



# Preparation and characterization of zinc oxide nano rods for solar cell applications

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## ABSTRACT

This study involves the preparation and characterization of hydrothermally grown zinc oxide (ZnO) nanorods. Zinc acetate dihydrate, ethanol and de-ionized water were used to prepare seed layer. Zinc nitrate and hexamethylenetetramine solution were used for growth of ZnO nanorods. The ZnO nanorods were grown for 5 hours at three different temperatures of 80°C, 90°C and 100°C and annealed at 500°C in air atmosphere. Nanorod growth temperatures are varied and the corresponding changes in structural, morphological, optical and photoluminescence properties were reported. The ZnO nanorods were investigated by XRD, SEM, UV and PL studies.

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## Introduction

ZnO is an important semiconductor with direct band-gap of 3.37 eV and high exciton binding energy of 60 meV [1, 2]. Thus, zinc oxide can be a promising candidate for novel applications such as UV detectors [1], field emission devices [2], high sensitivity gas sensors [3], biosensors [4], dye-sensitized solar cells [5], photoluminescent materials [6], photocatalytic degradation of pollutants [7] and antibacterial purposes [8]. One of the key properties of ZnO is that when it is exposed to light, photoexcited electron-hole pairs will be generated. Thus, the ZnO nanostructure with narrower band is usually preferred.

Obviously, the size of ZnO nanorods play important role in optimizing the optical properties of ZnO nanorod array films. In this paper, ZnO nanorod films were prepared by hydrothermal method at the low temperature of 90°C. Effect of the growth temperature of ZnO nanorod films structure and morphology properties were investigated by XRD and SEM. A dip coating method was applied to deposit ZnO films on the glass as a seed layers. The grown ZnO nanorods were studied in detail.

## Experimental

Seed layers were deposited on the glass substrates by dip coating method. All the reagents used in the experiment were analytically pure and used without further purification. Prior to deposition, the glass substrates were cleaned with de-ionized water, acetone, chromic acid solution, sodium hydroxide solution, 2-propanol, ultrasonic agitator and finally dried in a hot air oven at 70°C for 10 minutes. 0.1 mol of zinc acetate was dissolved into 10ml of ethanol, wherein white floccules immediately appeared as soon as they were mixed. Then 0.25ml of distilled water was introduced drop by drop through syringe. Under stirring, the solution was transferred into a clear and homogeneous solution. The above solution was stirred continuously for 2 hours at room temperature. The seed solution was deposited on well cleaned glass substrates for five times at regular intervals of one minute at 70°C temperature. The five

layer films were annealed in a muffle furnace at 200°C for 1 hour.

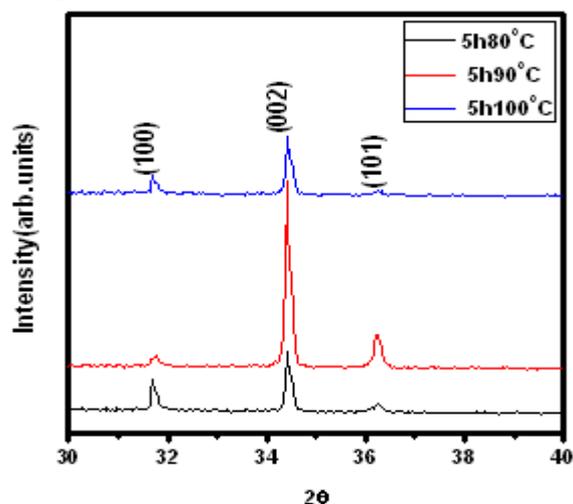
ZnO nano rods were grown on seed layer deposited glass substrates by hydrothermal method for 5 hours at 80°C, 90°C, and 100°C growth temperatures. Zinc nitrate hexa hydrate Zn (NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and hexamethylenetetramine (HMT) C<sub>6</sub>H<sub>12</sub>N<sub>4</sub>, were employed as precursors. The molar concentration of the precursors was taken in the ratio of 1:10 with 0.02 mol of zinc nitrate and 0.2 mol of HMT. The above solution was mixed through magnetic stirrer for 2 hours. In the growth process, the ZnO seed coated glass substrates were immersed in solution. The solution was heated with a hot air oven and maintained at different growth temperatures of 80°C, 90°C, and 100°C for 5 hours. At the end of the growth period, the substrates were removed from the solution and rinsed immediately with deionized water to remove the residuals from the surface and dried in air. Then the above films were annealed in muffle furnace at 500°C for 1 hour. The crystal structure and morphology of ZnO nano rods were investigated by X-ray diffraction (XRD) and Scanning Electron Microscope (SEM). The absorbance spectra have been recorded using a spectrophotometer JASCO V-570. The photoluminescence spectra of the prepared ZnO nanorods have been recorded using a HORIBA JOBIN YVON-Fluorolog at an excitation wavelength of 350 nm.

