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Effect of Deposition Temperature on Self-Catalyzed ZnO Nanorods via Chemical Vapour Deposition Method

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ABSTRACT

The morphological, structural, optical and electrical properties of ZnO nanorods are investigated as a function of deposition temperature. The ZnO nanorods were grown on ZnO seed catalyst layer at temperatures between 750^{o}C – 825^{o}C using thermal chemical vapour deposition method. Sample deposited at 825^{o}C showed the highest crystalline orientation. The FE-SEM micrographs and the intense peak along (002) direction in the XRD spectra of this sample implied that the nanorods possess c-axis orientation. PL spectra showed two common ZnO peaks which centered at 380 nm and 540 nm. Two-point probe I-V measurement revealed ohmic behaviour with the gold metal contact, whereby the current increase with the deposition temperature.

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1. INTRODUCTION

Zinc oxide (ZnO) is a II-VI semiconductor compound with a direct band gap of E_g = 3.37 eV (at room temperature) [1, 2] which makes it suitable for application of shortwave length optoelectronics devices, such as light emitting diode and laser diodes. ZnO has high excitation binding energy of 60 meV, which is three times larger than GaN (E_b = 20 meV). This is the main advantage of ZnO as a light emitter, which permit excitonic recombination to dominate at room temperature [3]. ZnO is commonly available in white colour powder and has been used in so many products, such as in paints, ointments, adhesives, sealants, and many more not forgetting in many electronics devices. ZnO thin films are highly transparent in the visible wavelength, making it suitable for optoelectronics devices such as solar cells [4]. It has shown distinguished properties which are semiconducting, piezoelectric, and pyroelectric properties [6]. It is chemically and mechanically stable, non-toxic, and high abundant.

ZnO nanostructures such as nanorods and nanoflowers [5] have been grown using many deposition methods. Among them are hydrothermal method [6], thermal chemical vapor deposition method [7], magnetron sputtering [8], electrochemical deposition [9] and many more. Among these methods, CVD has become one of the most favorable method to grow ZnO nanorods due to good crystalline structures of the samples. In a conventional vapour–liquid–solid (VLS) growth mechanism to grow the ZnO nanostructures, metals such as gold are used as the catalyst layer. Consequently, nanorods deposited by the VLS mechanism typically contain catalyst nanoparticles at their tips [10]. However the metal catalysts will unavoidably affect the purity of the products, and furthermore could affect the efficiency of electronics devices [11, 12]. According to Wang *et.al* [13], metal catalysts are not necessary needed during the growth process of the ZnO nanorods. Many research reported on the growth of ZnO nanorods directly on substrates such as silicon wafer, sapphire, graphite and etc. However, there are constraints of this type of growth process which limits the selection of the templates. The lattice mismatch between substrate/ZnO nanorods could lead to increase of strain in the ZnO nanorods [14]. Furthermore, sapphire is rather expensive.

Self-catalytic ZnO nanorods and nanowires became an alternative method to the metal-catalysed nanorods. For this type of growth, vapour-solid (VS) growth mechanism was proposed by many. Growths of the self-catalysed ZnO nanorods were done at various growth conditions. The substrates' positions, growth temperature, precursors, and gas pressures were among the affecting parameters [15].

In this work, we have employed CVD method to synthesize self-catalyzed ZnO nanorods by varying the deposition temperature (750^{o}C to 825^{o}C). ZnO thin films were firstly coated on the surface of quartz substrates which act as the seed layers. With different deposition temperatures, we observed the obtained ZnOmorphological, structural, optical and electrical properties.

2. EXPERIMENTAL

ZnO nanorods were grown using thermal chemical vapor deposition method using zinc powder and oxygen gas as the precursor. Layer-by-layer ZnO thin films were firsty was firstly coated on top of the quartz substrate which act as the seed catalyst layer and it has been presented elsewhere [16]. The growth process was carried out in a quartz tube in a horizontal tube furnace. Zinc powder and ZnO coated quartz substrate were placed in a boat, which was then inserted into the quartz tube and placed at the centre of the furnace as shown in Figure 1. Double tube insertion gas (one for argon and one for oxygen) were applied in this system to ensure the good growth of the ZnO nanorods.

The carrier gas, Argon was firstly fed into the alumina tube for 15 minutes to ensure that all other gases were flowed out and to maintain a stable environment inside the tube. Oxygen was not fed at this step to prevent unintended or unnecessary oxidation effects of the seed layer as well as deposition of amorphous phase ZnO or by-products synthesized on the substrates at low temperature while raising the temperature of the furnace. In this work, the gas was flown into growth tube which was not pre-evacuated.

