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***Research paper***

# Effect of Growth Temperature on Zno Nanostructures Thin Film Fabricated using Tcvd Method

**R.A.Rahman[1], S.A.Karim[2], A.B.Rosli[3], M.A.Zulkifli[4], Z.Zulkifli[5], D.Kamaruzzaman[6*]**

*[12345]Nano-Electronic Centre (NET), Faculty of Electrical Engineering, Universiti Teknologi MARA, Shah Alam, Malaysia*
*[6] Faculty of Electrical Engineering, Universiti Teknologi MARA, Terengganu, Malaysia*
**Corresponding author E-mail: dayana620@uitm.edu.my*

## Abstract

The objective of this study is to explore the effects of ZnO growth temperature on the formation of the nanostructures. ZnO nanostructures was grow on the ITO coated glass substrate with the application of double furnace system of thermal chemical vapor deposition (TCVD) method. During growing process, the growth temperatures were varied in 50 ºC interval temperature (500 ºC-650 ºC) while the other parameters such growth time, precursor temperature, annealing time and temperature were remain constant. After the growing and annealing process were completed, all of the films were characterized physically, electrically and also optically using field emission scanning electron microscope (FESEM), surface profiler, I-V measurement and also ultraviolet visible (UV-Vis). FESEM results reveal that all growth temperature shows a formation of nanotetrapod ZnO film. The highest of growth temperature exhibited long and thin leg of nanotetrapod, with the lowest thickness value of 14.90 nm. As the growth temperatures increase, ZnO nanostructures change with the decreasing thickness value. Other than that, I-V results indicate that resistivity of the films increase when the growth temperatures were raised, so as the optical energy band gap values. Highest growth temperature shows highest value of resistivity and optical band gap with the value of 32.49 x $10^3$ Ω.cm and 3.32 eV. Overall, the results obtained proved that the growth temperature affect the characteristics of the film, where the morphology, thickness, I-V, transmittance, absorbance and optical band gap changes with the increasing growth temperatures.

***Keywords***: *nanostructures; TCVD; growth; precursor; annealing*

## 1. Introduction

The distinctive and mesmerizing characteristics of nanostructured materials have triggered extraordinary attraction among scientist in order to explore their capabilities to be applied in technology applications. In particular, their structural, electronic and optical properties have become motivation for researchers to be studied due to their potential application in the fabrication of microelectronic and optoelectronic devices [1-3].

There are numerous number of nanostructured materials that gain researchers attraction. As for example, E. Zalnedzad et al. reported, titanium dioxide ($TiO_2$) nanotube was applied in biomedical field [4]. Nanostructured of numerous materials was used in myriad applications such as bio medical field, sensor material, and so on. Nanostructured films are preferable and significance to be applied in many field due to its high surface area. For instance, S. M. Ingole studied about the application of $SnO_2$ nanostructures as gas sensor which demonstrate high response of $SnO_2$ nanostructures towards gas and other excellent properties [4].

Among the most studied nanostructures materials, zinc oxide (ZnO) has fascinating attraction to explore and study. Many researchers focus on depositing and fabricating ZnO nanostructures since ZnO itself has very distinctive properties [5-7]. ZnO is a groups II-VI semiconductor compound which has a wide direct band gap (3.37 eV). Furthermore, ZnO become more attractive because it is inexpensive, chemically stable and non-toxic material. In form of stability, ZnO can be used in quite high temperature (~1800ºC), due to the Young's Modulus (bulk crystal) characteristic. ZnO also offer variations of nanostructures, which can be obtained by various deposition methods [8].

ZnO nanosheet, is one of the nanostructures that can be produced from ZnO through electrophoretic method [9]. Besides nanosheet, Z. Shi et al. investigate the morphology of ZnO nanoflower, where this type of ZnO nanostructures was growth by using chemical bath deposition [10]. Other than that, the most common ZnO nanostructures that has been explored is ZnO nanorod [11-12]. In order to divert from the common nanostructures, some scientist and researchers choose to investigate ZnO nanotetrapod to be applied in their application [13-15]. ZnO tetrapod nanostructure are usually grown or deposited by using chemical vapor deposition (CVD), as claimed by [16]. Besides CVD, nanotetrapod can be grown using some other methods such as fast microemulsion-based hyrothermal [17] and pulse laser deposition [18]. Among these method, thermal-CVD (TCVD) is preferable due to simple preparation, simpler crystal growth technology and give high performance solid material [19].

