Effect of Growth Time on the Characteristics of ZnO Nanorods

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Abstract. ZnO nanorods were successfully synthesized via two stages, that is deposition of ZnO seed layers on ITO substrate and growth of ZnO nanorods via solvothermal method. A characterization by using XRD was employed to investigate the structure and size of the crystals. SEM characterization was used to study the size and morphology of the particles. UV-Vis and FTIR characterizations were used to investigate the bandgap and functional group of the samples. The data analysis presented that the ZnO particles had a crystal structure of hexagonal with rod morphology. The diameter size of the ZnO nanorods growth on the substrate surface for the growth time of 4, 6, and 8 hours were respectively 138, 230, and 236 nm with the length of the rods of 570, 934, and 1280 nm, respectively. The bandgaps of the ZnO nanorods for growth times of 4, 6, and 8 hours were respectively 3.14, 3.12, and 3.05 eV, while the ZnO seed layers had 3.22 eV band gap. FTIR spectrum showed that the main peaks were 400-515, 870, and 1250 cm\textsuperscript{-1} showing the functional groups of ZnO and H-C-N.

Keywords: ZnO, nanorod, solvothermal, optical properties, band gap.

1. Introduction

The synthesis of ZnO semiconductor has become a topic that catches researchers’ attention in the few decades. Several unique characteristics offered by ZnO, such as its wide band gap energy of 3.37 eV, large exciton binding energy of 60 meV, and high electron mobility, make ZnO is a multifunction material [1]. Based on such characteristics, the ZnO semiconductor has been widely applied as, among others, the main component of numerous optical or electronic devices such as fluid sensor [2], gas sensor [3], UV emission devices [4], light emitting diode (LED) [5], a photocatalyst [6], and solar cells [7].

Along with nanoscience and nanotechnology development, the synthesis of nano-scaled ZnO has been a focus. It is due to the better electronic and optical characteristics offered by nano-scaled materials compared with the bulk materials [8]. Some researchers have performed synthesis of nano-
size ZnO in varied types of morphology for numerous applications. Some of such morphology include nanorod [9], nanowire [10], nanotube [11], nanoflower [12], nano comb-like [13], nanosheet [14], nanoflake [15], nanocastle [16], and nanoforest [17]. The formation of vertically oriented ZnO in rod morphology, among other types of morphology, on a substrate has been intensively studied until recently.

Vertically oriented ZnO nanorods have been successfully synthesized by several methods, either the vapor or liquid phase method. Several vapor-phase methods such as vapor-liquid-solid [18], metal-organic chemical vapor deposition [19], and chemical vapor transport [6] are proven to be effective in forming vertically oriented ZnO nanorods on a substrate. However, some of such vapor-phase synthesis methods have several drawbacks, i.e. their demand for a relatively high temperature, expensive operational cost, large energy consumption, and a relatively long synthesis time [18]. Compared to the vapor-phase synthesis method, liquid phase synthesis method is more economical and easier to be applied in a wider scale.

Some liquid-phase synthesis methods, such as sol-gel, hydrothermal, electrodeposition, and chemical bath deposition, are developed more intensively by the researchers [19]. By all of the methods, a hydrothermal method is chosen by many researchers due to its superiorities. This method is mostly used for directing the formations of various metal oxides since it requires a simple process, a low temperature, and it can be applied on a wide scale [20]. The performance of ZnO semiconductor could be improved by optimizing the rod length and diameter that will influence the surface area. A high surface area of the semiconductor applied as an indicator electrode in the solar cell allows more absorption of dye- sensitizers so that the solar cell energy conversion can improve [21]. The length and diameter of the rod can be optimized by varying the hydrothermal time during the synthesis process. It was reported that the synthesis of ZnO in nanoflower morphology was conducted using hydrothermal method. The hydrothermal time that was increased to a certain limit could improve the length of the rod that formed the nanoflower so that it would have a larger surface area [22].