Once the temperature stabled at the deposition temperature, oxygen gas was then injected into the tube with a flow rate 5 sccm. The gas flow rateswere controlled using a mass flow controller. The deposition time started when the oxygen was fed into the tube. Once the deposition was done, the oxygen was turned off and the temperatures of the furnace were turned off. The furnace was cooled down with the argon gas maintained flowing during the cooling process. The sample was taken out and ready for characterizations.

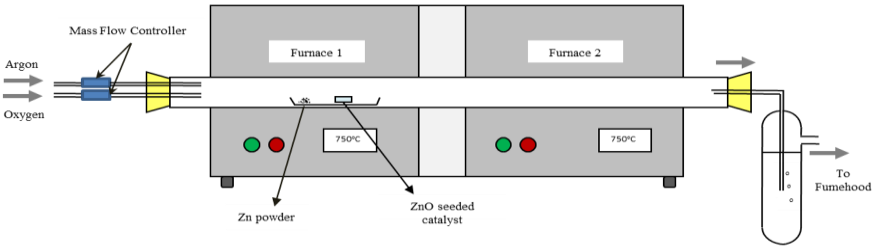

Figure 1. Schematic Diagram of Thermal Chemical Vapour Deposition System

The morphological properties were investigated by a field emission scanning electron microscope (model: JEOL, JSM-7600F), while the crystallinity properties were measured by an X-ray diffraction (XRD; model: Rigaku Ultima IV) using Cu Kα radiation (λ=1.5418 Å). For the optical properties, photoluminescence spectra were obtained on a spectrophotometer (PL, Horiba Jobin Yvon HR8) equipped with HeCd laser at excitation source of 325 nm. 2 point-probe I-V measurement was used to obtain the electrical properties.

3. RESULTAND ANALYSIS

3.1. Morphological and Crystallographic Properties

We firstly present the surface morphological of the ZnO nanorods with effect of various deposition temperature. For this experiment, the deposition temperatures were varied at 750^{o}C, 775^{o}C, 800^{o}C and

825^{o}C. The surface morphologies of the ZnO nanorods at different deposition temperature were checked using FE-SEM and shown in Figure 2 (a) – (d), while Figure 2 (e) shows the surface morphology of the ZnO seed layer. Here, we have proven that we have succeeded to grow self-catalyzed ZnO nanorods using CVD method at atmospheric pressure without using any metal catalyst.

The FE-SEM images showed that the growth of the nanorods shows a dependency on the deposition temperatures. As the temperature increased, it is found that the diameter of the nanorods increased from the range of 30 – 80 nm for sample deposited at 750^{o}C to 40 – 170 nm for samples deposited at 825^{o}C. The nanorods diameters are tabulated in Table 1. The presented results prove that the morphology of the ZnO products can be controlled by adjusting the furnace temperature during the deposition of ZnO nanorods.

