Investigation of ZnO Nanotetrapods at Different Evaporation Temperatures by Thermal-CVD Method for OLED Applications

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ABSTRACT

Organic semiconductors have been discovered for various applications such as in organic light-emitting diodes (OLEDs). Zinc oxide (ZnO) nanostructures have been discovered and received much attention in various applications such as in organic light-emitting diodes (OLEDs), solar cells, sensors and so on. The metal oxides such as ZnO provide an interesting alternative for conventional metal that as low work function as electron injection layer in OLEDs. This study focuses on the synthesization of ZnO nanotetrapods at different evaporation temperature using double furnace thermal chemical vapor deposition (CVD). The ZnO nanotetrapods was produced from synthesized of Zn powder (≥99.9% purity, Sigma Aldrich). From X-Ray Diffraction (XRD) pattern, it is confirmed that (101) diffraction peak successful growth nanotetrapods structure. The ZnO (101) diffraction peak indicates that the nanotetrapods exhibit good crystalline quality. The ZnO nanotetrapods were characterized using field emission scanning electron microscope (FESEM). It shows that the diameter size of ZnO nanotetrapods range in nanometer. Meanwhile, the length of nanotetrapods was around 1.15µm. Photoluminescence of nanotetrapods shows the highest intensity for sample temperature of 750ºC at visible emission. It can be seen that the highest at visible emission was due to the oxygen vacancy or Zn

interstitial effects. These properties will provide better performances and it is suitable for optoelectronic device especially in OLED.

Keywords: *ZnO, Evaporation Temperature, Thermal-CVD, Optical Properties*

Introduction

Zinc oxide (ZnO) is a metal oxide semiconductor material that has large exciton binding energy (60meV) [1] at room temperature and direct band gap (3.37 eV) [2–4]. This metal oxide has used in various application such as light-emitting diode [5], sensor [6, 7], solar cell [8] and others. The ZnO had received attention for organic light emitting diode because of intrinsic and extrinsic defect in UV and visible emission. Over past few years, one-dimensional (1D) single-crystalline ZnO nanostructures material such as nanorod, tetrapod, nanobelt, and nanowire [3, 9–11] have been introduced in optoelectronic devices. The ZnO nanotetrapods have special optical properties and potential applications in semiconductor electronic device. These structures have attracted a lot attention due to high crystalline quality.

The synthesized zinc oxide has been achieved through many methods such as thermal chemical vapor deposition [12-13] and hydrothermal method [14]. Among these methods, the thermal chemical vapor deposition is widely used to synthesize ZnO nanotetrapods due to low cost, simplicity and fewer necessary apparatuses. The ZnO nanotetrapods were produced on the lab scale directly from Zn powder when tetrapods are collected in a boat. Direct synthesis from the metal vapor method has advantages using a low temperature process with high yield.

Moreover, by optimizing parameter such as evaporation temperature is necessary to control the functionalities of metal oxide properties. In this work, we investigated the performance of ZnO nanotetrapods at different evaporation temperature. We discussed the effect of ZnO nanotetrpods on surface morphology, structural and optical properties using thermal-CVD.

Experimental

Synthesization Technique

ZnO nanotetrapods were synthesized and grown using thermal-CVD in a horizontal quartz tube. 1gram of zinc powder (99.9% purity; Sigma-Aldrich) was placed in an alumina boat at the centre of the tube of furnace 1 and furnace 2. The zinc powder was spread in the boat at furnace 1 as indicate in Figure 1. The temperature of furnace 1 was set at 750°C while furnace 2 was increased to 500°C in order to control growth temperature of ZnO

nanotetrapods. The oxygen gas was supplied into the tube at flow 5 sccm. The growth time was 30 minutes under a constant flow of 100 sccm of argon gas with pressure of 1bars. The furnace was cooled down to room temperature.

