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Optical properties of ZnO nanorods derived from chemical bath deposition process with different seeds solution concentration

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Abstract. Owing to their high surface to volume ratio and fast electron transfer, zinc oxide (ZnO) nanorods have been well-known as potential nanostructured material for various applications including sensors, dye sensitized solar cells, optoelectronic, transparent heater and biomedical devices. Among other synthesizing techniques for obtaining ZnO nanorods, chemical bath deposition (CBD) has been thought as a simple and low-cost method. However, there are several processing parameters that need to be investigated for the above-mentioned applications where the highly optical transparency of thin film ZnO nanorods grown on glass substrates is one of important targets to be achieved. In this work, ZnO nanorods were synthesized through CBD process at low temperature (0°C) by using seed solution prepared by dissolving 1: 1 equimolar zinc nitrate tetrahydrate and hexamethylene tetraamine. For investigation purposes, three different concentration of seed solutions i.e. 0.005, 0.025 and 0.05 M were used. Thin films containing ZnO nanoseeds were formed by spin coating the precursors on the glass substrates, followed with annealing at 200°C for 5 minutes. Finally, the ZnO nanorods were further grown at 90°C for 3 hours in the beaker glass using the same solution. X-ray diffraction (XRD) analysis showed that all ZnO nanorods demonstrated a strong (002) peak belong to wurtzite phase. It was found that the estimated crystallite size and band gap energy (E_g) for ZnO nanorods derived from the seed solutions of 0.005, 0.025 and 0.05 M were 21.42, 137.11, 171.39 nm, and 3.60, 3.20, 3.18 eV, respectively. However, the optical transparency was adversely lowered from about 75 to 40 % as a result of increased coverage of ZnO nanorods on the glass substrate. For transparent heater application where, a desired combination of high optical transparency and suitable electronic properties is needed, the current results were considered to be promising.

1. Introduction

The development of technology in various area today cannot be separated from the use of semiconductor materials. One of the most widely used semiconductor materials is zinc oxide (ZnO). ZnO has unique properties such as direct band gap energy of 3.37 eV, high-electrochemical stability, high thermal and mechanical stability at room, nontoxic, excellent optical and electrical properties, and easily formed into nanostructured materials [1]. These unique properties make the material useful for optoelectronic devices such as sensors, solar cell energy, laser technology, optoelectronics, and transparent conducting oxide [2]. ZnO nanorods is one dimensional (1D) nanostructured material that has received considerable



attention for photovoltaic devices due to its unique optical and electrical properties including much higher surface to volume ratio and faster electron transfer.

ZnO nanorods have been synthesized by using different physical and chemical methods such as chemical bath deposition (CBD) [3,4], RF sputtering [5], spray pyrolysis [6], metal chemical vapor deposition [7], vapor phase transport [8] and pulsed laser deposition [9]. Among these fabrication techniques, chemical bath deposition (CBD) has been considered as versatile one because it can offer many advantages such as easily available equipment, affordable cost, simple process, and harmless. In addition, the synthesis process takes place at low temperatures which make it suitable for producing large areas of thin film.

There are several important CBD parameters that significantly influences the formation of ZnO nanorods. These include precursor concentration, pH of the solution, bath temperature, thickness of the seed layer, type of substrates and time. It has been reported that the precursor concentration has affected the size and morphology of the formed ZnO nanorods [10]. For various optical applications, the size, shape and morphology of the ZnO nanorods is of importance and they need to be optimized. In this paper, therefore, we report the influence of seed solution concentration on the nanostructural characteristics and optical property of ZnO nanorods.

2. Methodology

2.1. Preparation of Seed Solutions and Layer Deposition

Prior to seed solutions preparation and seed layer deposition, the glass substrates as a growth medium for the ZnO nanorods formation were ultrasonically cleaned in beakers containing deionized water, acetone and ethanol, respectively for 8 minutes each and dried in water. The seed solution concentration starting from 0.005, 0.025 and 0.05 M were prepared by dissolving 1: 1 equimolar zinc nitrate tetrahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, Merck) and hexamethylene tetraamine ($\text{C}_6\text{H}_{12}\text{N}_4$ / HMTA, Merck) in water at 0°C for 1 hour. Thin films containing ZnO nanoseeds were obtained through spin coating the precursors on the glass substrates with 2000 rpm for 20 seconds, followed with annealing at 200°C for 5 minutes.

