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STRUCTURAL, OPTICAL AND ELECTRICAL PROPERTIES OF ZnO NANOROD ARRAY PREPARED BY HYDROTHERMAL PROCESS

NANDA SHAKTI*, SUNITA KUMARI, P.S. GUPTA
Department of Applied Physics, Indian School of Mines, Dhanbad – 826004, Jharkhand, India

ZnO nanorods were synthesized on sol-gel prepared ZnO seed layer over p-Si substrate. The X-ray diffraction (XRD) of nanorods showed c - axis orientation perpendicular to the substrate. The Field emission scanning electron microscopy (FESEM) of the surface of the ZnO film showed vertical ZnO nanorods with hexagonal crossection. The diameter of the nanorods was of the order of 200 nm. The optical reflectance of the nanorod showed an absorption edge at the band gap of ZnO. The photoluminescence of nanorods showed UV emission at room temperature. The intensity of emission showed dependence on nanorod diameter. The current-voltage characteristics of ZnO nanorod films showed rectifying behaviour.

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1. Introduction

ZnO is a semiconducting material having direct wide band gap of 3.37 eV and high excitonic binding energy of 60 meV at room temperature. These features make it a promising material for transparant electronics, solar cells and other optoelectronic devices [1-3]. Growth of ZnO nanostructures such as one-dimensional rods, wires, tubes etc., has received increasing attention for its specific properties and for the fabrication of nanoscale devices. Many different techniques were employed for the growth of nanostructures; these include vapour-liquid-solid (VLS) epitaxy [4], chemical vapour deposition (CVD) [5], pulse laser deposition (PLD) [6], thermal decomposition [7], hydrothermal synthesis [8], etc. The hydrothermal method is a simple and cost effective process for the growth of ZnO nanorods. It has low growth temperature below 100ºC, catalyst free process and is suited for the uniform growth of ZnO nanorods over large area of the substrates. The structural and optical properties of the nanorods prepared by hydrothermal process shows strong dependence on conditions such as seed layer crystallinity, choice and concentration of surfactant used and reaction time for growth. Ma *et al.* [9] had reported the effect of annealing substrates on the density of ZnO nanorod array. Wu et *al.* [10] had studied the effect of addition of NaOH on the diameter of ZnO nanorods grown by hydrothermal method. Liu *et al.*[11] had synthesized ZnO nanorods on sputtered ZnO seed layer.

In this work we have synthesized ZnO nanorods on sol-gel prepared ZnO seed layer [1] over p-Si substrate. The structural properties of the nanorods were studied by X-ray diffraction (XRD). The nanorods showed c- axis orientation perpendicular to the substrate. The surface morphology of the nanowires was studied by Scanning electron microscopy (SEM) and Field emission scanning electron microscopy (FESEM). The surface of the ZnO film showed vertical ZnO nanorods with hexagonal crossection. The diameter of the nanorods was of the order of 200 nm. The optical properties of the samples were studied by UV-Vis spectrophotometer and spectroflurophotomer. The reflectance of the nanorod showed an absorption edge at the band gap of ZnO. The photoluminescence of nanorods showed UV emission at room temperature. The

* Corresponding author: nash_cbsa@yahoo.co.in

intensity of emission showed dependence on nanorod diameter.The current-voltage characteristics of ZnO nanorod films showed rectifying behaviour.

2. Experimental

The ZnO thin films were deposited on the Si substrate by a sol-gel method [12] which served as the seed layers for the growth of nanorods. For sol preparation, 1gm of zinc acetate dihydrate [Zn $(CH_3COO)_2.2H_2O$] was dissolved in 10 ml of boiling isopropanol at 84ºC on the magnetic stirrer. The solution became milky white. The turbid solution was cleared by adding 5-6 drops of diethanolamine (DEA). The resulting solution was aged for 2hrs to make a homogeneous stable colloidal solution.

For the film preparation, a p-type Si wafer was mounted on the spin coater (SCU 2005 Apex Inst.Co.). With a 5ml dropper, 6-7 drops of the sol was coated on the wafer while it was spinning at the rate of 3000 rpm for 20sec. The wet film was dried at 100ºC for 10 min and subsequently annealed at two different annealing temperatures of 400 ºC and 600 ºC for 1 hr. This process was repeated 8 times to form multilayer ZnO films.