In relation to the above fact, another work reported that among the variety of nanostructures, the formation of ZnO nanorods that is vertically oriented on the substrate has been an extensively studied topic until recently [21]. It is also crucial to increase the electron transport that has an impact on the improvement of indicator electrode photosynthesis. Such rod-like 1-dimension nanostructure has been greatly studied and it is known that the morphology of such nanostructure could increase the diffusion of an electron in the photoelectrode film by directly providing the conduction pathway. Such direct pathway along the nanostructure is expected to be able to reduce the charge recombination that is likely to occur on randomly-oriented conventional polycrystalline nanoparticles [23].

According to the above descriptions, the development of synthesis methods to produce ZnO nanorods in a variety of shapes and sizes in order to boost the performance becomes crucial. One way that could be taken is varying the growth time of the ZnO synthesis on the substrate. The particle structure, morphology and size, functional group, and band gap were certainly included in this research.

2. Experimental Methods

The primary materials of Zn(II) acetate dihydrate (Zn(CH₃COO)₂·2H₂O), PA, Ethanol C₂H₅OH (EtOH), Monoethanolamine C₂H₇NO (MEA) were used in the synthesis of ZnO nanoparticles as seed layers. The materials used for the ZnO nanorods growth were Zinc Nitrate Tetrahydrate (Zn(NO₃)₂·4H₂O), Hexamethylenetetramine C₆H₁₂N₄ (HMT), Deionized Water, and Indium Tin Oxide (ITO) as a substrate. The following process was the formation of ZnO solution by dissolving Zn(CH₃COO)₂·2H₂O in ethanol. For the Zn(CH₃COO)₂·2H₂O to be completely dissolved, a hot plate magnetic stirrer was utilized at 70 °C for 45 minutes. Such process was followed by an addition of MEA into the solution while stirred at a constant temperature of 70 °C for 2 hours. The molar ratio concentration of Zn(CH₃COO)₂·2H₂O: MEA was 1:1. Then, the solution was stored at room temperature for 24 hours until a homogeneous and transparent solution was formed. Next, the ITO substrate was put on the spin coater during the formation process of seed layer ZnO thin films. After that, the solution was dropped on the ITO substrate to be then spun at 2500 rpm for 25 seconds,
continued by the preheating process at 150 °C for 10 minutes. After the third repetition of such process, an annealing process was performed at 550 °C for 2 hours. Then, after the coating of seed layer ZnO thin films was grown on the ITO substrate, the ZnO nanorods were grown by using the hydrothermal method. The solution growth was performed using Zinc Nitrate Tetrahydrate (Zn(NO₃)₂·4H₂O), HMT, and Deionized Water. The utilized precursor concentration was 75 mM, with a molar comparison between Zn(NO₃)₂·4H₂O and HMT of 1:1. The solution was then stirred by a magnetic stirrer for 45 minutes at room temperature. Then, the seed layer ZnO film was dipped into the prepared solution. During the growth process, the solution was heated at a temperature of 90 °C with the growth-time variation of 4 hours, 6 hours, and 9 hours for each concentration. The sample was rinsed by Deionized Water to remove the impurity from the surface area to be then dried at room temperature. Subsequently, the ZnO nanorods on the ITO substrate were annealed at a temperature of 550 °C for 2 hours.

The ZnO nanorods were characterized using X’Pert Pro XRD with Cu-Kα 1.540 Å to identify the structure of the crystal, while INSPECT-S50 SEM-EDAX Type FEI characterized the morphology, elemental composition, and size of the samples. FTIR, with Shimadzu IR Prestige 21 brand was utilized to determine the functional group. Further, a test by using UV-Vis Spectrophotometer was conducted to characterize the band gap.

3. Results and Discussion

The diffraction patterns of X-ray films of ZnO nanorods/ITO with a precursor concentration of 75 mM for a growth time variation of 4, 6, and 8 hours using the solvothermal method are shown in Figure 1. The ZnO nanorods phase analysis informed that the formed diffraction patterns were in good agreement with standard JCPDS card No. 36-1451 with zincite phase, which had a space group of P 63 m c, hexagonal crystal systems, unit cell of a = 3.2533 Å and c = 5.2073 Å. The phase that was formed in accordance with the research findings reported by Rai et al. (2014) stating that ZnO nanorods were formed in the zincite phase [24]. Figure 1 shows the diffraction peaks located at the (100), (002), and (101) plans. The peak at (002) plane is the highest peak intensities and increases by increasing growth times. This phenomenon indicates that ZnO nanorods growth along c-axis with excellent crystallinity. It is in agreement with the research result reported by Selvan et al. (2014) [25].

