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Optical and Structural Properties of Zinc Oxide Nanowires Fabricated by Hydrothermal Method

Kanchana Shahi¹, R S Singh², Ajay Kumar Singh³

¹ Department of Physics, Bhilai Mahila Mahavidyalaya, Bhilai Nagar

² Department of Physics, Govt Danveer Tularam College, Utai

³ Department of Chemistry, Govt. V Y T P G Autonomus College, Durg

Abstract: Nanocrystalline film of Zinc Oxide (ZnO) nanowires were prepared on glass substrate at a low temperature using a low cost, simple hydrothermal method. We used different concentration of ZnO nanowires precursor solution and studied the effect on its structural, morphological and optical properties. The morphology and structural properties of the ZnO nanowires were studied using scanning electron microscopy (SEM), and x-ray diffraction (XRD) respectively. Scanning electron microscopy (SEM) and X-ray diffraction (XRD) results confirm that the nanorods were single crystals with the wurtzite structure. Optical transmittance (UV-Vis) and photoluminescence (PL) properties of ZnO nanorods have been characterized at room temperature.

Index Terms: Zinc Oxide, Nanowires, sol-gel, Hydrothermal Photoluminescence.

I. INTRODUCTION

Zinc oxide (ZnO) is a wide direct band gap (3.37 eV), n-type semiconductor, has a large exciton binding energy (60 meV) and a chemically stable material [1]. Because of its unique properties, it is suitable for several practical optoelectronic device applications such as photo detectors, light emitting diodes, UV light emitters, solar cells [2-7]. Many different techniques used for ZnO nanostructure growth include molecular beam epitaxy (MBE), chemical vapour deposition (CVD), Vapour-liquid-solid (VLS), RF sputtering, and pulsed laser deposition (PLD) [8-14] etc. The preparation of ZnO nanostructure via CVD, MBE and sputtering are expensive techniques, while PLD has limitations in scaling up. In order to fabricate the low cost device, it is necessary to prepare high quality ZnO nanostructure via a relatively low cost route for various device applications. Amongst the different ZnO nanostructures synthesis methods, the hydrothermal method is simple and low cost, and also environment friendly. In this paper, we report on the fabrication of ZnO nanowires using two different solution concentration and investigate their optical properties. PL and optical transmittance are demonstrated here.

II. EXPERIMENTAL

ZnO nanowires were prepared by wet chemistry method in two steps. In first step the ZnO seed layer deposited on glass substrate using sol-gel spin coating method and after that the ZnO nanowires grown on this seed layer by hydrothermal method. Prior to seed layer deposition, the glass substrate cleaned with detergent, double distilled water, ethanol, methanol sequentially. To prepare seed layer solution 0.01 M Zinc acetate dehydrate [$\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$] and 0.03M sodium hydroxide [NaOH] were dissolved in methanol [CH_3OH] stirred at 60 °C for 2h. Many layers were deposited on each substrate by spin coating method at the rate of 2500 rpm for 30 s. All the films were drying after each spin coating process at 110 °C for 10 minutes in the oven. After the seed layers deposition, the coated substrates were calcinated at 150°C for 1h. The seed layer coated substrate was immersed in the solution prepared by equimolar hexamethylenetetramine (HMT) [$(\text{CH}_2)_6\text{N}_4$] and zinc nitrate hexahydrate [$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$] with different concentration of 10mM and 20mM. Both samples kept in oven at 80 °C for 5 hours. After growth, the nanorods samples were dried at room temperature.