ZnO nanorods were grown by hydrothermal method. The aqueous solution was prepared by dissolving 50mM zinc nitrate hexahydrate $[Zn(NO_3)_2.6H_2O]$ and 50mM hexamethylenetetramine (HMTA) $[C_6H_{12}N_4]$ in a beaker covered with a Petri dish. The molar ratio was 1:1. The solution was preheated to a constant temperature of 75ºC in a water bath. For the growth of ZnO nanorods samples were immersed at the bottom of the beaker by keeping film side up at a constant temperature of 75ºC for 4hrs and was stirred mechanically. The substrates were then rinsed with deionised water for several times and were dried at 60ºC for 1 hr to remove any residual salts and organic materials.

The structural properties of ZnO nanorods films were studied by X-ray diffraction (XRD) (Panalytical Xpert pro) using Cu K_α radiation $\lambda = 1.54060$ Å. The surface morphology of the ZnO nanorods was observed by Scanning electron microscopy (SEM) (JSM-6390 PC-SEM, JEOL/EO) and Field emission scanning electron microscopy (FESEM) (JEOL). The reflectance spectrum of the ZnO nanorod was measured using UV – Vis spectrophotometer (HR 4000 Ocean Optics). The Photoluminescence properties were studied by using Fluorescence spectrophotometer (Hitachi). The electrical properties of the films were measured using 2400 Keithley Source meter.

3. Results and discussion

3.1 Structural properties

From figure 1 we observe that the peak position in the XRD spectrum of nanorods corresponds to the hexagonal wurtzite ZnO with lattice constants a = 0.325 nm and c = 0.521 nm as given in JCPDS card no. 75-0956.

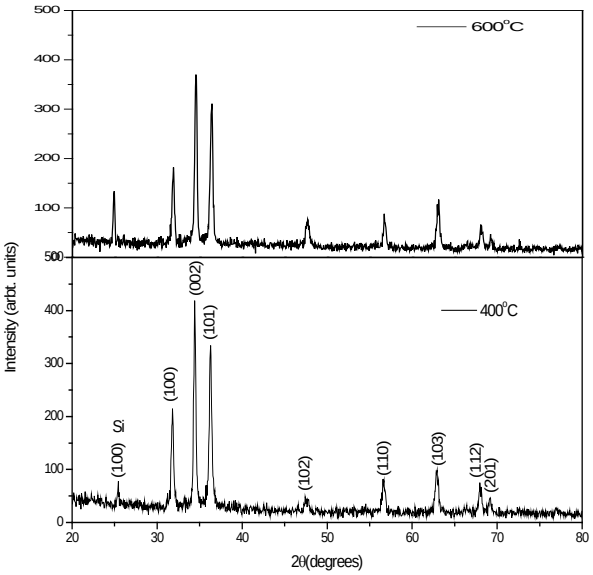

Fig1. XRD of ZnO nanorod films annealed at 400ºC and 600ºC.

The ZnO nanorod samples annealed at 400ºC and 600ºC are polycrystalline with preferred orientation along c-axis perpendicular to the substrate surface. The degree of c-axis orientation is defined by expression

$$P = \frac{I(002)}{\Sigma I(hkl)}$$

Where P is the degree of crystal orientation along the (002) direction, *I* (002) is the intensity of the (002) diffraction peak and *I* (hkl) is the intensity of all diffraction peaks. Using this expression the degree of crystal orientation along different diffraction planes is calculated and plotted in figures 2(a) and 2(b) which shows that the nanorods have preferential growth along c- axis for both the annealing temperatures.

