Structural, Optical & Surface Morphology of Zinc Oxide (ZnO) Nanorods in Molten Solution

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Abstract: ZnO (Zinc oxide) nanorods have been developed by using molten solution using the spin coating technique at low temperature. Zinc acetate dehydrate, Zinc nitrate hexahydrate and hexamethylenetetramine (HMT) were used as a base material. The ZnO seed layer was first deposited by spin coated of ethanol zinc acetate dehydrate [Zn(CH3COO)2.2H 2O] solution on a glass substrate (RI ~1.522). ZnO nanorods were grown on the ZnO seed layer from zinc nitrate hexahydrate and hexamethylenetetramine solution, and their diameters, lengths were controlled by precursor solution concentration and film developing time. Optical study was done with the help of UV-Vis-NIR V670JASCO spectrophotometer. Structural properties showed the highly oriented nature of ZnO nanorods. The FESEM (Field emission scanning electron microscope) was used to measure diameter of ZnO nanorods.

Key words: XRD (X-ray diffraction), zinc oxide, nanorods, FESEM (Field emission scanning electron microscope).

1. Introduction

ZnO is extensively used in the development of optoelectronic devices due to its versatile properties, such as a direct bad gap of 3.37 eV, a high exciton binding energy of 60 MeV, an optical grain of 300 cm$^{-1}$ and high mechanical and thermal stability. The controlled morphology, growth parameters and physical properties of these structures are being intensely discussed by many researchers. So many efforts have been made to control the morphology and methods to achieve better alignment and well-controlled morphology of ZnO nanostructures [1].

ZnO has been widely used in few applications such as in catalysis, solar cells, short-wavelength LED’s (Light-emitting devices), transparent conductors, chemical sensors, and piezoelectric nanomaterials [2]. The use of well-aligned ZnO nanorods in the development of a UV laser has strongly motivated researchers to study the alignment of ZnO nanostructures, such as nanorods, because the controlled morphology has a significant effect on the working performance of the nanoscale-based optoelectronics devices.

An XRD (X-ray diffraction) analysis has indicated the orientation of the nanorods perpendicular to the substrate by exhibiting only the characteristic diffraction peaks for the patterned arrays of the ZnO nanorods [3]. In this work ZnO nanorods have been produced by using the solution, zinc acetate dehydrate in ethanol as a seed layer. The growth of ZnO nanorods, diameter and length are controlled by changing the solution concentration and immersion time in equimolar of zinc nitrate hexahydrate and hexamethylenetetramine (HMTA) in deionized water at a 90 ºC and their morphologies, preferential orientation and optical properties were examined [4].

2. Results and Discussion

2.1. Optical Properties of ZnO Nanorods

Fig. 1 shows the optical transmittance spectrum of nanocrystalline ZnO nanorods at 90 ºC for precursor concentration 35 mm from immersion time 180 minutes annealed at 450 ºC for 30 minutes using UV-Visible region from 200 nm to 800 nm. The transmittance is over 80% in the visible region from 400 nm to 800 nm for all the samples. Sharp absorption
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Fig. 1 The transmittance spectrum of ZnO nanorods at 90 °C for precursor concentration 35 mm from immersion time 180 min.

Fig. 2 Plot of $(\alpha h\nu)^2$ vs photon energy $h\nu$ of ZnO nanorods.

edge is located at 380 nm which is due to the fact that the ZnO is a direct band gap semiconductor [5]. The corresponding optical band gap of ZnO thin film is estimated by extrapolation of the linear relationship between $(\alpha h\nu)^2$ and $h\nu$ according to Eq. (1):

$$\alpha h\nu = \frac{A(h\nu - E_g)}{2} \quad (1)$$

where, $\alpha$ is the absorption coefficient, $h\nu$ is the photon energy, $E_g$ is the optical band gap and $A$ is a constant.

Fig. 2 depicts the plot of $(\alpha h\nu)^2$ versus photon energy $h\nu$. The value of the direct optical band gap $E_g$ is calculated from the intercept of $(\alpha h\nu)^2$ vs $h\nu$ curve had also been plotted. The presence of a single slop in
the plot suggests that the ZnO nanorod has direct and allowed transition [6]. The band gap value of ZnO nanorod is found to be 3.3 eV which is slightly smaller to bulk ZnO (3.37 eV).

This difference is due to the fact the values of band gap $E_g$ depend on many factors, e.g. the granular structure, the nature and concentration of precursors, the structural defects and the crystal structure of the films. Moreover, departures from stoichiometry form lattice defects and impurity stats. It has been reported that the band gap difference between the thin film and crystal is due to the grain boundaries and the imperfection of the polycrystalline thin films. It was reported that this band gap difference between the film and bulk ZnO is due to the grain boundary, the stress and the interaction potentials between defects and host materials in the films.