III. RESULT AND DISCUSSION

The SEM, XRD characterizations done for studying structural and morphology respectively. To study the optical properties UV visible and PL studies were done

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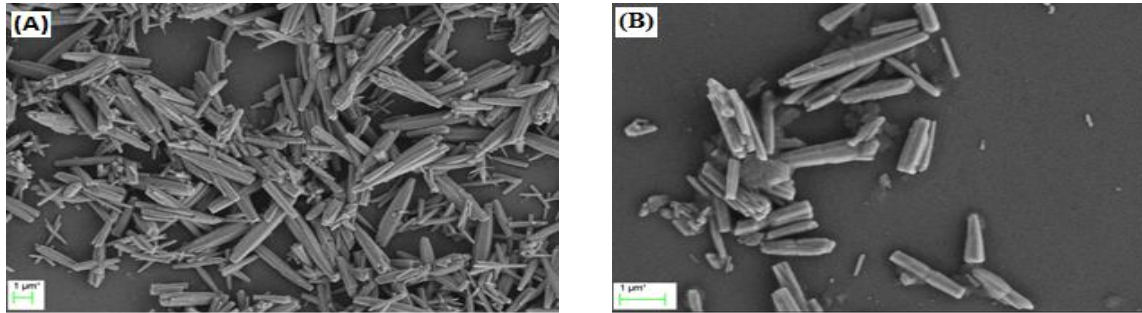


Fig.1 (A) ZnO nanowires on Glass substrate (Precursor concentration 10 mM) (b) ZnO nanowires on Glass substrate (Precursor concentration 20 mM)

The SEM images (Figure 1) show the morphology of ZnO nanowires grown on the Glass substrate with two different precursors concentration. The SEM images of both samples show hexagonal nanowires while nanorods density is low for precursor concentration 20 mM. The diameter of the ZnO NWs ranged from 110 nm to 129 nm, and the length ranged from 1 μm to 3 μm for sample- A. For sample – B the diameter and length ranged from 155 nm and diameter range from 504 nm to 962 nm respectively. SEM images show hexagonal structure of the ZnO nanowires. The ZnO nanorods diameter can be increased with increasing the concentration of precursor solution.