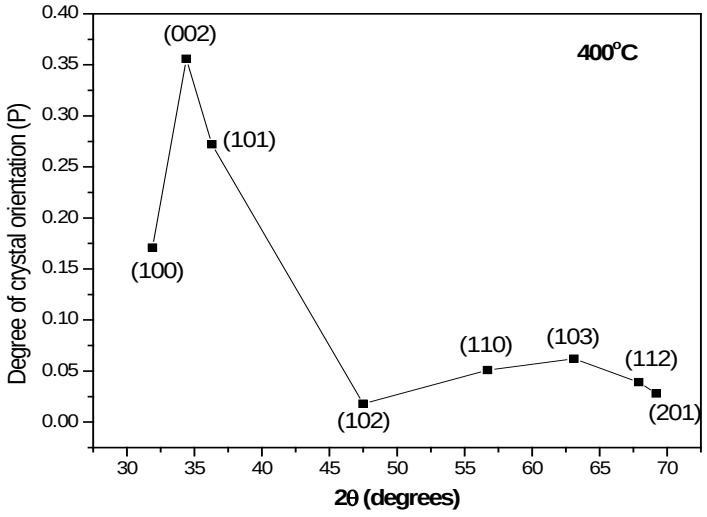

Fig 2(a). Degree of crystal orientation of various planes of ZnO nanorod film annealed at 400ºC

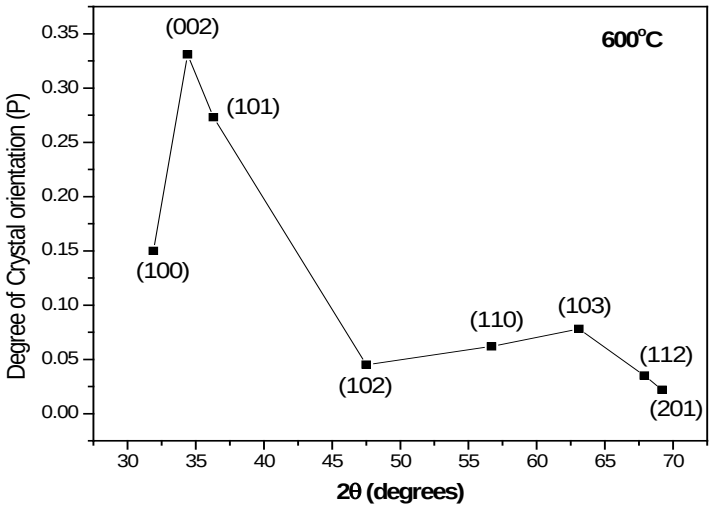

Fig 2(b). Degree of crystal orientation of various planes of ZnO nanorod film annealed at 600ºC.

Figures 3a, 3b show the FESEM micrographs (top view) of ZnO nanorods by hydrothermal process at annealing temperatures 400ºC.

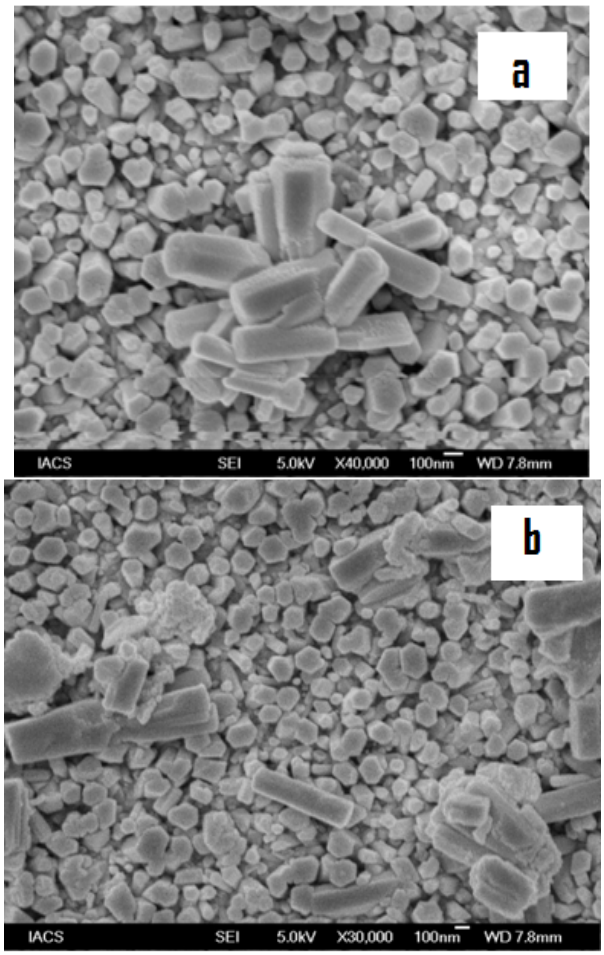

Fig 3(a, b). FESEM image of ZnO nanorod film annealed at 400ºC.