### 2.2. Structural Analysis of ZnO Nanorods

Fig. 3 depicts the XRD pattern of the crystal structure and orientation of the nanocrystalline ZnO nanorods deposited on glass substrate using spin coating at 2,000 rpm, pre-heated at 150 °C and annealed in air at 450 °C. From the XRD pattern, one can clearly observe a diffraction peak at $2\theta = 34.426°$. Strong preferential growth is observed along $c$-axis, i.e. (002), suggesting that the prepared ZnO nanorods have the wurtizite structure.

The unit cell “$a$” and “$c$” of the crystalline ZnO nanorods with (002) orientation is calculated using the relation Eqs. (2) and (3):

\[ a = \frac{1}{3\sin \theta} \]  \hspace{1cm} (2)

\[ c = \lambda \cdot \sin \theta \]  \hspace{1cm} (3)

The values obtained for the unit cell $a = 3.007 \, \text{Å}$ and $c = 5.21 \, \text{Å}$ are calculated.

From the XRD spectrum, grain size ($D$) of the film is calculated using debay scherrer formula.

\[ D = \frac{k\lambda}{\beta \cos \theta} \]  \hspace{1cm} (4)

where, $k$ is a constant to be taken 0.49, $\lambda$ is the XRD wave length ($\lambda = 1.5406 \, \text{Å}$), $\beta$ is the FWHM (Full width at half maximum) and $\theta$ is the Bragg angle. By inserting the different values from Table 2 in the Scherrer formula grain size of (002) oriented thin film is 44.12 nm which is same as reported in literature.

The dislocation density ($\delta$), which represents the amount of defects in the crystal, is estimated from the following equation:

\[ \delta = \frac{1}{D^2} \]  \hspace{1cm} (5)

Fig. 3  X-Ray diffraction of the ZnO nanorods grown at 90 °C for 180 min from the 35 mM precursor concentration.
Fig. 4 Surface FESEM images and diameter of hexagonal ZnO nanorods grown at 90 °C various concentrations (a) 15, (b) 20, (c) 25, (d) 30 and (e) 35 mM precursor concentration for 180 min.

Fig. 5 Surface FESEM images and length of hexagonal ZnO nanorods grown at 90 °C for immersion time (a) 60, (b) 90, (c) 120, (d) 150 and (e) 180 min from precursor concentration 35 mm.
The strain ($\varepsilon$) of the thin film is determined from the following formula:

$$\varepsilon = \frac{\beta \cdot \cos \theta}{4}$$  \hspace{1cm} (6)

3.3. Morphological Analysis of ZnO Nanorods

In Fig. 4, the FESEM shows the average diameter ($d$) of the ZnO nanorods increases from (57, 64, 83, 120 and 230 nm) as the precursor concentration increase from 15, 20, 25, 30 and 35 mM, respectively, where the immersion time is fixed for 180 min at 90 °C. The length of the grown ZnO nanorods is about 1 μm regardless of concentration, which indicates that changes in the precursor concentration at the fixed immersion time can affect only the diameter of the hexagonal ZnO nanorods. The rate of increase diameter of the ZnO nanorods is estimated to be approximately 34.4 nm/mM. The length of ZnO nanorods can also be varied when the immersion time changes in the fixed concentration.

Fig. 5 shows that the average length of the ZnO nanorods increases from (241, 459, 522, 820 nm and 1.2 μm) as the immersion time $t$ increases from 60, 90, 120, 150 and 180 min, respectively, at the precursor concentration of 35 mM. The length of ZnO nanorods indicates that growth rate is 6.3 nm/min.

3. Conclusions

In this work, we have grown ZnO nanorods on glass substrates by solution processing hydrothermal method in low temperature using the spin coating technique. The structural, morphological and optical properties were investigated. The hydrothermal method is a relatively simple technique: there are many factors which affected the quality of the film. We have optimized different parameters to obtain a good crystalline structure of ZnO nanorods with intense and sharp peak. The optical transmittance is over 80% in the wave length range from 400-800 nm and the band energy band gap is found to be 3.300 eV. According to XRD results, the as deposited films exhibited a hexagonal wurtized structure with (002) preferential orientation after annealing at 400 °C in air ambiance for 30 min. The XRD pattern consists of a single (002) peak which occurred due to ZnO crystals and grows along the $c$-axis. The grain size estimated to be 44.46 nm. The average diameter and average length of the ZnO nanorods obtained from the FESEM. The average diameter of ZnO nanorods, which are increasing from (57, 64, 83, 120 and 230 nm) as the precursor concentration increases at 90 °C for immersion time 180 min, and the average length of ZnO nanorods increases from (241, 459, 522, 820 nm and 1.2 μm) when the immersion time was increased at 90 °C for precursor concentration 35 mM. The EDX analyses of the samples clearly show that the sample prepared by above route has pure ZnO nanorod phases.

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