

Effect of Post-Annealing Treatment on the Morphological and Optical Properties of ZnO Thin Film Fabricated by Spraying Deposition Method

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ABSTRACT

This work investigated the effect of post-annealing treatment on the fabrication of zinc oxide (ZnO) thin film by spraying deposition method. Based on SEM analysis, the annealed ZnO thin film at 400°C presented better uniformity as compared to the non-annealed film. Further measurement by UV-Vis revealed that the lowest optical band gap energy (E_g) (3.22 eV) was achieved by 400°C sample. These results confirmed that post-annealing treatment enhanced the optical and morphological properties of the fabricated ZnO thin film.

Keywords: ZnO; thin film; spraying; band gap energy.

INTRODUCTION

Zinc oxide (ZnO), a wide band gap (E_g) semiconductor material has attracted a lot of interest due to its several advantages for various optoelectronic application, such as transparent conductive oxide (TCO). An ideal TCO should possessed high optical properties, i.e. high transmittance over the visible light and low E_g value^[1]. In order to fabricate the desired ZnO thin films, several effort have been done including its fabrication method. Sol-gel^[2,3], chemical vapour deposition, sputtering^[4,5], laser ablation, spin or dip coating^[2,6], and spraying deposition^[7-10] were commonly used to fabricate ZnO thin film. Among them, spraying deposition offered a simpler fabrication method, inexpensive equipment, controllable films thickness, and suitable for large area deposition^[7,11]. Commonly, high substrate temperature was needed during spraying process to evaporate the solvent. Cho et al. (2019) using 400°C substrate temperature and the spraying process was done for 15 mins^[8]. Meanwhile, higher substrate temperature of 400, 450, and 500°C were performed by Suárez et al. (2020) to fabricate ZnO:Mn thin film. They found that higher substrate temperature resulted thicker film and the changes in particle's size and shape^[9]. High substrate temperature also resulted a cracked to porous structure^[12].

In order to further improve the film's properties, post-annealing treatment has commonly carried out by varying its time duration or temperature. Nadarajah et al. (2013) annealed the sprayed ZnO thin film from 300 to 500°C for 2 h. The results showed that annealing treatment affected the particle's grain size, film's thickness, and film's resistivity^[13]. Lower electrical resistivity (8.22 to 1.12 Ωcm) and E_g value (\sim 3.275 from 3.289 eV) of the fabricated ZnO thin film were also observed by using annealing temperature of 450 and 500°C for 30 mins^[14]. Therefore, in this study, ZnO thin film was fabricated via spraying

deposition method with lower substrate temperature and annealed with various temperature.

METHODS

ZnO thin film was fabricated by spraying deposition method as described in the previous study. In brief, zinc acetate dihydrate was dissolved into methanol under constant stirring at room temperature for 1 h. The prepared 0.1 M ZnO solution was then sprayed to the preheated clean glass substrate (250°C) with the spraying distance of 20 cm. The sprayed film was then annealed for 1 h by different temperature (300, 350, 400, 450, and 500°C) and further used for characterization.

RESULTS AND DISCUSSION

The morphological properties of the fabricated ZnO thin film annealed at 400°C is presented in Figure 1 (a) and (b). Based on Figure 1 (a), it was clearly seen that the film's surface presented many holes. Meanwhile, the non-annealed ZnO thin film presented rough surface with river-like surface (Figure 1 (c)). This was believed caused by different solvent evaporation process during the deposition process and the absence of post-annealing treatment. Further cross section observation revealed the flat and smooth surface all over the substrate as the effect of post-annealing treatment (Figure 1 (b)). The uniformity of annealed film's thickness was observed in the range of $\sim 5 \mu\text{m}$. In contrast, rough surface was observed for the non-annealed ZnO thin film with the thickness ranged from 6.87 to 30.4 μm (Figure 1 (d)). Smoother surface morphology of annealed film was in a good agreement with others report^[14–16].

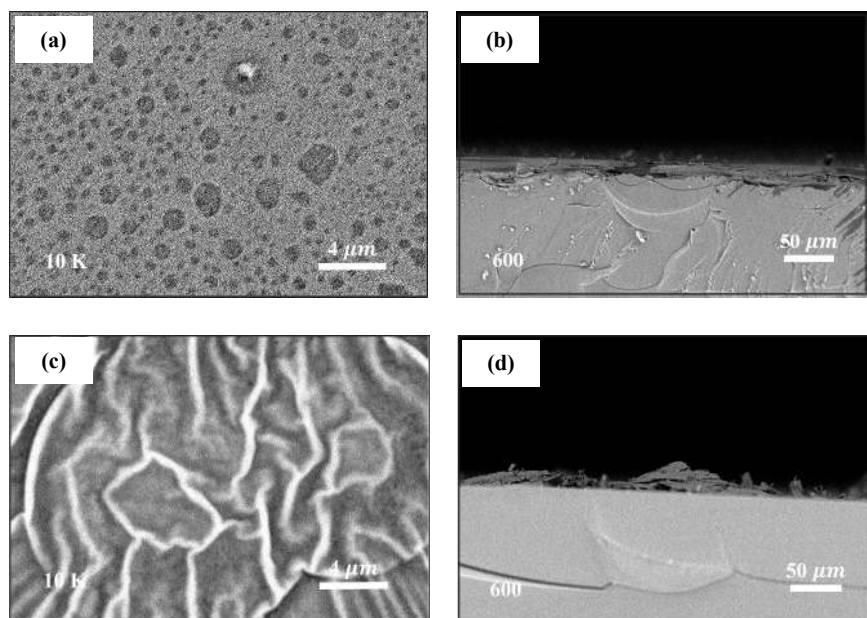


Figure 1. Top and cross section's SEM images of the fabricated ZnO thin film; (a)–(b) annealed at 400°C and (c)–(d) non-annealed

