

## OPTICAL PROPERTIES OF TETRAPOD NANOSTRUCTURED ZINC OXIDE BY CHEMICAL VAPOUR DEPOSITION

R. A. Rahman<sup>1</sup>, S. S. A. Karim<sup>1</sup>, D. Kamaruzaman<sup>2\*</sup>, and Z. Zulkifli<sup>1</sup>

<sup>1</sup>NANO-ElecTronicCentre (NET), Faculty of Electrical Engineering, Universiti Teknologi MARA, 40450 Shah Alam, Selangor, Malaysia

<sup>2</sup>Faculty of Electrical Engineering, Universiti Teknologi MARA Cawangan Terengganu, 23000 Dungun, Terengganu, Malaysia.

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### ABSTRACT

Tetrapod nanostructured zinc oxide (ZnO) thin films have been deposited onto indium tin oxide (ITO) coated glass substrate by thermal chemical vapor deposition (TCVD) technique. This work studies the effects of annealing temperature ranging from 100–500 °C towards its physical and optical properties. FESEM images showed that the structural properties of tetrapod nanostructured ZnO thin film were affected by the annealing temperature. The thickness of thin film is strongly support the FESEM analysis. The optical band gap energy ( $E_g$ ) was evaluated at 2.78 – 3.06 eV, which the ZnO thin film was found to be influenced by the change of interatomic spacing of semiconductor. The result shows that the higher annealing temperature greatly affects the physical structure of tetrapod nanostructured ZnO thin film to become narrow and longer length.

**Keywords:** tetrapod; TCVD; synthesizing; annealing; zinc oxide.

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Author Correspondence, e-mail: [dayana620@uitm.edu.my](mailto:dayana620@uitm.edu.my)

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## 1. INTRODUCTION

Recently, zinc oxide (ZnO) had attract many researcher's interest due to its excellent and noble properties, compared with other materials. ZnO had become a preferable metal oxide among investigators not only due to its properties, but also because of low cost and can be found abundantly. ZnO is an n-type semiconductor, which has wide bandgap (3.37 eV) at room temperature and large exciton binding energy, which is 60 meV [1]. This superior characteristics comes from the representative of II-VI semiconductor compound, other than has a stable wurtzite structure with lattice spacing constant of  $a = 0.325$  nm and  $c = 0.521$  nm [2] [3] [4]. The direct and wide band gap properties also suggest that ZnO may have a high breakdown voltage, lower noise and could be used in high power and high temperature applications.

Versatility of the ZnO properties make it become an attractive material to be applied in both commercial and scientific area. For instance, gas sensor based on nanostructure semiconducting metal oxide is expected to exhibit better performance compared with bulk or thin film gas sensor [5]. Besides gas sensor, ZnO is also used as chemical sensor [6]. ZnO was fabricated in order to be used as pH sensor, ethanol sensor, and also hydrogen sensor [6] [7] [8]. ZnO was chosen as sensing material due to its property that can sense ions. Generally, the surface of metal oxides has OH group that plays an important role since it can act as an effective adsorptive or reactive site for adsorbed substance [9].

Aside from its outstanding characteristics, various preparation methods also make ZnO is preferable among researchers. As for example, ZnO can be deposited by using atomic layer deposition (ALD) [10]. Commonly, ALD is based on the sequential use of gas phase chemical process. This method is similar with chemical vapor deposition technique. However, ALD requires high cost maintenance, thus, scientist usually prefer other methods. Sol-gel is one of the methods that become an attraction to researchers [11] [12] [13]. This is due to the low-cost and the easy handling process requirement during deposition process. Unfortunately, sol-gel spin coating technique has few drawbacks which can influence the performance of the thin film.

Typically, different deposition methods produce different type of ZnO nanostructures. As example, ZnO nanorod can be prepared by using chemical bath deposition [14]. Other than

nanorod structure, ZnO nanoflower can also be produced by this method [15]. In this study, thermal chemical vapor deposition (TCVD) was chosen to deposit the ZnO on ITO substrate to obtain the desired type of ZnO nanostructure. By applying this method, ZnO tetrapod was produced, and the annealing temperatures after deposition process were varied. The influence of different annealing temperatures towards the surface morphology of the thin film was observed, besides of its thickness, transmittance and absorbance characteristics.