2.2. Growing of ZnO Nanorods with Chemical Bath Deposition Method

Further growth of ZnO nanorods was carried out by soaking the glass substrate in each seeding solution for 3 hours at 90°C. Furthermore, the glass substrates were cleaned using distilled water and dried in air. The morphology of ZnO nanorods derived from different seed solution concentration was characterized by using field emission scanning electron microscopy (FE-SEM JEOL JIB tipe 4610F), while the crystal structure was investigated using X-ray diffraction (XRD, Pan Analytical X-Pert Pro). For analysis purposes, the crystallite size was calculated based on Debye-Scherrer method [11]. The optical absorbance-and transmittance of the ZnO nanorods for different seed solution concentration was obtained by using spectrometer UV-Vis (Shimadzu UV, 2450), while the resulting band gap energy, E_g of nanorods was calculated by using Tauc equation [12].

3. Results and Discussion

3.1. XRD Pattern of ZnO Nanorods with Different Seed Solution Concentration

Figure 1 shows XRD patterns of ZnO nanorods thin film with different seed solution concentration. The films are polycrystalline with hexagonal wurtzite ZnO according to JCPDS No. 36-1451. The (002) peak intensity of ZnO nanorods thin film increased significantly with the increase of seeding solution concentration. These results indicate that different seed solution concentration has affected the crystallinity of ZnO nanorods formed in this work. This can be attributed to the nucleation velocity of ZnO nuclei in the higher concentration which was faster than that of in the early stages with lower one, which resulted in bigger formation of ZnO crystallites. To obtain a more quantitative data on the crystallites growth, the diffraction data was processed further by using Debye-Scherrer method and the

calculation results shows that crystallite size of nanorods increased significantly from 21.42 to 137.11 and finally 171.39 nm when the seed solutions concentration was added from 0.005 to 0.050 M were, respectively.

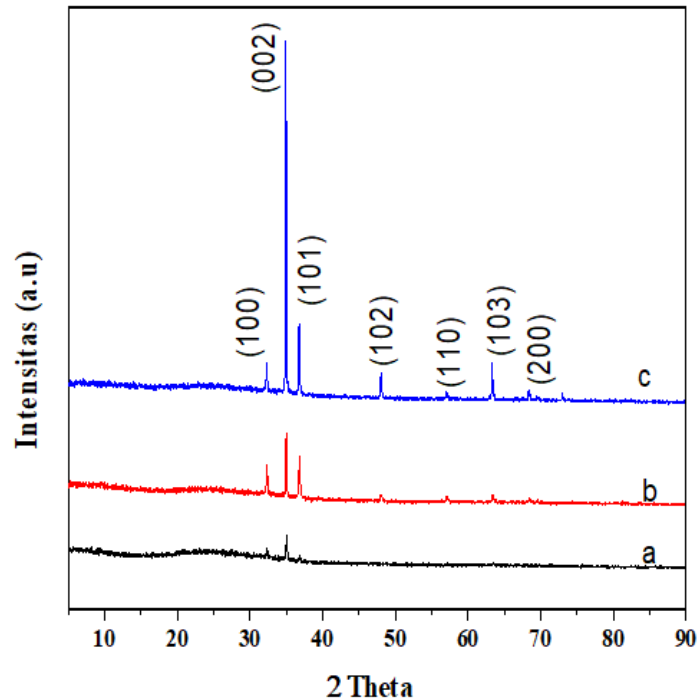


Figure 1. X-ray diffraction patterns for ZnO nanorods thin films with variation in seed solution concentration of: (a) 0.005, (b) 0.025, and (c) 0.050 M.