In this study, ZnO nanostructures was studied by deposited using double furnace system thermal chemical vapor deposition. ZnO was chosen as the growth material, since it has various advantages, with the strong endurance towards temperature. Generally, TCVD method usually involved high temperature during the growth process. Growth temperatures during deposition process in this study were varied. Physical, electrical and optical properties of the deposited ZnO nanostructures.

## 2. Experimental procedures

### 2.1. Cleaning substrate process

Indium tin oxide (ITO) was used as a substrate. Prior to ZnO growth on the substrate, ITO need to be cleaned first to remove all the stains and contaminants. ITO (2x2) cm was immersed in ethanol and sonicated in sonicator (Hwashin Technology Powersonic 405 Ultrasonic Cleaner) for 10 minutes at 50 ºC. Then, followed by the deionized (DI) water, with the same duration and temperature. Before blowing process took place, the cleaned ITO was rinsed, also using DI water. After that, all of the moistures were blown by using argon gas.

### 2.2 ZnO nanostructure growth process

Then, argon (Ar) gas was introduced into the quartz tube as purposed to remove and avoid all the contaminants during the growth process. To evaporate the Zn powder, furnace 1 (precursor) was set to 750 ºC, and temperature at furnace 2 (substrate) was raised up 500 ºC. After the temperatures at both furnaces were stable, oxygen ($O_2$) gas was purged into the quartz tube with the flow rate of 5 sccm. This growth process was fixed to 30 minutes.
When the growth process was completed, deposited sample was cool down until the temperature reached below than 60 ºC. This sample then was annealed at 600 ºC. In order to observe the characteristics of ZnO towards growth temperature dependency, all of these steps were repeated with the different growth temperature (furnace 2) which are 550 ºC, 600 ºC and 650 ºC. TVCD with double furnace system used in this study is illustrated in Figure 1.

### 2.3 Characterization process

All samples were characterized by using few characterizations in order to verify their physical, optical and electrical properties. Field emission scanning electron microscope (FESEM) was used to observe the morphology of the thin film. The optical properties of the films were explored by using UV-VIS-NIR spectrometer, while the thickness of the deposited films was measured by surface profiler. Other than that, for the electrical properties of the films, I-V measurement was conducted, with Aurum (Au) acted as the metal contact during the measurement process.