Furthermore, the results of crystal size measurement based on the XRD data are presented in Table 1. The crystal size was estimated using Scherrer equation along (002) plane. Table 1 presented that there was an increase in the crystal size along with the improved growth time of nanorods from 44.2 nm to 51.3 nm for growth times of 4 hours and 8 hours, respectively. However, the growth speed rate of ZnO nanorods at growth time 4 hours and 8 hours decreases respectively from 11.05 nm/h to 6.41 nm/h.

| Table 1. Crystallite sizes of the ZnO nanorods. |
| Sample                      | FWHM (rad) | Crystal Size (nm) |
|-----------------------------|------------|-------------------|
| ZnO nanorods 4 hours        | 0.003282   | 44.2              |
| ZnO nanorods 6 hours        | 0.002973   | 48.8              |
| ZnO nanorods 8 hours        | 0.002827   | 51.3              |

| Table 2. Dimensions of the ZnO nanorods. |
| Type of Sample   | Length (nm) | Diameter (nm) |
|------------------|-------------|---------------|
| ZnO nanorods 4 hours | 570         | 138           |
| ZnO nanorods 6 hours  | 934         | 230           |
| ZnO nanorods 8 hours  | 1280        | 236           |
Figure 1. SEM images of the ZnO nanorods in variation of the growth time of (a) 4 hours, (b) 6 hours, and (c) 8 hours.

Figure 1 shows the cross-section and top-section morphology of ZnO nanorods films with a variation of growth time of 4, 6, and 8 hours. The results of SEM characterization identified the formation of a hexagonal rod structure on the entire surface of the substrate. The SEM characterization results were analyzed and tabulated in Table 2.

It can be seen in Table 2 that the rod diameters on the variation of growth time of 4, 5, and 8 hours were 138 nm, 230 nm, and 236 nm, respectively, while the rod lengths were 570 nm, 934 nm, and 1280 nm, respectively. A longer the ZnO nanorods growth time produced a larger and a higher length of rod diameter. The nanorods diameter was controlled by the precursor concentration. A higher concentration would create a larger nanorods diameter [26], while the length of the nanorods was controlled through by the length of the growth time. A longer growth time would result in a longer rod [27]. The varied diameter sizes were due to the combination of the adjacent rods forming new rods with larger diameters. It was possible to happen when the distance between one rod and another became shorter along with the increased solvothermal period. Besides, it was also enabled by the influence of the different substrate position during the growth process. The ZnO films with the up-facing substrate would have longer rods compared with the ZnO films with the down-facing substrate. The morphology of nanorods with a higher density can be seen in the ZnO nanorods synthesized for a growth time of 8 hours. The longer growth time by hydrothermal method affects the increased density of the Nanorods, which was formed along with the growing length of the rods.
Such results were in accordance with the statement pointed out by Baruah and Dutta (2009) stating that nanorods growth is initiated by the initial nucleation process that took quite long time to be then followed by the growth process at a relatively faster rate until it reached the maximum rod length. Finally, there was not any growth in the rate because the content of Zn$^{2+}$ ion in the solution phase was reduced. The further radial growth did not cause the increase on the diameter size, yet by the combinations of several single nanorods forming new nanorods resulted from the increasing density of rods along with the addition of the hydrothermal period. In the following step, there was an excessive deposition when the reactant was still available in the solution phase while, on the other hand, the substrate could not provide a place for the initial nucleation process of the ZnO nanorods [28]. The increased density of rods had positive impacts on the orientation and direction of rods formed on the substrate. Nanorods with a more compact structure could result in a vertical orientation. It was possible since the rods with a more compact structure would support each other so that the possibilities of them to tilt or fall could be minimized.