3.2. The Morphology Properties of ZnO nanorods with Different Seed Solutions Concentration

The FE-SEM results of ZnO nanorods morphology for each seed solution concentration is shown in Figure 2. It shows that at concentration of 0.005 M the ZnO nanorods have not resulted in a good coverage on glass substrate (Figure 2a and b). It can be understood since at low concentration the supersaturation level of ZnO nuclei was still weak. The growth of nanorod was thus retained due to slow nucleation and growth rate. With an increase in the precursor concentration up to 0.025 M, the morphology of sample was improved where a quite uniform distribution of nanorods with hexagonal shape was obtained (Figure 2c and d). Furthermore, with a higher concentration up to 0.050 M the coverage of ZnO nanorods appeared much more uniform where the nanorods grew in a hexagonal vertical direction. It was found that the average diameter for ZnO nanorods was increased from 161 to 205 and finally 427 nm when the above seeding solution concentration was increased. This is in agreement with the previous results of XRD analysis on the crystallite size growth of the nanorods.

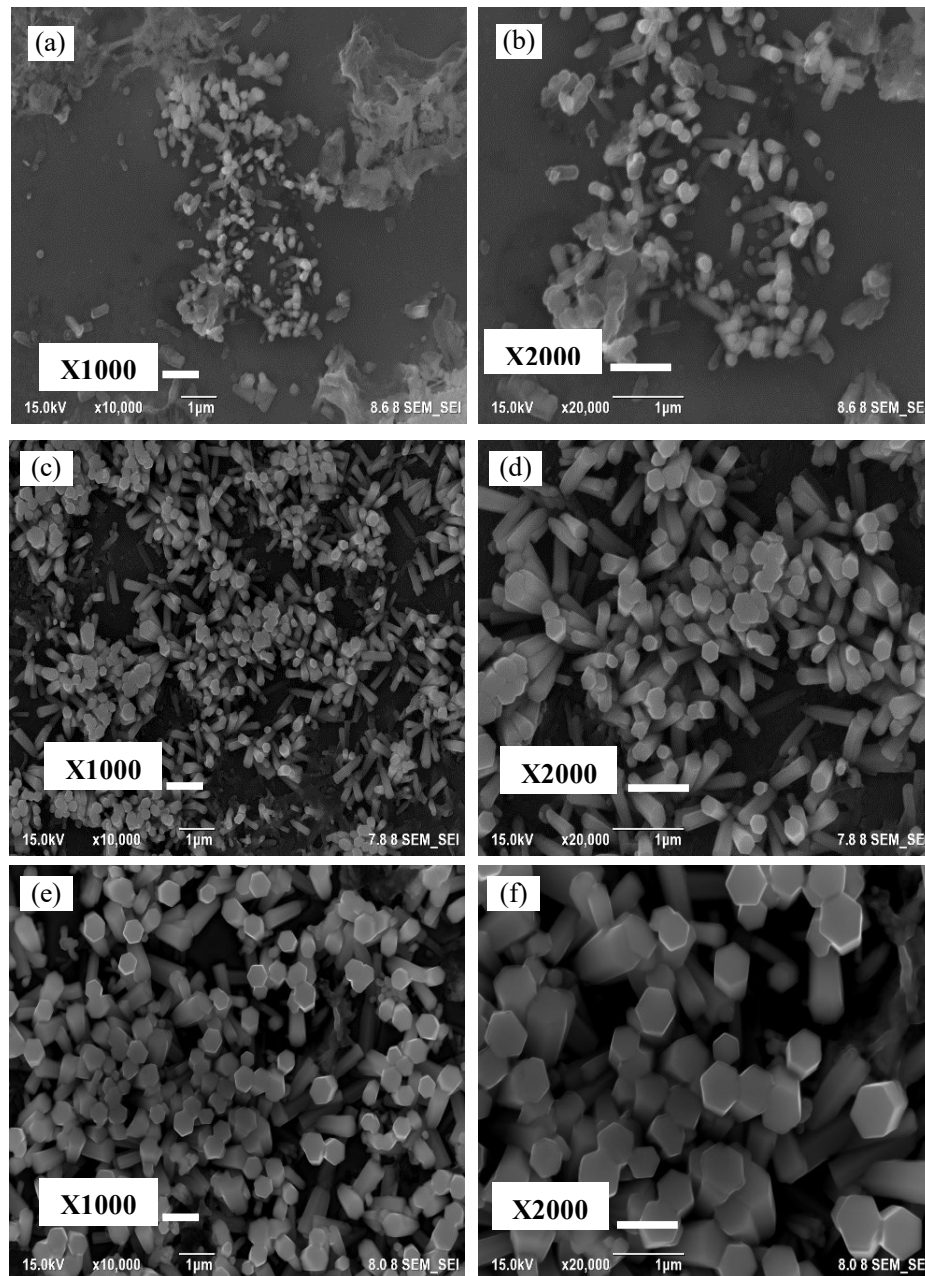


Figure 2. FE-SEM images of ZnO nanorods grown on the glass substrate with different seed solution concentration of: (a-b) 0.005, (c-d) 0.025 and (e-f) 0.050 M. The left figure is provided with magnification of 1000 X, while the right one with magnification of 2000 X.

3.3. The Optical Properties of ZnO Nanorods with Different Seed Solutions Concentration

Figure 3 shows the optical absorbance spectra of ZnO nanorods derived from different seed solution concentration. All the samples provided quite high transparency in the visible range (400-800 nm) and started to demonstrate absorption edge at around 380 nm. Sample with a seed solution concentration of 0.050 M has the highest absorbance in comparison to the other two samples, this result can be related to the higher crystallinity of nanorods with bigger crystallite size as has been studied by previous XRD analysis.

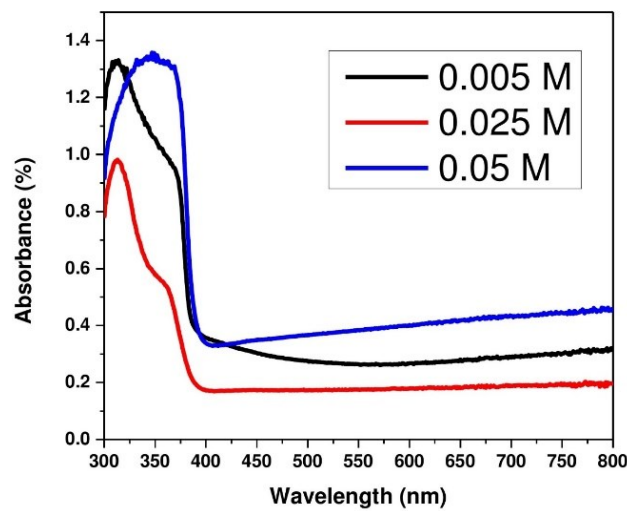