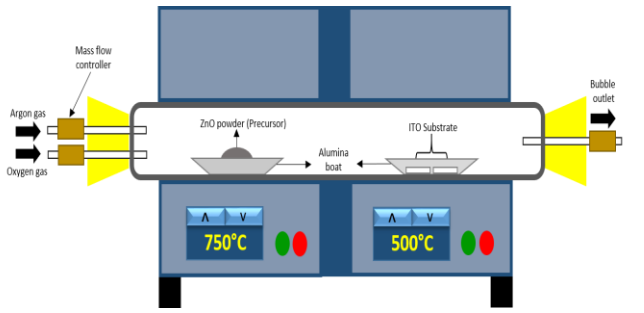


**Fig. 1:** TCVD with two double furnace system used to deposit ZnO nanostructures

## 3. Result and discussion

### 3.1. Physical and electrical properties

Physical characteristics of ZnO nanostructures deposited by TCVD were confirmed by using FESEM and surface profiler. To explore the surface morphology of the ZnO structure, the characterization process was observed using FESEM at 30K magnification after the annealing process was conducted. Different surface morphology was observed for each sample showing that the morphology was affected by the growth temperature. However, the annealing temperature used in this study was a constant temperature, which is 500 ºC. By observing the image in Figure 2 (a), ZnO nanostructure deposited at lowest temperature (500 ºC) shows nanowires form. When the temperature was raised to 550 ºC, ZnO nanostructure growth and shows nanotetrapod structured. This nanotetrapod can be observed in Figure 2 (b).
Again, when the growth temperature was increased to 600 ºC, ZnO nanotetrapod grow with longer tip, compared with ZnO deposited at lower temperature. ZnO nanotetrapod with longest tip and brunch can be discovered when further temperature was raised up (650 ºC). This ZnO nanotetrapod can be seen in Figure 2 (d). The modification of the structure that occurred between all of the deposited ZnO nanostructures film may be reasoning to the growth rate that influenced by the substrate temperature [20]. This growth rate affected by the phase transition from amorphous to crystalline phase [21]. Since the substrate temperatures were increased, the growth rate of the film also increased with the phase transition occurrence, thus lead to the ZnO nanostructures growth, as observed from the FESEM images. Based on these morphological structure, ZnO was suitable to be growth as ZnO nanotetrapod using TCVD method since ZnO exist in zinc blende and wurtzite structure. It is proved that this material is suitable to produced nanotetrapod because the four hexagonal wurtzite arms are branch out from the central of zinc blend during nucleation [22]. Other than that, some other elements such as thickness, structure and resistivity were also affected by growth temperature.

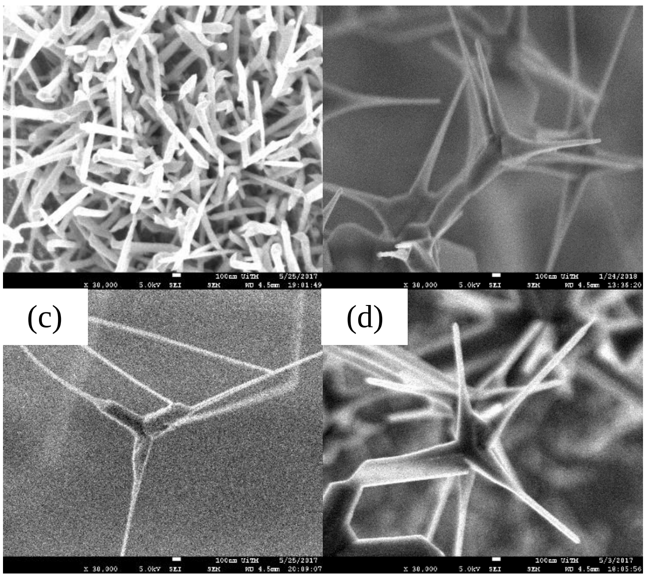


**Fig. 2:** FESEM images for ZnO nanostructure deposited at (a) 500 ºC, (b) 550 ºC, (c) 600 ºC and (d) 650 ºC

**Table 1:** Thickness, Resistivity and Conductivity Value for each of the ZnO Nanostructures Deposited at Different Growth Temperatures

| Growth temperature (°C) | Thickness (nm) | Resistivity, ρ (Ω cm) | Conductivity, σ $(\Omega\ cm)^{-1}$ |
|---|---|---|---|
| 500 | 33.83 | $1.56 \times 10^{6}$ | $6.30 \times 10^{-7}$ |
| 550 | 23.83 | $1.29 \times 10^{6}$ | $7.80 \times 10^{-7}$ |
| 600 | 17.92 | $2.52 \times 10^{6}$ | $3.97 \times 10^{-7}$ |
| 650 | 14.90 | $32.49 \times 10^{8}$ | $4.02 \times 10^{-9}$ |

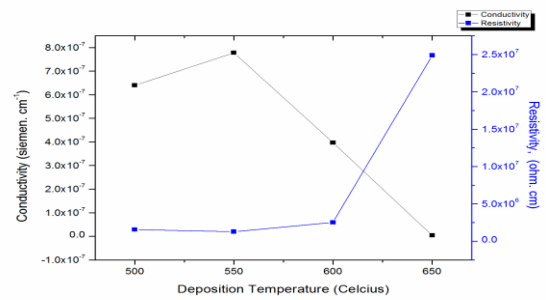


**Fig. 3:** Resistivity and conductivity values obtained from I-V measurement

Besides, the thickness of the deposited ZnO nanostructures also affected by the growth temperature. The thickness of the ZnO nanostructures decline when the temperature of the growth process incline. Table 1 include the thickness value of the ZnO nanostructure film, which ranging from 33 ~ 14.00 nm. The decrement of the ZnO nanostructures might due to crystallization process that occurred during the growth process. [23] reported that the film prepared at high substrate temperature have crystalline structure, in comparison with film prepared at lower temperature [23]. A crystalline film has better atom arrangement as to non-crystalline film, hence, might alter the thickness of the film.