Next, the optical band gap energy (E_g) is determined based on absorption spectrum fitting (ASF) method by plotting $(\text{Abs}_{(\lambda)}/\lambda)^2$ vs $1/\lambda$ data as shown in Figure 2^[17]. The λ_g value was obtained from its linear extrapolation and further used to calculate E_g value by using the following equation;

$$E_g = 1239.83/\lambda_g \quad (1)$$

Based on the calculation, lower E_g value (3.23–3.27 eV) was obtained compared to the non-annealed film (3.95 eV) obtained in the preliminary work. This was believed due to the decrement of amorphous phase and the improvement of film's crystallinity after post-annealing treatment^[15]. Among the annealed films, ZnO thin film annealed at 400°C presented the lowest E_g value of 3.23 eV which indicated better electron mobility^[18]. This might be caused by the excess charge carriers which were activated during annealing treatment^[13]. This result was in a good agreement with Periasamy et al (2010) who found that 400°C resulted the lowest E_g value (3.05 eV) compared to higher temperature (3.26 eV for 600°C)^[19]. Further higher post-annealing treatment (450 and 500°C) increased the E_g value of 3.27 and 3.26 eV.

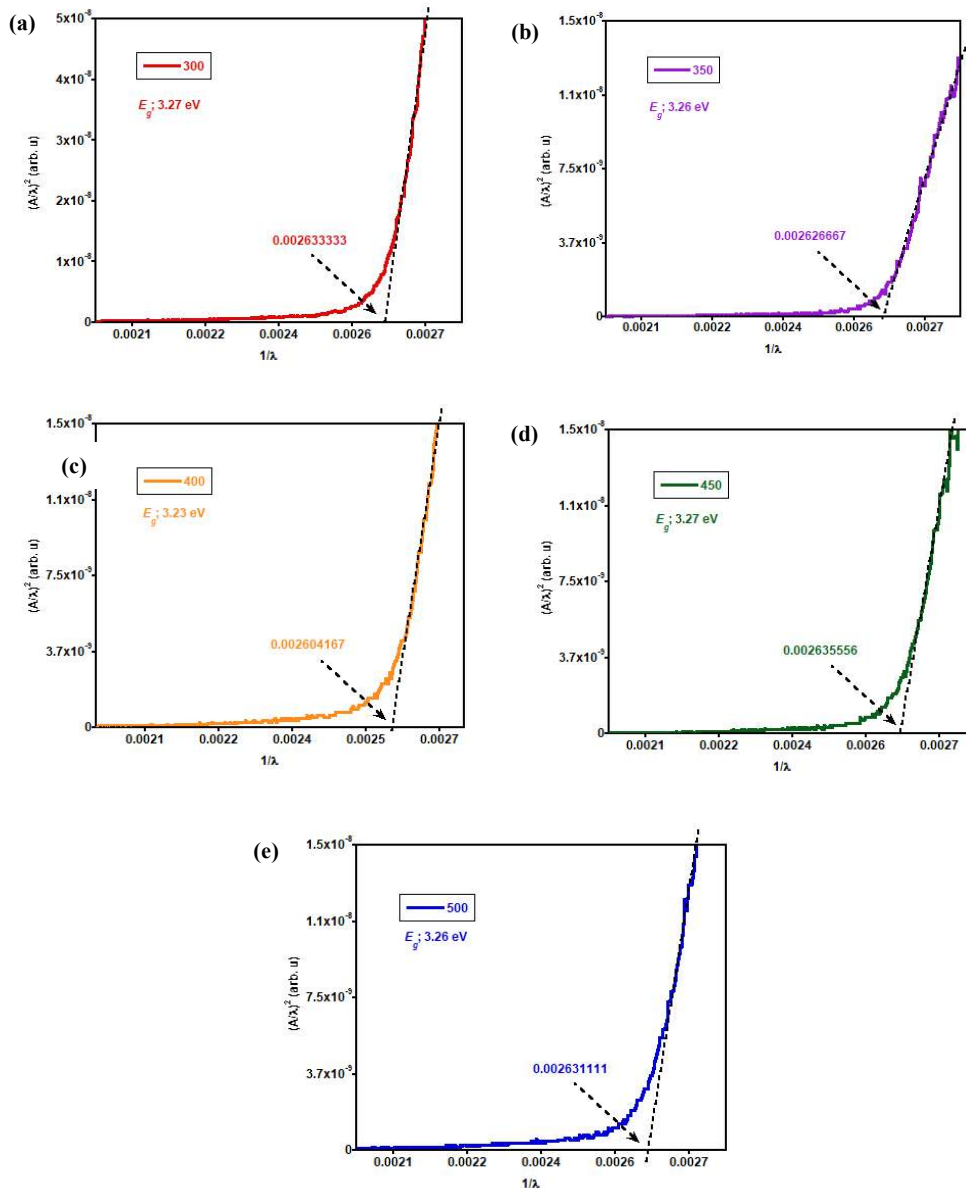


Figure 2. E_g value measurement based on ASF plot for ZnO thin films annealed at; (a) 300, (b) 350, (c) 400, (d) 450, and (e) 500°C

CONCLUSION

Various ZnO thin films have been successfully fabricated via spraying deposition method by varying post-annealing temperature. Better morphological and optical properties were achieved by annealed film. This was caused by crystallinity enhancement (lower amorphous phase) as the consequence of post-annealing treatment. Based on the characterization, ZnO thin film annealed at 400°C presented the lowest E_g value (3.23 eV) as compared to the non-annealed or other annealed films.

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