Absorbance dependence of ZnO thin films on post-heating temperature

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Abstract. We have prepared ZnO thin films on indium tin oxide (ITO) glasses using dip-coating at room temperature. Post-heating has been performed by different temperatures i.e. 450 °C, 500 °C, 550 °C, and 600 °C under atmosphere ambient. The effect of post-heating temperature on the structural properties and absorbance of ZnO thin films have been investigated. Structurally, we observed ZnO thin films under a post-heating temperature of 450 °C, 500 °C, and 550 °C have polycrystalline hexagonal wurtzite structure. Meanwhile, at the temperature of 600 °C, it has an amorphous structure. Optical absorbance spectra of ZnO thin films confirmed that amorphous structure has the highest intensity compared to polycrystalline hexagonal wurtzite structure.

1. Introduction
In the past two decades, ZnO as n-type semiconductor material has become interested subject to be investigated. All scientists believed that ZnO with a hexagonal wurtzite structure is a potential semiconductor material for optoelectronic devices. It is due to a wide direct bandgap energy (3.4 eV) and strong exciton binding energy (60 meV) \[1,2\].

As a metal oxide, ZnO thin films have high transparency over 80% in the visible range \[3\]. Meanwhile, ZnO thin films have demonstrated as potential photocatalytic and antibacterial against the Escherichia Coli bacterium \[4\]. Further investigation reported that the photocatalytic activities of ZnO thin films can be enhanced by Al dopant which acts as a charge trapping \[5\]. On the other hand, uniformity, thickness, porosity, and morphology of the ZnO thin films are still interesting to be investigated. Muthukrishnan et al believed that the structural modification of ZnO thin films without any dopants to get tailored surface can be potentially used as gas sensing \[6\]. However, due to asymmetry effect \[1\], ZnO thin films have been deposited on different substrates such as silicon (Si), Al\(_2\)O\(_3\), GaAs, SiC, indium tin oxide (ITO), etc. \[7,8\]. Among these substrates, ITO has many superior properties i.e. optically transparent, good electrical conductivity, high visible and near infra-red transmittance, reflection in the infrared range, and uniform transmission homogeneity \[9\]. The difference substrate affects the crystal growth behaviour of the films due to the lattice mismatch between the ZnO thin films and the substrate \[10\]. Teng et al reported that ZnO thin film growth on ITO glass...
substrates exhibits good crystal quality because it has lattice mismatch 3% [9]. Furthermore, the deposition technique of ZnO thin films has been demonstrated with various methods such as metal-organic chemical vapor deposition (MOCVD) [11], ultrasonic spray pyrolysis (USP) [12–14], sputtering [15], laser ablation [16], etc. Among these methods, dip-coating possesses the advantages, i.e. simple, low cost, fast, cover a large surface area, and controllable [6]. Furthermore, the morphology of the films can be controlled by some parameters during dip processes such as sol concentration, withdrawal speed, and post-growth annealing treatment [5].

To the best of our knowledge, the post-growth annealing treatment can be used to control intrinsic defects and improve the crystallinity of ZnO [17]. Hang et al. believed, the high-quality ZnO material can be obtained by proper annealing. In our previous report, we have confirmed that the proper growth temperature is an effective way to obtain a well-aligned ZnO structure [2].

In this paper, we report the ZnO thin films deposited by dip-coating with different post-heating temperature (450 °C, 500 °C, 550 °C, and 600 °C) on ITO substrate. Then, the study of post-heating temperature on the crystal structure and optical absorbance properties will be discussed.

2. Experimental details
The deposition processes of ZnO thin films on indium tin oxide (ITO) glass substrate have been demonstrated by the dip-coating method [18]. To obtain sols of 0.2 M concentration we have prepared zinc acetate dehydrate [C4H6O4Zn.2H2O] into 15 mL of isopropanol, 30 mL of monoethanolamide (MEA) which acts as a stabilizer, and 30 mL of de-ionized (DI) water. The solution was then stirred at 65 °C for 4 hours to accelerate the hydrolysis reaction. To obtain transparent sol, then the solution was cooled down for 24 hours and we obtained coating sol. ZnO thin films were deposited on ITO glass substrates by the dip-coating method. All the samples were performed with a constant withdrawal speed of 0.5 cm/min under room temperature. This process was repeated 4 times. After the coating process, then the films were dried at 225 °C for 15 min to completely evaporated the solvent. As coated films were subsequently annealed at different post-heating temperature i.e. 450 °C, 500 °C, 550 °C, and 600 °C for 1 h under atmosphere ambient. It is to remove undesired species and to obtain a good quality ZnO thin films [4]. Further, we will indicate the sample at a different post-heating temperature of 450 °C, 500 °C, 550 °C, and 600 °C as ZnO-A, ZnO-B, ZnO-C, and ZnO-D, respectively.

The structure and optical absorbance properties of the samples have performed using X-ray diffraction (XRD) measurement with CuKa radiation (PAN-analytical) and UV-Vis spectrophotometer UH 5300, respectively.

3. Results and discussion
Figure 1 shows XRD pattern of ZnO thin films at different post-heating temperatures of 450°C, 500°C, 550°C, and 600°C which are stated as ZnO-A, ZnO-B, ZnO-C, and ZnO-D, respectively. We observed six peaks with the (hkl) are (100), (002), (101), (102), (110), and (103).
According to the inorganic crystal structure database (ICSD) number #98-002-6170, the ZnO-A, ZnO-B, and ZnO-C possess polycrystalline hexagonal wurtzite structure. Meanwhile, at a post-heating temperature of 600 °C (ZnO-D), we cannot observe any peaks. Hence, we believed that the pattern indicates an amorphous structure. In order to determine prefer orientation, we have calculated quantitative coefficient of texture [19].

