gap energy at much lower annealing temperatures.

The smaller E_g values resulting from the Moss-Burstein shift are usually attributed to O content on the surface of the films [28, 34]. We propose that most annealing treatments cause evaporation of oxygen and the sample become more Zn-rich. Since the O-rich samples usually have lower band gap energy, relatively more Zn-rich samples after annealing due to the evaporation of excess oxygen from the surface will have higher band gap energies in comparison to the as-deposited samples. On the other hand, the authors of references [15, 17] have observed a decrease in band gap energy from 3.38 eV to 3.27 eV after air annealing treatment at 500 °C

for 1 h. We propose that this discrepancy might be resulted from the air annealing conditions where oxygen loss from the surface is impossible so that the material may become relatively more O-rich at the annealing temperatures and has lower band gap energy after annealing. As a result, we have applied an effective way of annealing at relatively low temperatures, causing the blue shift in the band gap energy, improving the crystalline quality and enlarging the grain sizes of the films on the conductive ITO substrate.

4. Conclusion

We investigated the effect of relatively low temperature annealing treatment on ZnO/ITO thin films grown by the ECD technique under a cathodic potential of -0.9 V from a simple zinc nitrate aqueous solution at 65 °C. The optical and structural characterization on both non-annealed and annealed samples have shown that the thermal treatment carried out at 300 °C has a great influence on the physical parameters of the grown structures. It has been observed that the direct band gap energy was increased from 3.23 to 3.37 eV after annealing at 300 °C for 30 min under N_2 flow. We proposed that this increase in band gap energy may be due to the low oxygen content of the sample surface after thermal treatment.

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