A characterization by UV-Vis spectrometer on the wavelength ranged from 350-800 nm was performed to identify the transmittance spectrum and the optical properties of ZnO nanorods shown in Figure 2. Figure 2 indicates that all ZnO nanorods with 75 mM precursor concentration with a variation of growth time of 4, 6, and 8 hours showed the highest excitonic absorption peak at the wavelength of ~376 nm. The results of this study were closely in agreement with the results obtained by Foo et al. (2014) with the highest peak of excitonic absorption at the wavelength of 378 nm [29]. Such a peak indicated that ZnO nanorods have a good optical quality and a strong exciton binding energy. The strongest peak of ZnO nanoparticle film was found at the wavelength of ~360 nm, such wavelength was the sharp peak from the free exciton. Exciton is a combination of neutral bond electron and hole that causes a rapid increase on the peak absorption. The absorption coefficient ($\alpha$) of the ZnO nanoparticle film's transitional directions is formulated through the Equation 1.

$$\alpha = \frac{ln(I/T)}{d}$$  

(1)

Where $T$ represents the transmission of ZnO film and $d$ is the thickness of the film [29].

The characterization of the energy bandgap ($E_g$) was done based on the Kubelka Munk equation for direct band gap semiconductor, which is determined from a Tauc plot between $(ahv)^2$ vs. $hv$, as can be seen in Figure 3. Based on the interpretation of Figure 3, the intersection between the line extrapolation and x-axis shows a thin energy band gap in each film. the band gap values of ZnO nanorods were obtained to be 3.14 eV, 3.12 eV, and 3.05 eV. In general, the bandgap of ZnO nanorods are lower rather than ZnO bulk (3.37 eV) due to optical confinement effect of the formation of ZnO nanorods [30]. The bandgap decreases with increasing growth time due to reduction of surface area [31].

![Figure 2. UV-Vis spectra of ZnO nanorods with variation of growth time.](image)
Figure 3. Touch graph of ZnO nanorods with variation of growth time.

Figure 4. FTIR Spectrum of ZnO nanorods with variation of growth time.

Figure 4 shows the FTIR Spectrum test results on ZnO seed layer (A) and ZnO nanorods/ZnO seed layer/ITO with a precursor concentration of 75 mM with a variation of hydrothermal growth periods of 4 hours (B), 6 hours (C), and 8 hours (D) in the wavelengths ranged from 400-500 cm\(^{-1}\) at room temperature. Figure 8 identified three main peaks on the wavelengths ranged from 400-515 cm\(^{-1}\), 870 cm\(^{-1}\), and 1250 cm\(^{-1}\). Generally, ZnO absorptions were found in the wavelengths ranged from 500-515 cm\(^{-1}\), in line with a report made by Gayen et al. (2010) [32], while the H-C-N functional groups formed at the wavelengths of 870 cm\(^{-1}\) and 1250 cm\(^{-1}\) from HMT material with a chemical formula of C\(_6\)H\(_{12}\)N\(_4\), as reported by Cottin et al. (2002) [33] and Garcia et al. (2010) [34].

4. Conclusion
ZnO nanorods have been successfully synthesized through ZnO seed layer deposition on the ITO substrate surface by solvothermal method. The crystal structure formed in ZnO nanorods is hexagonal zincite. The crystal sizes formed by employing 75 mM precursor concentration and with a variation of growth time of 4, 6, and 8 hours were 44, 48, and 51 nm, respectively. Also, the respective band gap values were identified to be 3.14, 3.12, and 3.05 eV. The SEM results showed that the rod diameter of each sample was 138, 230, and 236 nm, while the respective rod lengths were 570, 934, and 1280 nm. There were three primary peak absorptions on the wavelengths ranged from 400-515 cm\(^{-1}\), 870 cm\(^{-1}\), and 1250 cm\(^{-1}\) showing that the ZnO absorption was identified on the wavelengths ranged from 400-515 cm\(^{-1}\), while the absorption of H-C-N functional group was identified at the wavelengths of 870 cm\(^{-1}\) and 1250 cm\(^{-1}\).

5. References
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