## 2. METHODOLOGY

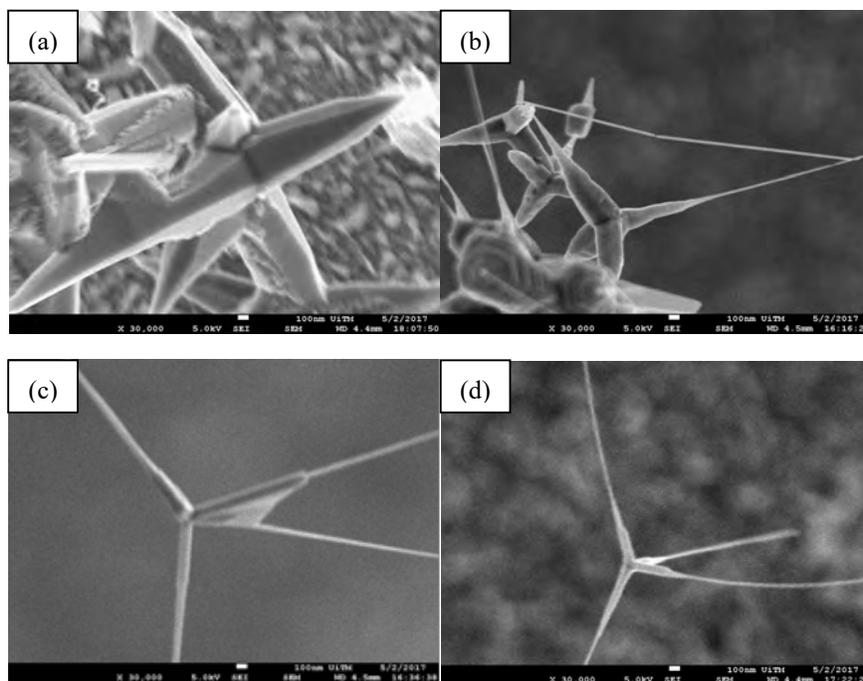
ZnO thin films were deposited using the thermal chemical vapor deposition (TCVD) method onto indium tin oxide (ITO) coated glass substrate (10mm×10mm×1.1mm, 10Ω/□). Before the deposition process, the ITO coated glass was first cleaned with acetone and methanol to eliminate stains and contaminants. Standard cleaning process was conducted, where the ITO substrate was first sonicated using sonicator (Hwashin Technology Powersonic 405 Ultrasonic Cleaner) with acetone and methanol for 10 min, respectively. Then, followed by rinsing in deionized water (DI) for another 10 min and blown by using nitrogen gas to remove all the moistures on the ITO substrate. After substrate cleaning process was conducted, the deposition process using TCVD method, with double furnace system was carried out. ZnO tetrapod nonastructure were synthesized through the evaporation of pure Zinc (Zn) powder. Alumina boat contained of 500mg Zn powder (99.9% purity; Sigma-Aldrich) was inserted to the centre of a horizontal quartz tube in furnace 1, while the other furnace, which is the centre of furnace 2, substrate holder consist of well-cleaned ITO substrate was placed in. Silicon stopper with the gas inlet was encapsulated at both end of quartz tube.