## Results And Discussion

Fig. 1 shows the XRD patterns of the product of the thin films with growth solution Zinc nitrate and Hexamethylenetetramine (HMT), with different growth temperatures of 80°C, 90°C and 100°C for 5 hours. All the diffraction peaks can be indexed within experimental error as hexagonal ZnO phase (Wurtzite-structure) which matches with the JCPDS card no: 036-1451.

The strong and narrow diffraction peaks indicate that the material has a good crystallinity. The XRD patterns of the films at growth temperature of 80°C and 100°C for 5 hours annealed

at 500°C shows that, it has a moderate (002) peak, weak (101) and (100) peak.



**Fig. 1: XRD pattern of ZnO thin films at 80°C, 90°C and 100°C for 5 hours.**

The XRD pattern growth temperature of 90°C for 5 hours annealed at 500°C has a very strong (002) peak and weak (100) and (101) peak. From the above XRD patterns it is clearly seen that, at the growth temperature of 90°C the diffraction peaks were oriented strongly along the (002) peak. This implies that the grown nanorods show perfect c-axis orientation which is in accordance with SEM images. The average size of the ZnO particle is calculated using Debye Scherer formula  $d_{avg} = 0.9\lambda / \beta \cos\theta$

where  $d_{avg}$  = average crystal size,  $\lambda$  = Wavelength of incident beam (1.5406Å),  $\beta$  = FWHM in radians and  $\theta$  = scattering angle in degree. The grain size of the nano particles are found to be 108.88nm, 109.709nm and 113.137nm for growth temperatures of 80°C, 90°C, and 100°C respectively. This implies that growth temperature influences the particle size.

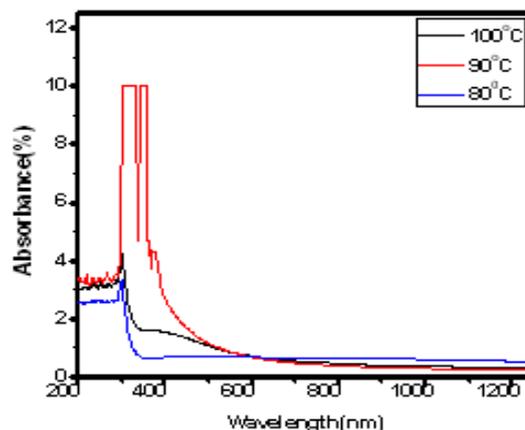
The SEM images of the products are given in Fig.2(a), Fig.2(b) and Fig.2(c). Many rod-like hexagonal structures can be clearly seen. The sizes of the products are homogeneous and the mean size is about 100 - 300 nm.



**Fig2(a) 5hour80°C Fig2(b) 5hour 90°C Fig2(c)5hour100°C**  
**Fig 2. SEM image of ZnO nanorods**

The images can be indexed as hexagonal Wurtzite-structural ZnO, which is very consistent with the analysis of XRD. As stated in the XRD patterns, the SEM images of the ZnO nano rods indicates that the length of the ZnO nano rods is maximum when the growth temperature is at 90°C. It indicates that the samples grown in same solution experienced different growth rate of nano rods at 80°C and 100°C. The growth rate is defined along with growing length per growth temperature. Fig.2a and Fig.2c shows SEM images of ZnO nanorods grown at 80°C and 100°C in which rods have grown in all directions in a flower like pattern, which reveals the XRD patterns, where all three peaks are moderately reflected. Fig.2b shows SEM image of ZnO nanorods grown at 90°C. These rods show hexagonal structure with increase in diameter and its length towards c-axis