Figure 1. XRD pattern of ZnO thin films at different post-heating temperature.

Figure 2 shows the coefficient of texture (TC) of ZnO thin films at different post-heating temperature. According to the TC value, ZnO thin films have preferred orientation in (002) plane. It can be seen from figure 2, in (002) plane, the ZnO-B and ZnO-C have a TC values of 1.4 and 1.7, respectively. It is higher than ZnO-A which has TC value of 1.08. A post-heating temperature improves preferred orientation in (002) plane which parallels along the c-axis of the thin films. We believed that the increasing of post-heating temperature will gain enough energy and growth along (002) plane as it possesses the highest
atomic packing density and minimum surface energy [20,21]. Hence, (002) plane as a preferred orientation will be considered.

**Table 1.** Calculation results of XRD pattern in (002) plane.

| Sample | FWHM (degree) | Crystallite size(nm) |
|--------|----------------|----------------------|
| ZnO-A  | 0.3192         | 28.4731              |
| ZnO-B  | 0.1524         | 78.2069              |
| ZnO-C  | 0.2933         | 19.6206              |

By using Scherer’s equation, we have used the value of full width at half maximum (FWHM) to estimate the crystallite size of ZnO thin films at different post-heating temperature [8]. As well known, the FWHM value relates to the crystallinity of the ZnO thin films. Therefore, as seen in table 1, the FWHM of the samples tend to decrease by increasing post-heating. It’s implied that the crystallinity of the ZnO thin films was improved by post-heating temperature. Even though, at the post-heating temperature of 600 °C, the ZnO thin films become an amorphous phase. Furthermore, the crystallite size of ZnO thin films was increased for ZnO-B. It’s believed due to a post-heating treatment induced coalescence of small grains by grain boundary diffusion [20,22]. Meanwhile, the decrease in crystallite size for ZnO-C is predicted due to the reformation of the new ZnO-like structure at the temperature of 550 °C [23].

**Table 2.** Lattice parameter and residual stress of ZnO thin films in (002) plane.

| Sample | a(Å) | c(Å)     | ε (dyne/cm²) |
|--------|------|----------|--------------|
| ZnO-A  | 3.2487| 5.1731   | 29.2971 × 10⁹ |
| ZnO-B  | 3.2513| 5.2071   | - 0.0086 × 10⁹ |
| ZnO-C  | 3.2514| 5.2107   | - 3.1976 × 10⁹ |

Moreover, post-heating temperature also induce variation in lattice parameters, it is seen in table 2. Hence, it will introduce lattice distortion and stress in ZnO thin films structure. By using biaxial strain model [24], residual stress in (002) plane has been estimated. The ZnO-A is ZnO thin film with the higher positive residual stress. Meanwhile, ZnO-B and ZnO-C, have negative value of residual stress. The negative values of residual stress correspond to the comprehensive residual stress, whereas the positive value correspond to the residual tensile stress in the films [25]. Hence, we predict the residual stress cause change in native internal defect. Chan et al believe that residual stress can improve number of charge carriers in ZnO thin films [25]. As well known, the native defects in ZnO thin films mainly due to oxygen vacancy (Vo) [26].

![Figure 3. UV-Vis absorbance spectra of ZnO thin films at different post-heating temperature.](image-url)
Figure 3 shows the UV-Vis absorbance spectra of ZnO thin films at different post-heating temperature. It can be seen from figure 3, all samples have strong absorption in ultraviolet (UV) range and weak in the visible range. The ZnO-D as amorphous ZnO has the strongest absorbance. It’s predicted that the higher degree of disorder induces strong absorption than that of polycrystalline ZnO thin films [27]. Meanwhile, the UV absorbance peaks are not linearly dependent on the increasing post-heating temperature. The absorbance peak of ZnO-B is higher than ZnO-A and ZnO-C. Even though there is a reformation of the new ZnO-like structure, we predict the ZnO-C with a post-heating temperature of 550 °C induces increasing some defects i.e. oxygen vacancy. During the heating process, there is re-evaporation of oxygen which produces an oxygen vacancy. Hence, it is immediately ionized and releasing two electrons in the conduction band [23]. Furthermore, by increasing a post-heating temperature, desorption of adsorbed oxygen molecules might occur from the grain boundaries and we believe it causes deterioration of UV absorbance.

4. Conclusion
In conclusion, we have deposited ZnO thin films at a different post-heating temperature of 450 °C, 500 °C, 550 °C, and 600 °C for 1 h under atmosphere ambient. The ZnO thin films with a post-heating temperature of 450 °C, 500 °C, 550 °C, and 600 °C are called ZnO-A, ZnO-B, ZnO-C, and ZnO-D, respectively. According to the inorganic crystal structure database (ICSD) number #98-002-6170, the ZnO-A, ZnO-B, and ZnO-C possess polycrystalline hexagonal wurtzite structure, meanwhile, ZnO-D is amorphous. A post-heating temperature induces variation in lattice parameters and introduces stress in ZnO thin film structure which indicates the native internal defect change. Hence, it affects the absorbance property of ZnO thin films i.e. the absorbance peak of ZnO-B is higher than ZnO-A and ZnO-C, meanwhile, the ZnO-D as amorphous ZnO has the strongest absorbance.

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