In addition, the thickness of the ZnO nanostructures film influence the electrical properties of the film. According to the data obtained from the I-V measurement, the resistivity of the deposited ZnO nanostructure film decrease when the thickness of the film increased. This result can be observed in Table 1, which explains the values of resistivity, ρ, for all of the ZnO nanostructures deposited at different growth temperature, while Figure 3 present the graph plotted to shows differentiation. The declination of the resistivity value when there is inclination of the film thickness might be subjected to the carrier concentration contained in deposited film [24]. B. Z. Dong et al. described in their study that film with thickness < 50 nm have correlation with changes of carrier concentration, thus attribute to the raise of Hall mobility [24]. Results attained in this study were an agreement to this description since all of the films in this study have the thickness value below than 50 nm. The raise of the Hall mobility stated might be due to the growth changes of the thin film nanostructure [24], which can be seen from the FESEM images.

### 3.2. Optical properties of ZnO nanostructures

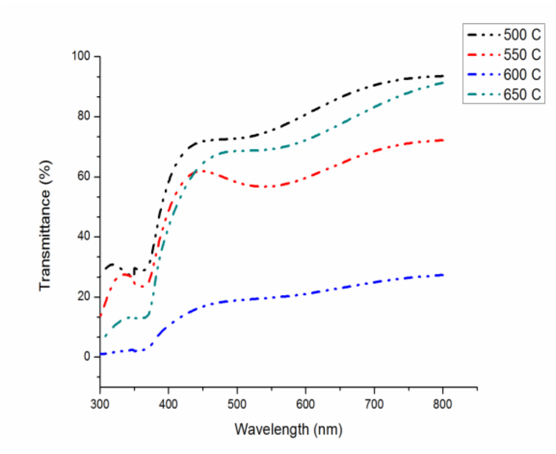


**Fig. 4:** Transmittance spectra for all ZnO nanostructures deposited

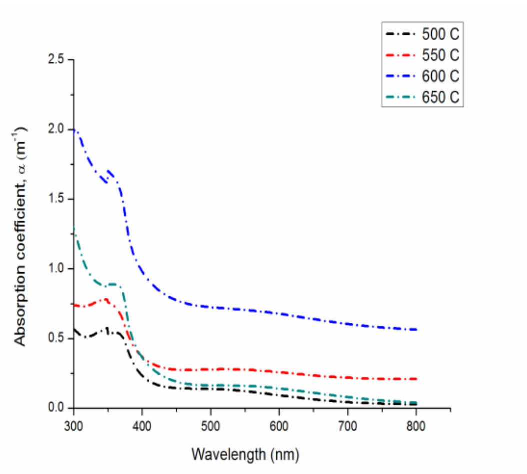


**Fig. 5:** Absorption coefficient ZnO nanostructures deposited at various temperatures

Figure 4 reveal the UV-Vis spectrum results for all of the deposited ZnO nanostructures thin film. In Figure 4, the optical transmittance spectra with different growth temperature in the wavelength range of 300 – 800 nm was shown. According to the plotted graph, the transmittance spectra indicate that all of the films have the percentage below than 40% transparency. This percentage decrease when the growth temperatures were increased. This reduction might due to the absorption of light by excitation and migration of electrons from the valence band into the conduction band of ZnO nanostructures. On the other hand, Figure 4 shows the absorption coefficient of ZnO nanostructure at UV region of 300 – 800 nm. The absorbance spectra displayed high absorption properties below than 400 nm in UV region. In addition, deposited films also present low absorbance value in visible region which state that the samples deposited have good transparency in visible region. Based on the results, the transparency of the ZnO nanostructures film improve with the increasing growth temperature.