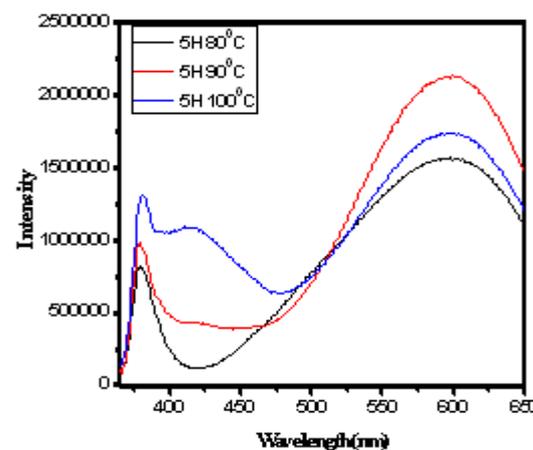
orientation. This result relates with the peaks as indicated in the XRD pattern.



**Fig.3 UV-Vis absorption spectra of ZnO at three different growth temperatures**

The optical absorption in the UV region and corresponding photo efficiency influences the use of ZnO nanorods for photo catalytic and solar cell activities [9]. Fig.3 shows the absorption spectra of ZnO nanorods. The optical absorption edge has a tendency to shift to an upper wavelength with increase in growth temperature. It is well identified that the optical absorption determines the optical band gap of ZnO films which has a direct band gap. The optical band gap of ZnO films at growth time of 5 hours for 80°C, 90°C and 100°C growth temperature was found to be 3.40 eV, 3.23 eV and 3.25 eV respectively. With the increase of growth temperature from 80°C to 90°C, the band gap decreases from 3.40 eV to 3.23 eV.

Considering the results, it is clearly indicated that as growth temperature increases the band gap decreases. The decrease in band gap of ZnO films may be attributed to the improvement in the crystalline quality of the films along with the reduction in porosity and increase in grain size.



**Fig.4. Room temperature Photoluminescence spectra obtained at three different growth temperatures**

The Room temperature Photoluminescence spectra of ZnO samples obtained with an excitation wavelength of 350nm for three different growth temperatures of 80°C, 90°C and 100°C is shown in the fig.4. The Ultraviolet (UV) emission peak in the range of 340-380 nm shows the PL spectra, with moderate intensity of peaks. The UV emission also called the near band edge emission (NBE) may originate from free excitonic emission in the ZnO materials as ZnO has a high exciton binding energy of 60meV at room temperature. Besides the medium UV emission peak, PL spectrum covers the surface related strong visible PL emission peaks which dominates all PL

spectra in the wavelength range of 550-650nm. The intensity of this broad visible PL emission is highly sensitive to the environment and mainly depends on the surface to volume ratio of the nano particles [10].

The obtained PL results of the samples indicate that the visible PL emission is enhanced while the UV emission is suppressed as growth temperature increases and particularly at 90°C, due to large competition from the defect emission and increase in both the oxygen vacancies and zinc interstitials [11].

#### Conclusion

ZnO nano rods had been successfully synthesized in a hydrothermal method at low growth temperature of 90°C for 5 hours and annealed at 500°C. The prepared ZnO nanorods were characterized by XRD, SEM, UV and PL. From the XRD results, it is clearly seen that, at the growth temperature of 90°C the diffraction peaks were oriented strongly along the (002) peak. The grain size of the nano particles are found to be increasing as growth temperature increases. SEM results clearly show that nanorods grown at 90°C have hexagonal structure with increase in diameter and length towards c-axis orientation when compared to 80°C and 100°C. The UV-Vis Absorption spectra show that band gap of the grown rods decreases from 3.40 eV to 3.23 eV as growth temperature increases. The PL spectrum shows two emission bands, near band edge emission in the UV region and high intensity broad emission in the visible region. From the results it is shown that the high quality ZnO nano rods can be grown using hydrothermal process and one can apply these high quality ZnO nano rods on the electrode of dye-sensitized solar cell to increase the contact area between ZnO and dye, follow-on in the enhancement of efficiency for dye-sensitized solar cell.

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