Characterization Technique

The surface morphology has been characterized using field emission scanning electron microscope (JEOL JSM-J600F). The photoluminescence (PL) for ZnO nanotetrapod was characterized by using FlouroMax3 Horiba Jobin Vyon. The crystalline structure of ZnO nanotetrapod was analyzed by X-ray diffraction (XRD, Broker AXS D8 Advance with Cu Kα radiation).
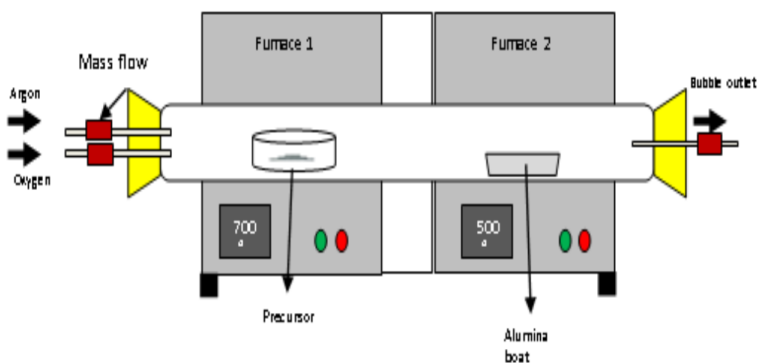

Figure 1: Thermal-CVD Process

Result and Discussion

Structural properties

Figure 2 shows the XRD pattern for ZnO nanotetrapods evaporate at 750°C. All the peaks of the sample was prepared at evaporation temperature correspond to the peaks of standard ZnO the Joint Committee on Powder Diffraction Standard (JCPDS Card No. 36-1451). The diffraction peaks can be indexed as the hexagonal wurtzite phase at lattice constants of a = b = 3.250 Å and c = 5.206 Å. The Figure 2 shows sample temperature of 750°C is strongly exhibited in the wurtzite structure. The relative intensities of the diffraction peaks for this sample was fair agreement with standard powder diffraction data. The peak (101) diffraction peak is located around 36.22°. The result was good condition at 750°C (4806.19 cps) which is highest intensity compared with others. The ZnO (101) diffraction peak indicates that the nanotetrapods exhibit good crystalline quality [15]. The increment of

others diffraction peak indicate the increment of grain boundaries density of sample.

For the samples temperature prepared at 750°C, the full width at half maximum (FWHM) of the (101) diffraction peak was 0.43°. The ZnO nanotetrapods grain size was calculated using Debye- Scherrer equation [16].

$$D = \frac{0.9\lambda}{\beta \cos\theta} \tag{1}$$

where D is grain size, 0.9 is Scherrer's constant, λ is the wavelength of X-rays, θ is the Bragg diffraction angle in degrees and β is the full width at half-maximum (FWHM) of the diffraction peak. For sample 750°C shows the crystallite size of ZnO is around 100 nm. This is due to the growth rate between the different crystallographic planes of ZnO [17]. The crystalline size of ZnO nanotetrapods is tabulated in Table 1.

Table 1: Crystallite Size of ZnO Nanotetrapods

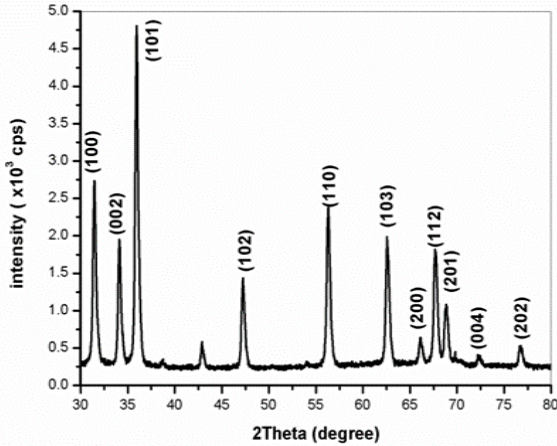| Evaporation Temperature (°C)	FWHM (m Rad)	2θ (°)	Crystallite size (nm)
750	0.43	35.93	19.51