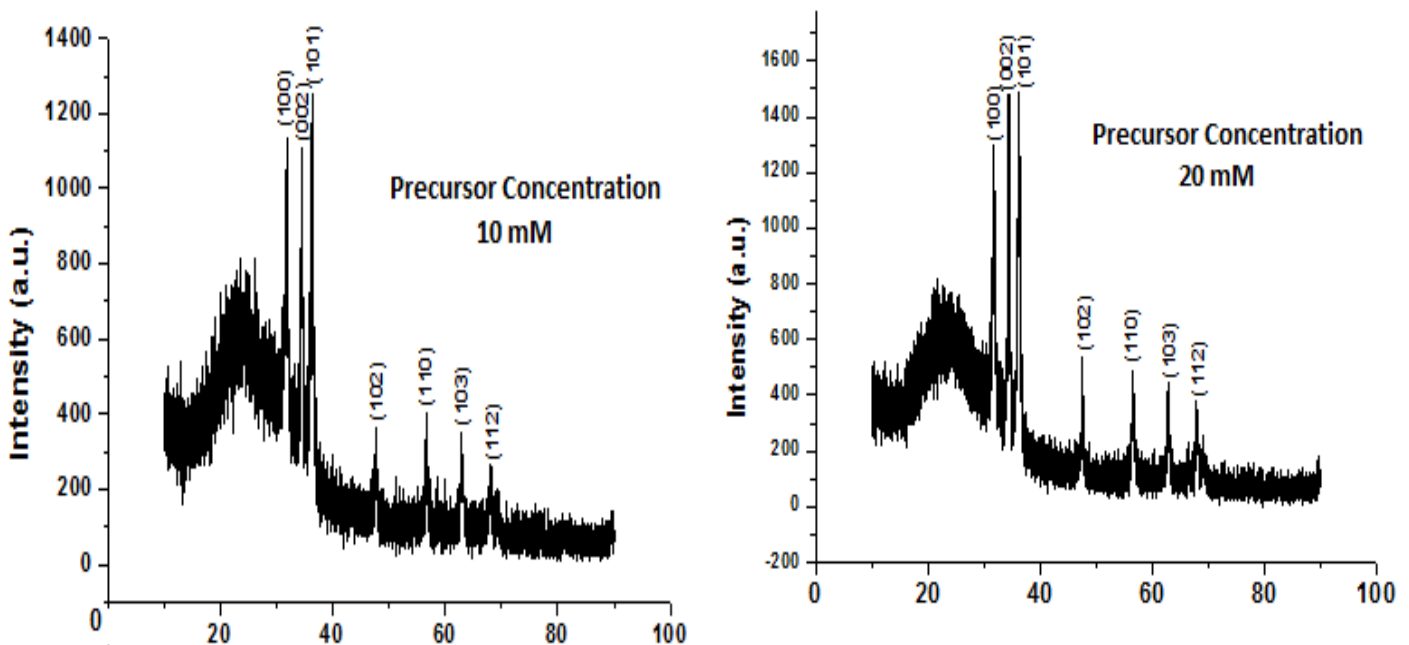


Fig 2. X-ray diffraction patterns of ZnO-NWs with different precursor concentration of nanowire solution (10 mM and 20 mM).

Figure 2. shows X-ray diffraction patterns of the hydrothermal growth of ZnO-NWs on seed layer coated glass substrates with different precursor concentration of nanowire solution (10 mM and 20 mM). All of the observed peaks indicated that ZnO NWs were successfully grown on two samples and indexed to the hexagonal phase with a wurtzite structure of ZnO in accordance with JCPDS 36-1451. It is noted that both the samples have good crystallinities with preferred orientations along the (100), (002) and (101) direction. The intensities of this diffraction peak increased as the precursor concentration of zno nanowires solution increased. This result indicates that the crystallinity of nanowires increases when the precursor concentration increases. The lattice parameters of ZnO nanowires calculated from XRD data are in good agreement with JCPDS card No 36-1451. The calculated lattice parameters are listed in Table 1.

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Data	2 Θ	(hkl)	d_{hkl} (Å)	Structure	Lattice Parameter (Å)
Prepared Sample - I	31.64 34.45	(100) (002)	2.826 2.606	Hexagonal	a = 3.264 c = 5.212 a/c = 1.5968
Prepared Sample - II	31.76 34.42	(100) (002)	2.769 2.563	Hexagonal	a = 3.239 c = 5.205 a/c = 1.607
JCPDS (36-1451)	31.770 34.422	(100) (002)	2.814 2.603	Hexagonal	a = 3.250 c = 5.207 a/c = 1.6021