It is observed that the nanorods are uniformly distributed over the ZnO film. The average diameter of the nanorods ~ 200 nm having hexagonal crossection. Figure 3c shows the edge view of the ZnO nanorod arrays over film annealed at 400ºC.

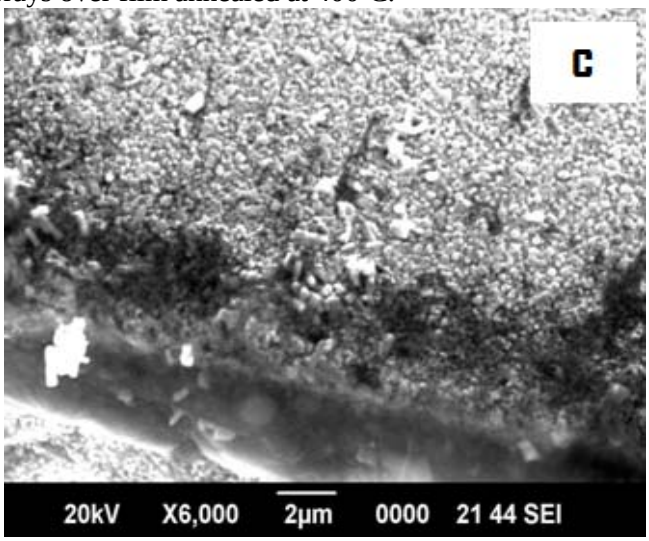

Fig 3(c). SEM image of ZnO nanorod film annealed at 400ºC (edge view).

The average length of the nanorods is ~ 1 µm. Figure 4a, 4b shows the top view of the nanorod arrays at annealing temperature 600ºC.

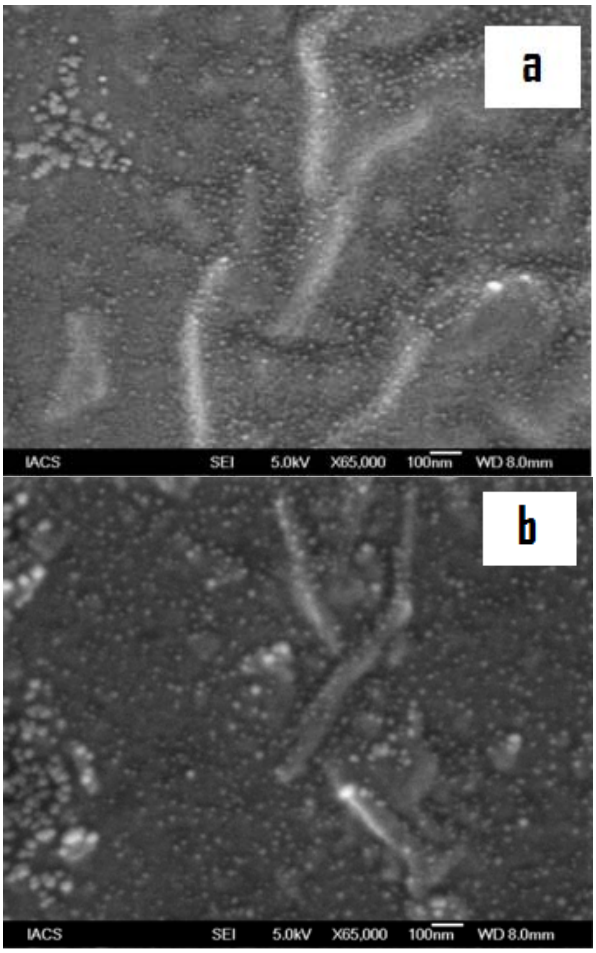

Fig 4(a,b). FESEM image of ZnO nanorod film annealed at 600ºC.