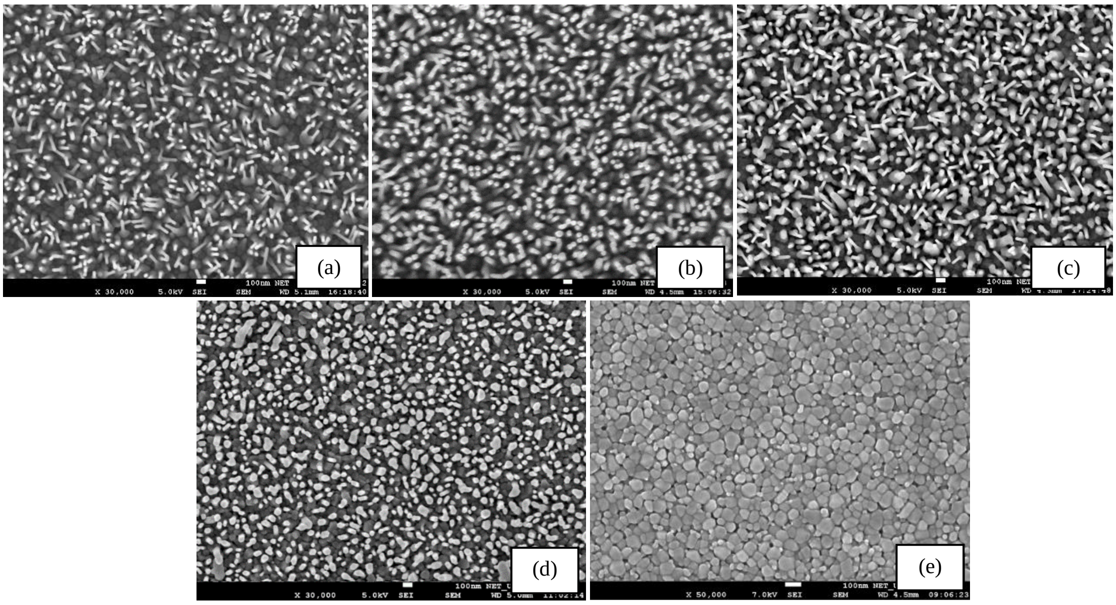

Figure 2. FE-SEM Micrographs of ZnO Nanorods at Different Deposition Temperatures of (a) 750^{o}C, (b) 775^{o}C, (c) 800^{o}C, (d) 825^{o}C, and (e) ZnO seed layer

Table 1. Film Thickness and Average Particle Size at Various Numbers of Layers

Number of Layers	Film Thickness (nm)	Average particles size (nm)
1	42.77	24.1
2	68.52	34.9
3	92.57	49.7
4	111.19	54.6
5	129.85	61.0
6	153.74	77.9

Figure 3 shows the XRD spectra of the ZnO nanorods at different deposition temperature. All samples exhibit crystalline structure that belongs to the hexagonal wurtzite type of ZnO (JCPDS #36-1451). Three diffraction peaks of (1 0 0), (0 0 2) and (1 0 1) at $2\theta = 31.90^o$, 34.57^o and 36.39^o were observed, as marked in the figure. This proves that the nanorods grew in the same orientation of the seeded catalyst layer films.

The overwhelming (0 0 2) peak of all samples indicate that the preferred orientation of the ZnO nanorods is along the c-axis with a good crystalline structure. The (0 0 2) peak intensity were found to become stronger with the increasing of the deposition temperature and maximized at sample of 825^{o}C. This is consistent with the FE-SEM image shown in Figure 2(d).

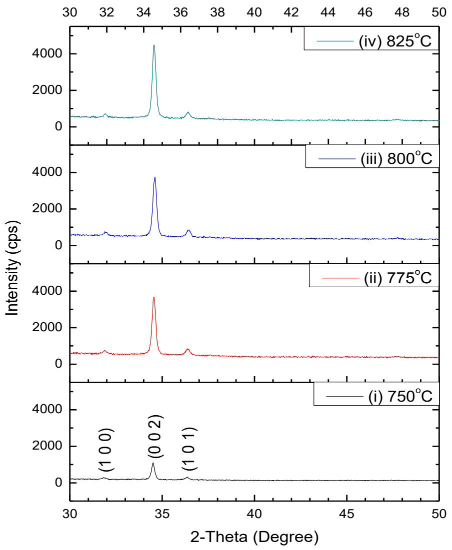

Figure 3. XRD Patterns of ZnO Nanorods at Different Deposition Temperatures

3.2. Optical Properties

Room temperature PL spectrometry with the excitation wavelength of 325 nm was used to measure the optical properties of ZnO nanorods deposited at different temperature. Figure 4 shows the PL spectra of the samples measured within the wavelength range of 330 nm to 800 nm. The usual peaks of ZnO were observed from all samples; which are the UV emission centred at 380 nm and broad visible emission (green) centred at 540 nm. It is reported by many [17, 18] that the UV emission is attributed to the exciton recombination process. The UV peak intensity gradually increased as the deposition increased. This result is in agreement with the crystalline quality of the ZnO nanorods which showed improvement with the increased of the deposition temperature.It is well known that the PL spectra strongly rely on the type and density of defects in the ZnO nanorods. According to Vanheusden et al [19], the green emission is attributed to singly ionized oxygen vacancy. It is also noticeable that the visible emission intensity increased with the deposition temperature with no peak shifting observed.The ZnO nanorods with larger diameters tend to exhibit PL spectra dominated by the broad green light emission due to the defects compared to the smaller diameter nanorods.