After that, Argon (Ar) gas was introduced and fed into the quartz tube for 15 min at 100 sccm flow rate to eliminate and remove all the other gases to avoid any contamination during the deposition process. The temperature at furnace 1 (vaporizing furnace) was set as 750°C, and the temperature of furnace 2 (substrate) was set to 600°C. Once the temperature of furnaces reached the desired temperature, the whole deposition unit was purged with oxygen (O<sub>2</sub>) gas at 5 sccm. The deposition time was set to a constant duration, 30 min. After that, the deposited ZnO thin films prepared for the annealing studies at various temperatures, 100 °C, 200 °C, 300 °C, 400 °C and 500 °C in separate set of experiments for 1h. The deposited ZnO thin film were

characterized by using field emission-scanning electron microscopy (FESEM, Model JSM-7600F, JEOL, Japan) to explore and observe the surface morphology. The transmittance was measured by UV-VIS-NIR spectrophotometer (Perkin Elmer, Lambda 750) in the range of 300-800nm for optical properties. The thickness of the deposited ZnO tetrapod nanostructure was measured by using Surface Profiler (Veeco, Dektak 150).

### 3. RESULTS AND DISCUSSION

The surface morphology of the ZnO tetrapod nanostructure was observed by using FESEM, at 5kV applied voltage and at a magnification of 30k. Fig. 1 presents the FESEM images of the annealed ZnO tetrapod nanostructure thin films. Different morphologies were obtained from different annealing temperatures (Fig. 1 (a) – (d)) prepared by TCVD method. These images reveal the growth of the cylindrical arms occur via the nucleation of a core structure which describe the formation of tetrapod nanostructured ZnO which deposited onto ITO substrate. It can be seen in Fig. 1 (a) that ZnO tetrapod nanostructure has the biggest size, compared with other samples. The diameter of the tetrapod is big, while the length is short. When the annealing temperatures were increased, the size of the tetrapod become smaller, with the tapered and tip shape. This characteristic can be observed in Fig. 1 (b)-(d). The size of the tetrapod nanostructured ZnO gradually decreased with the increasing annealing temperature. As can be seen from FESEM images, the length of the tip become longer when annealed at higher temperature. Annealing process was known to improve the crystallinity of a material and at the same time, influence the growth direction of the nanostructure. The increasing in the annealing temperature means that higher energy received by the atoms to rearrange themselves [16]. Therefore, it can be seen that the annealing studies has marked effects on morphologies of the ZnO tetrapod nanostructure which results in longer length and tip as the annealing temperature increases.



**Fig.1.** Surface morphology of ZnO tetrapod nanostructure annealed at (a) 200 °C, (b) 300 °C, (c) 400 °C and (d) 500 °C

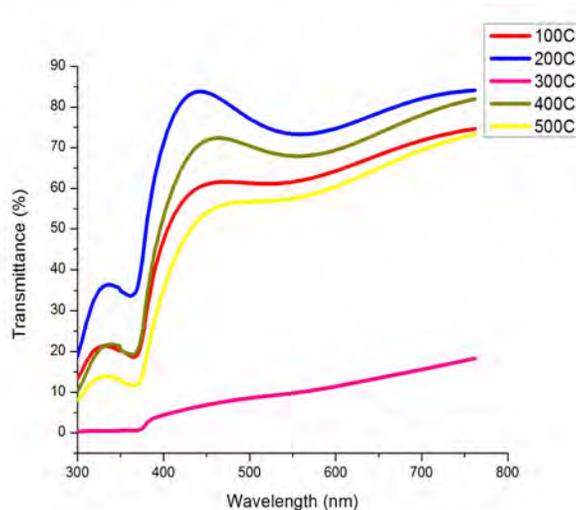
**Table 1.** Thickness of the annealed ZnO tetrapod nanostructure at different temperatures

Annealing temperatures (°C)	Thickness (μm)
100	28.59
200	24.26
300	8.866
400	1.676
500	1.465