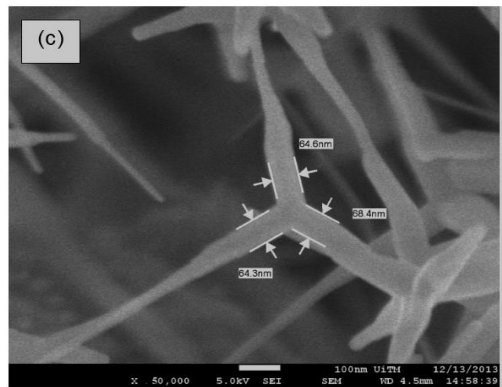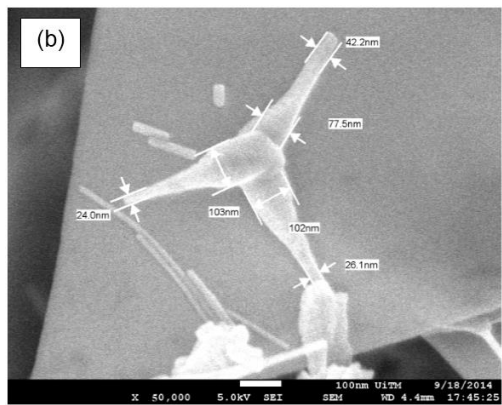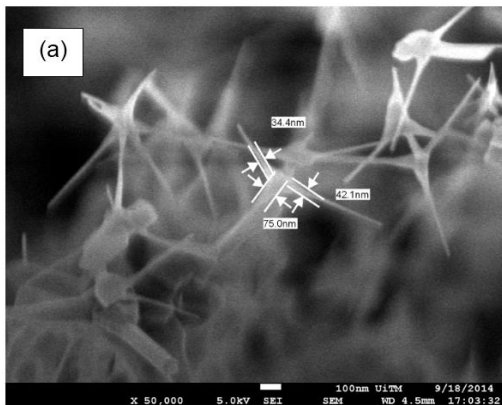Figure 2: XRD pattern of ZnO nanotetrapods

Surface Morphology

Surface morphology of ZnO nanotetrapods were measured using field emission scanning electron microscope (FESEM) at different evaporation temperature as shown in Figure 3. The images were taken at 5V and 50k magnification. The higher magnification image indicating that the growth of the nanotetrapods has sharp tips at the end with an average diameter of 100 nm. The average length of the ZnO nanotetrapods was estimated to be 1 µm. The Figure 3 (a) shows polycrystalline plate on ZnO nanotetrapods legs were obtained at temperature of 700°C. The nucleation and growth of ZnO nanotetrapods is understood to occur in the vapor phase during synthesis. The diameters and length of needle were increased as temperature increased. The diameters and lengths of needles were in the range 34 to 68 nm and 388 to 500 nm, respectively. At temperature of 750°C, the product of needles formed the ZnO nanotetrapods [18].

The ZnO nanotetrapods start to be formed at temperature around boiling point of ZnO (750°C) which metallic Zn are easily evaporated. The formation shaped of ZnO nanotetrapods occur because of Zn vapor react with oxygen in the thermal-CVD. When the temperature increases to 800°C, the diameter and length needles grow larger and longer. It can be seen that at higher vaporized temperature, the needle start to be formed larger. The good formation of ZnO nanotetrapods is good due to highly intensity for (101) diffraction peak in Figure 2. The length and diameter of ZnO nanotetrapods was tabulated in Table 2.

Table 2: Length and Diameter for ZnO Nanotetrapods at Various Evaporation Temperatures

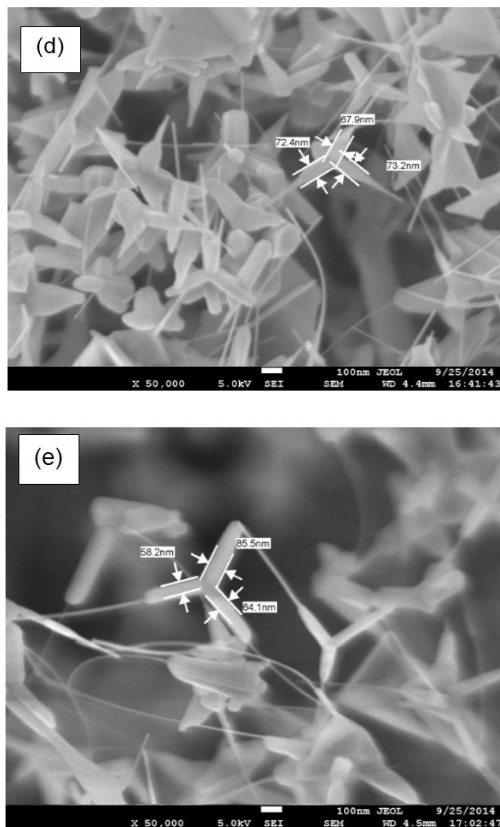| Evaporation temperature (°C)	Length (nm)	Diameter (nm)
700	342	34.4
725	356	42.2
750	463	64.6
775	512	72.4
800	748	85.5