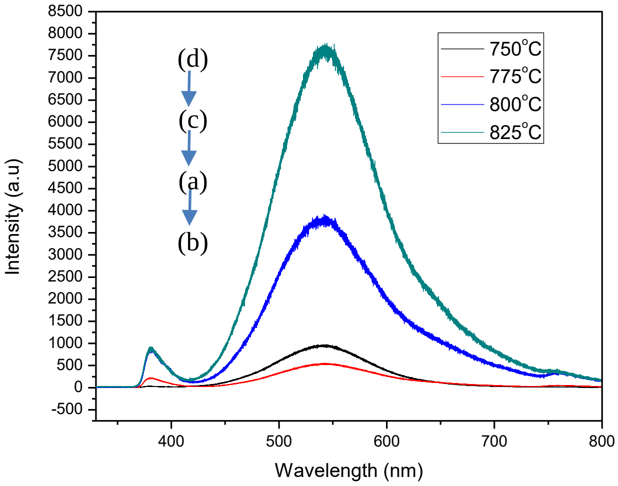

Figure 4. PL Measurements of ZnO Nanorods at Deposition Temperatures of (a) 750°C, (b) 775°C, (c) 800°C, and (d) 825°C

3.3. Electrical Properties

Electrical contacts were prepared to ZnO nanorod using gold metal for the *I-V* measurements. The *I-V* measurements were done at room temperature using two point probes and plotted as shown in Figure 5. All samples show a linear increased of currents with the increased of the voltage value, indicating an ohmic behaviour of the ZnO nanorods with the metal contact. The current values were found to increase with the deposition temperatures. At 5V of supplied voltage, the current values were found to be 4.20 x 10^{-4}Ω.cm, 1.96 x 10^{-3}Ω.cm, 5.29 x 10^{-3}Ω.cm and 9.12 x 10^{-3}Ω.cm for films deposited at750°C, 775°C, 800°C, and 825°C, respectively.

From the *I-V* measurement graph, the resistivity of the ZnO nanorods were calculated and presented in graph shown in Figure 6. As predicted from the *I-V* measurement, the resistivity of the samples decreased with the increased of deposition temperature. The resistivity decreased from 2.59 Ω-cm to 5.4 x 10^{-2} Ω-cm with the increased of deposition temperature from 750°C to 825°C. It is predicted that this phenomenon is due to the enhancement of film crystalline which is proven by the XRD results which is in good agreement with Chao et al [20]. According to Mosbah et al [21], the increase of deposition temperature led to the reduction in the scattering of the carriers at the grains boundaries and crystal defects, which increased the carrier mobility, and thus reduced the resistivity. Therefore, the optimized temperature for this parameter is at 825°C which showed highest crystalline structure and lowest resistivity value.

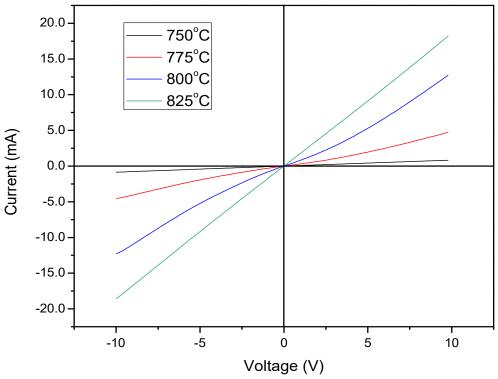

Figure 5. *I-V* Measurements of ZnO Nanorods at Different Deposition Temperatures

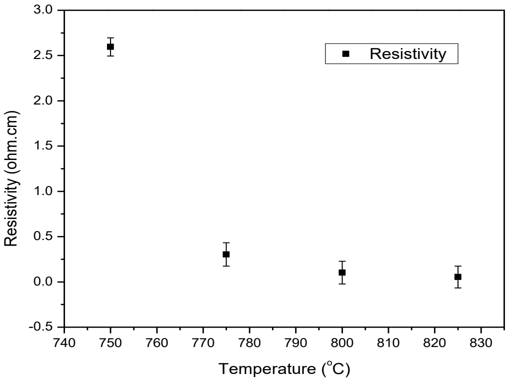

Figure 6. Resistivity of ZnO Nanorods at Different Deposition Temperatures

4. CONCLUSION

Self-catalyzed ZnO nanorods were successfully grown using TCVD method at different deposition temperature. Our results show that the ZnO nanorods grown at temperature of 825°C produced perfectly aligned nanorods with highc-axis orientation crystallinity, enhanced PL emission and lowest resistivity.The analysis of the morphology, structural, optical and electrical properties of ZnO nanorods implied that the growth of ZnO nanorods were directly controlled by the deposition temperatures.

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