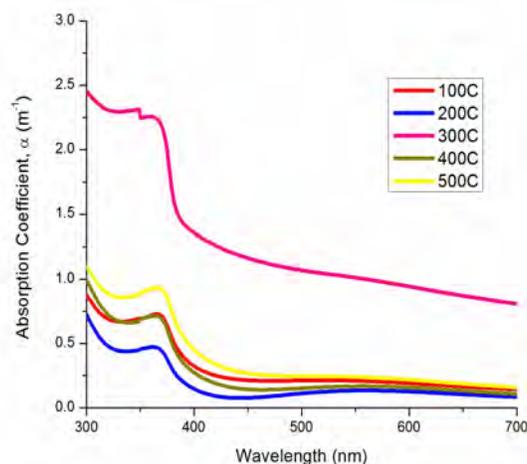
Other than the surface morphology, physical characteristic of ZnO tetrapod thin films were characterized by using surface profiler, in order to measure the thickness of the thin films. Results obtained from this measurement for thin film annealed at different annealing temperatures were recorded in Table 1. According to the data analysis, the thickness of the

thin film decreased significantly when the annealing temperature was increased. Annealing process done at elevated temperature would make the ZnO thin film thinner, as shown when the sample that annealed at 100 °C is the thickest, in comparison with the samples annealed at 200 °C, 300 °C, 400 °C and 500 °C. This is might due to the annealing process that influences the atomic structure of the thin film. Thermal energy supplied during annealing process enable atoms to diffuse and stack, thus restructuring process occur and influence the film to become thinner when the annealing temperature increase [17]. As reported by Fang et al., the decrease in thickness of ZnO thin film is affected by annealing temperature due to there were more energy supplied for the atom to diffuse and occupy the correct site [18]. Other than that, phase transition during annealing process also may attribute to the thickness changes of the thin films [19].

The optical properties of ZnO tetrapod nanostructure thin films annealed at various annealing temperatures were characterized by UV-VIS-NIR spectroscopy in the range of 300–800nm at room temperature.



**Fig.2.** Transmittance spectra for ZnO tetrapod nanostructure annealed at different temperatures



**Fig.3.** Absorption coefficient of ZnO tetrapod annealed at various temperature

Fig. 2 represents the optical transmittance spectra of ZnO tetrapod nanostructure annealed at different temperatures in the visible range. It can be observed that the ZnO tetrapod nanostructure thin films produce different optical transmittance spectra ranging from 70-10% as the percentage of transmittance was determined at the visible wavelength of 550nm. These spectra demonstrated that the ZnO tetrapod nanostructure thin film annealed at 100 °C, 200 °C, 400 °C and 500 °C shows a good optical transmittance (>50%) whereas the transmittance of ZnO tetrapod nanostructure thin film annealed at 300 °C is approximately 10%. This optical scattering might due to the annealing process at different temperature, which influences the phase transition of the thin film. The crystallinity of the thin films were improved as the annealing temperature was increased which might be caused by the lattice orientation of the ZnO *c*-axis [20]. Hence, the optical scattering of the thin film was closely related to the structural condition as could be seen in previous FESEM analysis.

Absorption coefficient of the thin films at different wavelength has been calculated from transmittance data. The absorption coefficient,  $\alpha$ , was determined using Lambert's Law as shown in Eq. (1),

$$\alpha = \frac{1}{t} \ln\left(\frac{1}{T}\right) \quad (1)$$

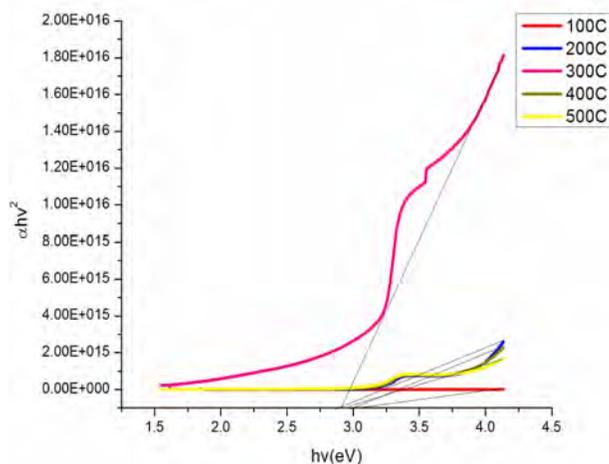
Where  $t$  is the thickness of the thin film measured using profilometer and  $T$  is the