Figure 3: FESEM images of ZnO nanotetrapods at (a) 700ºC, (b) 725ºC, (c) 750ºC, (d) 775ºC, and (e) 800ºC

Optical Properties

Photoluminescence (PL) spectra of ZnO nanotetrapods at different evaporation temperature were measured at room temperature in wavelength 325 to 800 nm as shown in Figure 4. The ZnO nanotetrapods were characterized under exciton of He-Cd laser (325 nm). The PL spectra was exhibited a strong emission at wavelength ~380 nm in UV ranges and 535 nm in visible region (green emission) respectively.

The peak at UV region also called as near-band-edge emission (NBE) is attributed to the free exciton recombination. The intensity of UV emission decreases with increasing temperature at 750ºC which is 2282.50 arbitrary units. The intensity decreases because of the thermal quenching effect [19].

The emission peak in UV region increases with increase in high evaporation temperature.

The Figure 4 shows the peak intensity of visible region tends to increase for the sample evaporate at 750°C which is 5676.98 arbitrary units. The peak intensity of visible region can be attributed to the defects of ZnO such as zinc interstitials and oxygen vacancies. It can be seen that stronger the intensity at visible emission may attributed to the singly ionized oxygen vacancy being from the recombination of electrons at the conduction band with holes trapped in oxygen-related defects [20]. The defect level slightly decreased when the temperature increased to 800°C.
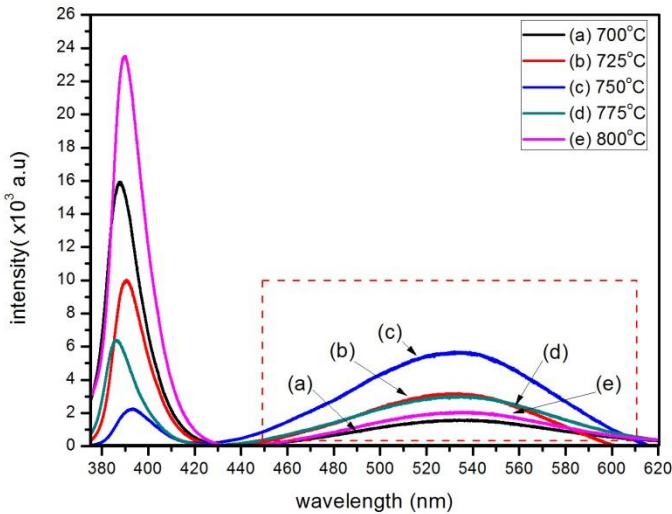

Figure 4: Photoluminescence spectra of ZnO Nanotetrapods

Conclusion

In this paper, the ZnO nanotetrapods were successfully prepared using thermal-CVD at different evaporation temperature. X-Ray Diffraction spectra related to the surface morphology of the sample was done. From the XRD spectra, (101) diffraction peaks for sample of 750°C was seen to be slightly high compared other peaks. The (101) diffraction peak on sample of 750°C was found to be 4806.19 cps. It is highly probable that the highest diffraction peak indicate good crystalline quality. From FESEM images show temperature of 750°C has the good formation of ZnO nanotetrapods due to Zn vapor react with oxygen in the thermal-CVD. The needles of ZnO

nanotetrapods interconnect each other. Moreover, the photoluminescence spectra found the highest peak intensity in visible region at temperature of 750ºC. The highest peak intensity was due to zinc interstitial and oxygen vacancy. This study focuses the optimum of ZnO nanotetrapods with temperature of 750ºC to obtain the high intensity as well. However, this parameter will be implied for the fabrication of MEH-PPV: ZnO nanocomposite for OLED devices.

Acknowledgement

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