Figure 3. Optical absorption spectrum of ZnO nanorods for difference seed solution concentration (a) 0.005, (b) 0.025 and (c) 0.050 M.

The results of plotting $(\alpha h\nu)^2$ versus photon energy ($h\nu$) of ZnO nanorods with three different seed solution concentrations by using Tauc equation is presented in Figure 4. It was found that with increasing seed solution concentration from 0.005 to 0.050 M the band gap energy, E_g decreased from 3.60 to 3.18 eV. The decrease in the band gap energy value can be correlated to the increase in the carrier concentration and the declining in the strain value [13,14]. Again, this complies with the XRD analysis previously showing the trend of increase in crystallite size. In nanometer regime, the smaller E_g is obtained with bigger nanocrystallite size of semiconductor materials, which relates to the electron excitation from valence band to conduction band. We already have observed this phenomena in our previous studies on conventionally annealed and post-hydrothermally treated TiO₂ nanoparticles derived from the sol-gel process [15], TiO₂ nanotubes [16,17], ZnO nanoparticles [18], and ZnO nanorods [19].

Figures 5a - c shows optical transmittance spectrum of ZnO nanorods thin films by using different seed solution concentration. It can be clearly seen that the transmittance value of the samples has decreased from 75 to 40% with the respective increase in the seed solution concentration. The drop of transmittance at higher seed solution concentration was due to the increase in photon scattering by increase of the roughness of the surface morphology [13]. Furthermore, the decrease in transmittance with increasing concentrations of seed solutions can also be associated to the increasing number of molecules involved in absorption of light energy [14]. Smaller band gap energy own by ZnO nanorods derived from higher concentration of seeding solution, as shown in previous analysis by Tauc equation, also confirmed the easiness of electron excitation from valence band to conduction band, resulting more absorbance and thus lower transmittance.