The optical band gap for all of the deposited ZnO nanostructures films were calculated using Tauc method below [20]:

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

$$(\propto hv) = A\,(hv - Eg)^{1/2} \quad (2)$$

$$(\propto hv)^2 = A(hv - Eg) \quad (3)$$

Referring to Eq. (1), t is the thickness of the films which obtained from the surface profiler, while T is the optical transmittance spectra measured by UV-Vis spectrometer. Besides, *hv* in Eq. 2 and 3 is the photon energy, A is constant based on electron-hole mobility and Eg is the optical band gap energy. Figure 5 present the graph plotted for $(\alpha hv)^2$ against photon energy *hv*. The optical band gap was calculated by extrapolating downwards the corresponding straight lines until the intersection with photon energy exist. Figure 6 and Table 2 describes the values of optical band gap belongs to ZnO nanostructures film. Based on the calculation and plotted graph, the optical band gap values increase with the increase growth temperature. This increasing trend can be observed in Figure 7. This means that the temperature affects the optical band gap of the film.

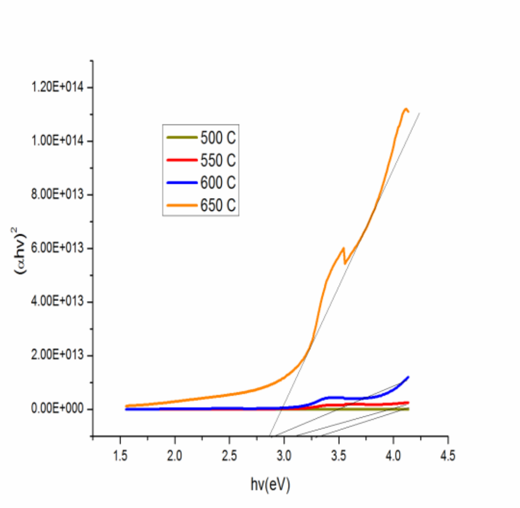


**Fig. 6:** Optical band gap for ZnO nanostructures film calculated using Tauc method

**Table 2:** Numerical energy band gap value for ZnO nanostructures growth at different temperatures

| Growth temperature (°C) | Energy band gap (Eg) |
|---|---|
| 500 | 2.87 |
| 550 | 2.93 |
| 600 | 3.14 |
| 650 | 3.32 |

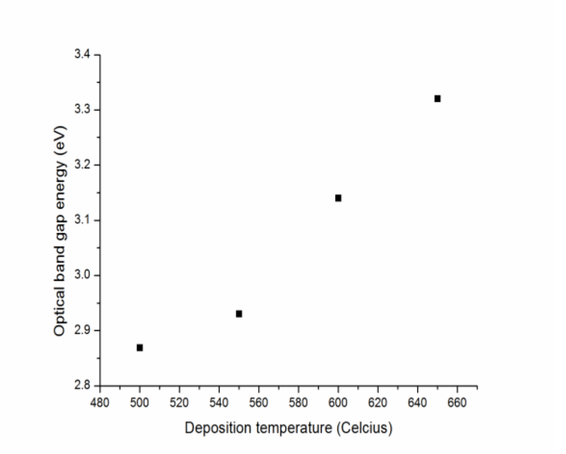


**Fig. 7:** Optical band gap differentiation between all ZnO nanostructures films

## 4. Conclusion

In summary, ZnO nanostructures films were successfully deposited on ITO coated glass substrate at different growth temperatures. The properties and characterizations of the films were conducted. FESEM images revealed that growth temperatures play an important role in order to determine the structure or morphology of the film. ZnO nanotetrapod tip and brunch become more longer when growth temperatures were raised. Besides, the thickness of the ZnO nanostructure films increase respectively with the increasing temperature, thus affect the electrical properties of the film. Resistivity of the film shows increment values when growth temperatures increase. The same trend was shows by optical band gap energy of the films, were the values increase (2.87, 2.93, 3.14 and 3.32 eV).

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