Table 1. lattice parameters of ZnO nanowires calculated from XRD data

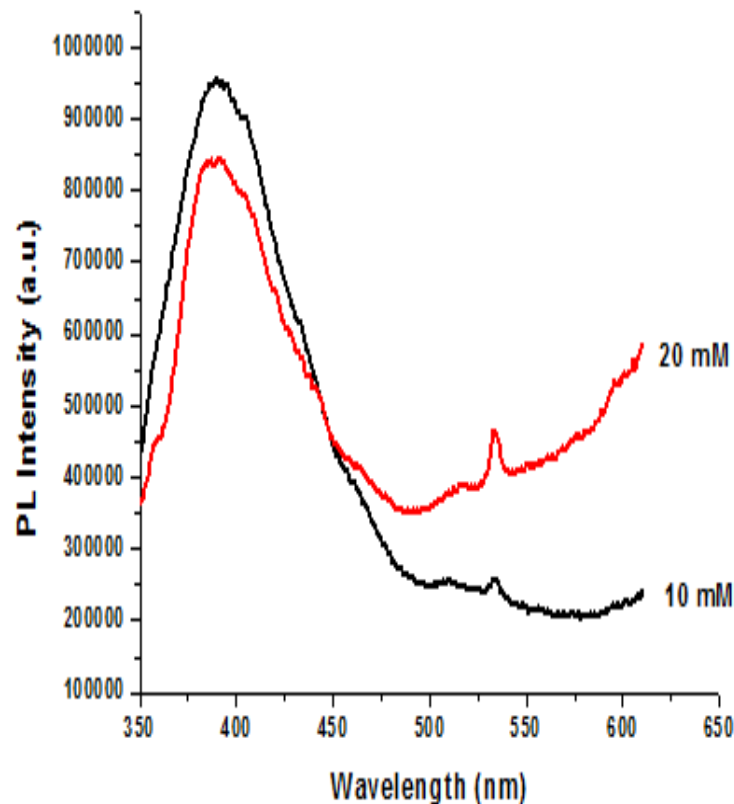


Fig. 3 Photoluminescence of ZnO nanowires prepared with 10 mM and 20 mM precursor concentration

Fig. 3 shows Photoluminescence spectra at room temperature. Graph reveals emission peaks in the ultraviolet region, namely at wavelength of 391.40 nm and one weak emission peak at 535.20 nm in the green yellow region for 10nm precursor concentration . The samples prepared with 20m M precursor concentration has reduced peak intensity in UV region, but high peak intensity in green yellow region. The ultraviolet emission shows by samples is usually due to emission from band-to-band transitions while the visible green yellow emission is related to deep level defects as oxygen and zinc vacancies and interstitials. . This PL spectra shows that ZnO nanorods grown with 10mM precursors concentration have the highest UV emission as compared to 20 mM precursor concentration.

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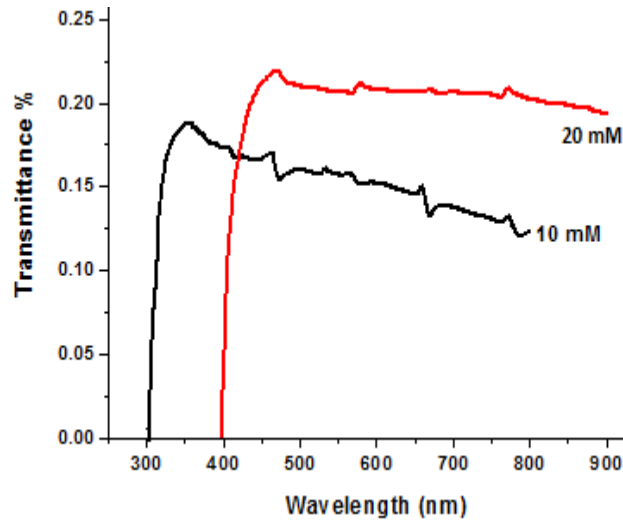


Fig. 4 UV visible transmittance spectra of ZnO nanowires prepared with 10 mM and 20 mM precursor concentration.

The change in precursor concentration shows shifting in range of transmittance. For 10 mM the transmittance range was 300 nm to 800nm, and for 20 mM the range was from 400 nm to 900 nm

IV. CONCLUSION

Hexagonal ZnO nanowires were synthesized on the seed layer coated glass substrates via low cost hydrothermal process where seed layers were deposited by sol-gel with spin coating method. The structural and optical properties of ZnO nanowires were studied with change in the precursor concentration. Both concentration shows hexagonal structure in SEM and both samples have very close crystalline structure with JCPDS 36-1451.

The sample which prepared with the 10mM precursor concentration shows the optical properties that are rather different from the other samples prepared with 20mM precursor concentrations. ZnO nanowires prepared using 20 mM precursor are found to grow with larger diameter as compared with 10 mM concentration but XRD pattern reveals that both samples have same crystallinity and their parameters are much close to JCPDS card 36-1451.

The transmittance spectra shows that the increase in precursor concentration results in the increase of optical transmittance. The Photoluminescence spectra shows increase in precursor concentration decrease in UV intensity while increase the visible green yellow, however there was no change in band gap with change in precursor concentration. This study will provide approaches to change the optical properties which can be used for optoelectronic applications

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