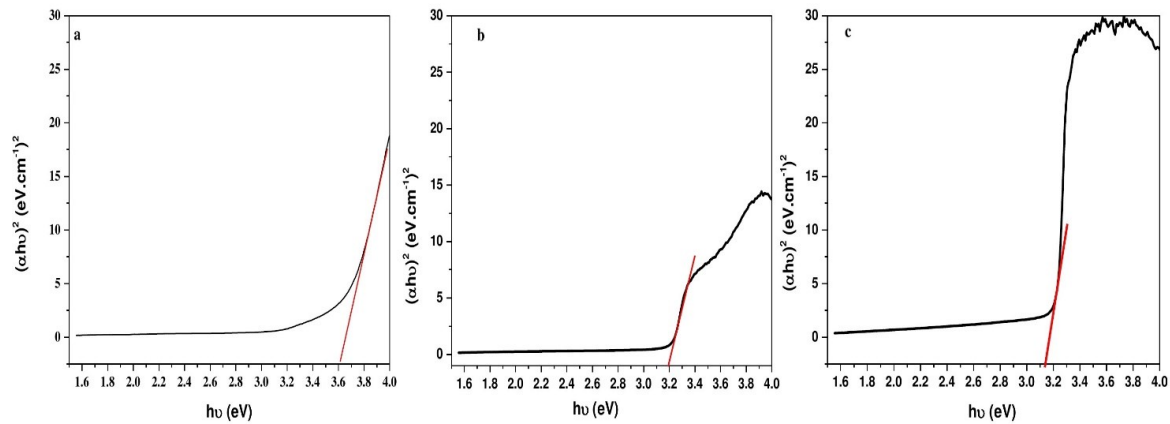


Figure 4. The plot of $(\alpha h\nu)^2$ versus photon energy ($h\nu$) of ZnO nanorods thin film with different seed solution concentration of (a) 0.005, (b) 0.025 and (c) 0.050 M.

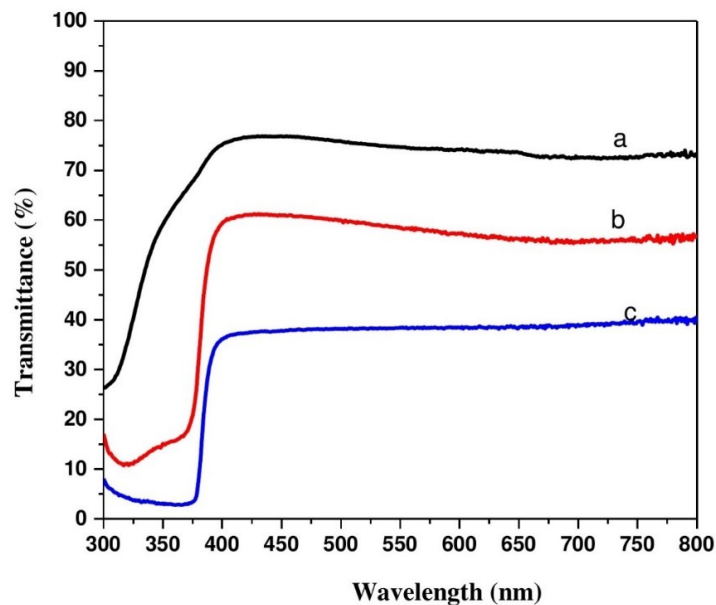


Figure 5. Optical transmittance spectra of ZnO nanorods thin film with different seed solution concentration of: (a) 0.005, (b) 0.025 and (c) 0.05 M.

4. Conclusion

The effect of seed solution concentration by CBD process on optical properties, morphological properties, and crystal structure of ZnO nanorods thin film have been studied in this work. The band gap energy from the thin film of ZnO nanorods decreased from 3.60 to 3.18 eV with increasing concentration of seed solution from 0.005 to 0.05 M. Meanwhile, the optical transmittance spectrum of ZnO nanorods was reduced to 40% as a result of bigger crystallite size causing more photon energy absorption. The average diameter of nanorods was found to increase from 161 to 427 nm as a consequence of crystallite growth within the nanorods.

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