transmittance spectra, measured UV-Vis spectrometer. Fig. 3 shows the absorption coefficient of the ZnO tetrapod nanostructure annealed at different temperatures, ranging from 100-500 °C. From the absorption coefficient ranging from 300-800 nm, it can be observed that the thin film annealed at different temperatures produced different absorption coefficient. The spectra show that all thin films have high absorption coefficient in the UV region (< 400 nm). The absorption coefficient obtained presents an agreement to the transmittance spectra discussed earlier. This suggests that the annealing process influence the changes in transmittance spectra and the absorption coefficient of the thin film. The effect of the annealing temperature towards ZnO tetrapod nanostructure can be observed by the change of the in optical band gap energy,  $E_g$ . The optical band gap energy,  $E_g$  for ZnO tetrapod nanostructure thin films were determined, by using Tauc method [21].  $E_g$  can be expressed by Tauc's relation as shown in Eq. (2) and Eq. (3),

$$\alpha h\nu = B(h\nu - E_g)^{\frac{1}{2}} \quad (2)$$

$$(\alpha h\nu)^2 = B(h\nu - E_g) \quad (3)$$

Where  $\alpha$  is absorption coefficient,  $h\nu$  is the photon energy,  $E_g$  is the optical band gap energy, and  $B$  is an energy-dependent constant ranging from  $1 \times 10^5$  and  $1 \times 10^6 \text{ cm}^{-1} \text{ eV}^{-1}$ , which is depending on electron-hole mobility [22]. Fig. 4 provides the graph of  $(\alpha h\nu)^2$  vs photon energy,  $h\nu$ . The  $E_g$  of the thin film was obtained by extrapolating the linear part of the curves  $(\alpha h\nu)^2$  as a function of incident photon energy,  $h\nu$  to intercept at the  $x$ -axis of the plotted graph. The determined  $E_g$  was recorded in Table 2.



**Fig.4.** Optical band gap of ZnO tetrapod nanostructure annealed at 100 °C, 200 °C, 300 °C, 400 °C and 500 °C

**Table 2.** Thickness of each of thin film annealed at different temperatures

Annealing temperatures (°C)	Optical band gap energy, $E_g$
100	3.06
200	2.95
300	2.87
400	3.01
500	3.02

The optical band gap obtained shows decreasing value when annealing process started from 100 °C to 300 °C, then started to increase again after the temperature was increased from 400 °C to 500 °C. It can be concluded that the optical band gap of semiconductor can be affected by increasing the annealing temperature [23]. The  $E_g$  is consistent with the trend in the transmittance and absorption coefficient results. The increased of  $E_g$  indicates that the compressive stress decreased as the annealing temperature increased from 400 °C to 500 °C [24]. This explains the compressive stress change the interatomic spacing of semiconductor that affects the  $E_g$ .

#### 4. CONCLUSION

In this study, ZnO tetrapod nanostructure thin films were successfully deposited by using TCVD method. Deposited thin films then were annealed at various temperatures (100 °C-500 °C) to investigate the effects of the annealing temperature towards its physical and optical properties. FESEM images revealed that annealing temperature influences the changes of the surface morphology of thin film, where ZnO tetrapod shows differentiation in size and shape when annealed at different temperatures. In addition, annealing process also altered the thickness of the ZnO tetrapod nanostructure thin films. The thickness of the thin films show decreasing pattern when being annealed at higher temperatures. Thin films become thinner when exposed to high temperatures, and this affects its optical properties. Based on the results from UV-Vis spectrometer, the optical transmittance of ZnO tetrapod nanostructure thin films ranged from 10~85%. Besides, the optical band gap was also influenced by the annealing process. In this study, the thin film annealed at 100 °C, 200 °C, 300 °C, 400 °C and 500 °C, have optical band gaps of 3.06 eV, 2.95 eV, 2.87 eV, 3.01 eV and 3.02 eV respectively. In summary, it was proven from the results obtained that the physical and optical properties of the fabricated tetrapod nanostructured ZnO thin films can be influenced by the variation in annealing temperature used.

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