The micrograph shows that nanorods are smaller in diameter (about 20 nm) than samples annealed at 400ºC. This may be due to the inversion of the substrate during stirring in the solution phase reaction.

3.2 Optical properties

Fig. 5 is the reflectance of the ZnO nanorod film annealed at 400ºC and 600ºC.

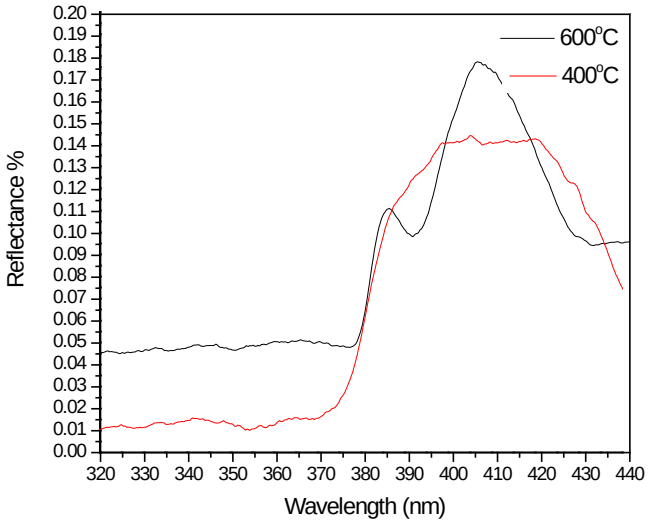

Fig 5. Reflectance of ZnO nanorod films annealed at 400ºC and 600ºC

We find that the reflectance of the ZnO nanorod film annealed at 600ºC is greater in the wavelength range 320-386 nm as compared to film annealed at 400ºC.The nanorod film annealed at 600ºC shows absorption edge at 376.9 nm while the film annealed at 400ºC shows absorption edge at 376.4 nm.
Using the relation,

$$\text{hv}\ (eV) = \frac{1.24}{\lambda(\mu m)}$$

The Optical band gap of the ZnO nanorod films annealed at 400ºC and 600ºC was found to be 3.294eV and 3.289 eV respectively.

The Photoluminescence properties of the ZnO nanorod films annealed at 400ºC and 600ºC were studied using Fluorescence spectrophotometer.The PL spectrum in figure 6 indicates that the films annealed at 400ºC and 600 ºC show strong UV emission at 386.4 nm and 388.3 nm respectively.

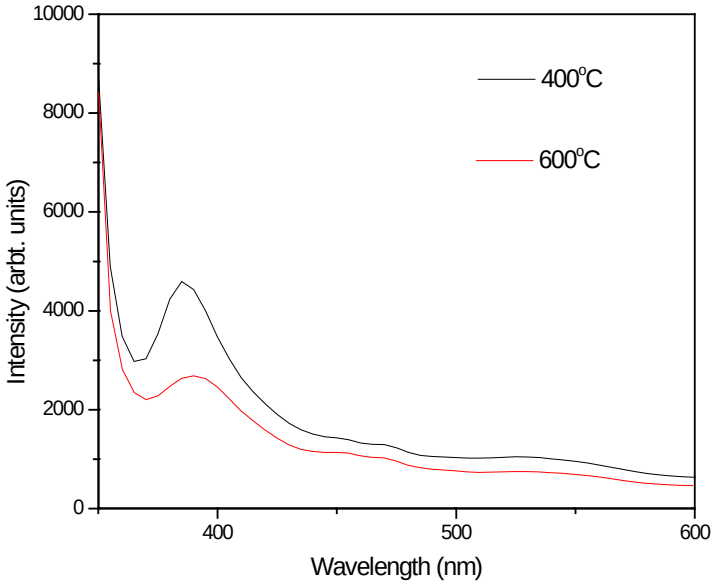

Fig 6. Room temperature photoluminescence spectrum of ZnO nanorod films annealed at 400ºC and 600ºC.

The origin of UV emission in ZnO is due to the recombination of electron–hole pair in free excitons .The UV emission peak intensity decreases for film annealed at 600ºC. This may be due to decrease in density of excitons as a result of thermal ionization and formation of free electron and free hole which in turn decreases the intensity of UV emission.

