Optical properties of zinc oxide thin film fabricated by spraying deposition method

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Abstract. Zinc oxide (ZnO) is a semiconductor material which commonly used for optoelectronic devices due to its several advantages. Various ZnO thin film synthesis or fabrication method have widely developed to produce the desired material with excellent properties, such as low resistivity, high transmittance, and simpler experiment procedures. This work focused on the utilization of spraying deposition as a new method to fabricate ZnO thin film. Based on UV-Vis measurement, all of the fabricated ZnO thin films presented high transmittance over 80%. In addition, the optimum spraying distance was found to be 20 cm which resulted transmittance and $E_g$ value of 98.6% and 3.95 eV, respectively. This method presented a lower cost and simpler method to fabricate ZnO thin film.

1. Introduction

Zinc oxide (ZnO) is a semiconductor material which commonly used for several electronic, optoelectronic, and sensor applications, such as solar cell [1–3], light-emitting-diode, ultraviolet (UV) sensor, and electrochromic windows [4]. This was due to its several advantages, such as non-toxic, low cost, and possessed high chemical and mechanical stability [5]. Various ZnO thin film synthesis or fabrication method were sol-gel [6], sputtering [7, 8], pulse laser deposition (PLD), and metal-organic chemical vapour deposition (MOCVD). PLD and MOCVD yielded high quality ZnO. However, these methods required high cost equipment and temperature during synthesis process.

Sputtering method offered a lower cost, simpler fabrication procedure, and lower synthesis temperature as compared to PLD and MOCVD methods. Previous ZnO thin film fabrication using direct current (DC) magnetron sputtering had resulted a wurtzite crystal structure and good resistivity of ZnO thin film [7,9]. Several parameters need to be considered in this method were Argon pressure, temperature, deposition time, and plasma power. However, this method still required relatively high cost equipment and longer deposition method due to the need on making the pallets as target prior to the deposition process. In order to further decrease the fabrication cost and shorten the synthesis procedure, the study of new ZnO thin film’s fabrication method need to be developed.

Spraying deposition method offered several advantages, such as low cost equipment and simpler synthesis procedure, can be applied to various type and kind of substrate, and also potential for large scale fabrication [10]. Firdaus et al. (2012) combined spray-spin coating method to fabricate different ZnO thin film’s thickness. The results showed that thicker ZnO thin film resulted higher band gap energy ($E_g$) and lower conductivity [11]. Gutkowski et al. (2014) also showed that spraying method resulted
homogeneous ZnO thin film as compared to doctor-blading method [10]. By just using methanol and zinc acetate to prepare ZnO solution, Hafdallah et al. (2017) showed lower ZnO growth rate by increasing the spraying distance [12]. Next, Cho et al. (2019) also successfully fabricated various ZnO thin film by varying the spraying pressure [13]. Apart from its simple fabrication method, some of the previous mentioned methods utilized high preheated temperatures (>300˚C) and longer spraying time during ZnO deposition. Therefore, the purpose of this research is to fabricate ZnO thin film by utilising the simpler proposed method of spraying deposition with lower preheated temperatures.

2. Methods
0.1 M of ZnO solution was initially prepared by dissolving zinc acetate dihydrate (Emsure) into methanol (Emsure, 99.9%) and stirred for 1 h at room temperature. Prior to the spraying process, the clean glass substrates were preheated at 250˚C on a hot plate (DLab MS-H280-Pro) for about 5 minutes. The ZnO thin film fabrication was then carried out by spraying the prepared ZnO solution with various spraying distance (10, 20, 30, and 40 cm) between an airbrush nozzle and substrate. The sprayed films were let to cool down at room temperature and ready for characterization. The fabricated samples were then characterized by using UV-Vis spectrophotometer (Shimadzu UV 2600) in order to measure the ZnO thin film’s absorbance. The obtained data was then used to measure the $E_g$ value using absorption spectrum fitting (ASF) procedure by using equation; $E_g = \frac{1239.83}{\lambda_g}$, where $\lambda_g$ was a wavelength corresponding to the optical band gap defined from linear extrapolating of ($\text{Abs}(\lambda)/\lambda$)$^2$ vs $1/\lambda$ graph [14].

3. Results and Discussion
The transmittance value of the fabricated ZnO thin films are presented in Figure 1. Based on the graph, all of the fabricated ZnO thin films presented high transmittance value over 80% in the visible region (400–800 nm). The sharp transmittance decrement around 380 nm observed for all samples was caused by the band gap absorption [11]. The lowest transmittance value of 85.5% was observed for 10 cm sample. The nearest spraying distance between the airbrush nozzle and substrate offered the high ZnO precipitation amount thus resulted the thickest film. The nearest spraying distance also resulted inhomogeneous film caused by different solvent evaporation time. Next, higher spraying distance of 20, 30, and 40 cm which caused lower ZnO precipitation amount resulted higher transmittance value of 98.6, 99.6, and 99.6%, respectively. Higher spraying distance let the solvent to evaporate thus hindered the agglomeration on the substrate. This result was in consistent with Hafdallah et al. (2017) that higher spraying distance presented lower growth rate of deposited film [12].

![Figure 1. Transmittance value of the fabricated ZnO thin film.](image-url)
The calculated $E_g$ of the fabricated ZnO thin film are presented in Figure 2. The lowest $E_g$ value (3.65 eV) was presented by 10 cm sample (Figure 2 (a)). However, the tail was observed in this sample with $E_{tail}$ value of 3.31 eV. This indicated that the fabricated 10 cm sample was still in amorphous state [15]. An agglomeration during spraying deposition process due to the closest distance between the airbrush nozzle and substrate also might affect this result. Meanwhile, similar $E_g$ value of 4.01 and 4.02 eV were observed for ZnO thin films fabricated with higher spraying distance; 30 and 40 cm, respectively. This high value was caused by lower ZnO growth or deposition on the glass substrate as proven by the highest transmittance value among the fabricated samples (refer Figure 1). The slightly lower $E_g$ value (3.95 eV) was then observed on 20 cm sample. This value was quite high as compared to the theoretical value of ZnO (~3.37 eV) due to the absent of post annealing treatment. However, the lowest $E_g$ value and the absent of tail on the graph among the fabricated samples lead to the conclusion that the optimum spraying distance was 20 cm. This result also confirmed that the proposed spraying deposition method was suitable to fabricate ZnO thin film with the advantage of lower cost and simpler experimental procedures.

Figure 2. $E_g$ measurement based on ASF plot for samples; (a) 10, (b) 20, (c) 30, and (d) 40 cm spraying distance.
4. Conclusion
Various ZnO thin film were successfully fabricated via spraying deposition method by varying the spraying distance between the airbrush nozzle and the substrate. Based on UV-Vis measurement, the optimum spraying distance was found to be 20 cm which resulted optimum ZnO growth or deposition thus hindered the agglomeration during deposition process. In addition, the lowest $E_g$ value was calculated to be 3.95 eV with the absent of tail. This confirmed that spraying deposition process was suitable to be applied as ZnO thin film fabrication method.

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