Fig. 6 also shows a weak blue-green emission band (~ 475-525 nm) for nanorod films annealed at 400ºC and 600ºC.This blue-green emission in ZnO may be due to defect related emission (O or Zn vacancy).For film annealed at 600ºC the weak blue-green emission is relatively less intense than for film annealed at 400ºC, this is attributed to the increase in crystallinity of the film with increase in annealing temperature, which in turn leads to the decrease in the concentration of structural defects in the crystal, thereby decreasing the defect related emission.

As, ZnO films are prepared at the atmospheric pressure, the oxygen vacancies density in these films are very low and hence we observe almost negligible green band in the PL spectrum as shown in figure 6.

3.3 Electrical properties

Figure 7 shows the current-voltage characteristics of ZnO nanorod films annealed at 400 ºC and 600 ºC.

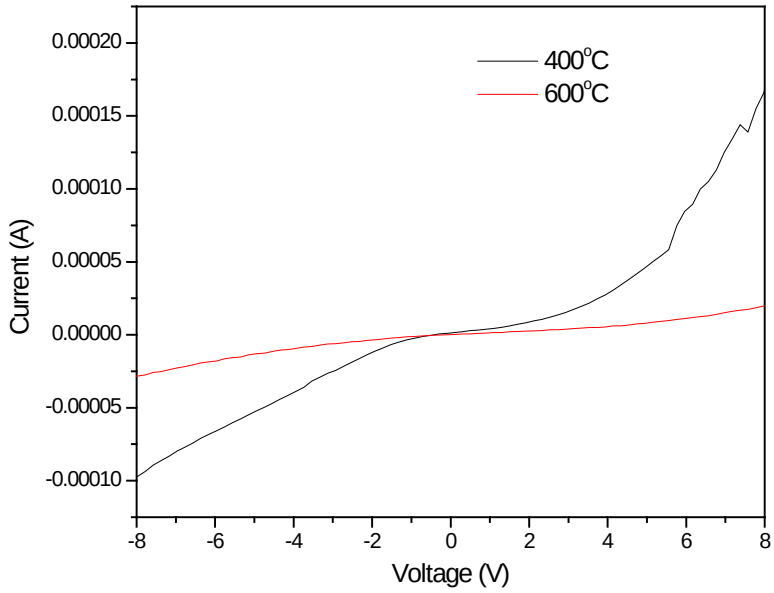

Fig 7. Current-Voltage Characteristics of ZnO nanorod films annealed at 400ºC and 600ºC.

From figure we observe that ZnO nanorod film annealed at 400 ºC shows more rectifying behaviour than that annealed at 600 ºC. The rectifying behaviour may arise due to the contact resistance developed at the interface of the nanorod film and silver paste that was used to make electric contact to the film. The more rectifying behaviour of film annealed at 400 ºC is due to large quantity of nanorods growth at its surface compared to that annealed at 600 ºC as seen in FESEM image.

4. Conclusions

ZnO nanorods were grown on sol-gel prepared ZnO seed layer over [1] p type -Si substrate by hydrothermal process. The structural properties of the nanorods were studied by X-ray diffraction (XRD). The nanorods showed c- axis orientation perpendicular to the substrate. The surface morphology of the nanorods was studied by Scanning electron microscopy (SEM) and Field emission microscopy (FESEM). The surface of the ZnO film showed vertical ZnO nanorods arrays with hexagonal crossection. The diameter of the nanorods was of the order of 200 nm. The optical properties of the samples were studied by UV-Vis spectrophotometer and fluorescence spectrophotometer. The reflectance of the nanorod showed a absorption edge at the band gap of ZnO. The photoluminescence of nanorods showed UV emission at room temperature. The intensity of emission showed dependence on nanorod diameter. The current-voltage characteristics of ZnO nanorod films annealed at 400 ºC and 600 ºC showed rectifying behaviour. Further we propose to extend the study to intermediate temperature range so that optimum growth conditions can be found which can be used in its device applications such as in solar cells and UV emitting devices.

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