



Effect of solvent on structural, morphological and optical properties of undoped ZnO nanorods

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ABSTRACT

In this work, ZnO nanorods were achieved by a simple chemical precipitation method in the presence of pure solvent of deionised water at room temperature. X-Ray Diffraction result indicates that ZnO nano rods have wurtzite hexagonal structure without any impurities. It has been seen that the growth orientation of the prepared ZnO nanorods were [101]. Here, we also compared the *d*-spacing and relative peak intensities from their standard values with different angles. The SEM image confirmed the size and shape of these nanorods. It has also been found that at room temperature ultra violet (UV-Vis) absorption band is around 364 nm (blue shifted as compared to bulk). Finally, the band gap is calculated using UV-absorption peak.

Keywords: UV-absorption peak, exciton binding energy, interplaner spacing, ZnO micro rods, relative peak intensities, optoelectronic

INTRODUCTION

One dimensional nanostructure materials like nanorods, nanowires, nanotubes have received more attention in recent years because of their remarkable properties. These properties are very useful in all fields like optoelectronics, electronic nanodevices etc. [1,2]. Some important semiconductor nanomaterials like GaN [3], CdS [4], Si [5], SnO₂ [6], TiO₂ [7], ZnO [8,9] and CeO₂ [10-13] have been widely studied due to the basic phenomena of quantum size effect on electrical, optical, mechanical and magnetic properties. Among them ZnO nanomaterials have been chosen because of their remarkable properties like wide and direct band gap (E_g ~3.4 eV) and large exciton binding energy (60 meV). In ZnO UV lasing action is possible at room temperature due to its wide band gap and large exciton binding energy [14]. At room temperature due to the extreme large binding energy, the excitons are thermally stable in ZnO. That's why ZnO has significant advantages in optoelectronic applications like ultraviolet (UV) lasing media [15]. For ZnO, the wide and direct optical energy band gap of 3.37eV is large enough to transmit most of the useful solar radiation. ZnO is an n-type semiconductor which belongs to II-VI group. It is very useful for transparent electrodes in flat panel displays, solar cells and promising material for short wavelength light emitting devices [16-18]. ZnO epitaxial films and nanostructures have been mostly studied for applications in UV-emitters, solar cells, gas sensors, varistors and surface electro-acoustic wave devices [19]. In the field of advanced devices low dimensional nanostructures are now being extensively used.

For the synthesis of nanomaterials there are various methods like, chemical vapour deposition [20], laser ablation [21], vacuum arc deposition [22], sputtering [23] and hydrothermal process [24,25]. But most of these fabrication techniques have complex steps, which require extremely sophisticated instruments, precise experimental setup and extreme experimental conditions. Hence, it is important to develop a very simple method to fabricate ZnO nanorods in laboratory environment. The chemical precipitation method provides a better route to fabricate multidimensional nanostructure in a very large scale. This technique is inexpensive, which does not require any complicated processing or huge infrastructures.

In this experiment, chemical precipitation method is used for synthesis of hexagonal zinc oxide rods at room temperature, which is simple and economical. In this method zinc acetate and poly vinyl pyrrolidone is used as a precursor and deionised water as a solvent. Further the sample is characterized by XRD and SEM, optical property is also discussed by UV-VIS spectroscopy.

EXPERIMENTAL SECTION

2.1: Materials

Zinc acetate dihydrate $Zn(CH_3COO)_2 \cdot 2H_2O$, Sodium Hydroxide (NaOH), Poly Vinyl Pyrrolidone (PVP) and absolute ethanol were used to synthesize undoped zinc oxide rods. All these chemicals were used as precursors which were obtained from MERCK chemical company. PVP is used as a capping agent. In this experiment, all the glass ware used was acid washed. The chemical reagents used were analytical reagent grade which needs no further purification. Ultrapure water was used for all dilution and sample preparation. All the fabrication process was done at room temperature.

2.2: Sample Preparation

In a typical experiment, 2.2g (0.2mol/l) of zinc acetate $Zn(CH_3COOH)_2 \cdot 2H_2O$ was dissolved in 50ml deionised water. The stirring rate of solution was taken as 1200rpm at room temperature. Then 1gm of PVP was dissolved in 50ml deionised water and was added drop by drop to the constant stirring solution for stabilizing the synthesized particles. The mixture was stirred at room temperature until a homogeneous solution was obtained. After that 0.4gm (0.2mol/l) of 50ml sodium hydroxide was added drop by drop to the above mixture which gives white voluminous precipitate. The Stirring process was continued for 3 hours till a white precipitate deposited at the bottom of the beaker. This solution was kept overnight for settlement of precipitate. Then the precipitate was filtered and washed 2-3 times with distilled water and 1-2 times with absolute ethanol by using Whatmann filter paper. After this process finally the products were dried in hot air oven at 100°C for 1h. The powder obtained was used for further characterization process.

2.3: Characterization

The X-Ray Diffraction (XRD) patterns of the undoped powered ZnO sample was recorded by XPERT-PRO Diffractometer system using $CuK\alpha$ radiation ($\lambda=1.54056$) at 45kV and 40mA. The morphology and size of the particles were determined by Scanning Electron Microscopy (SEM) by using JEOL-EO microscopy with accelerating voltage 20kV. The optical absorption spectra of the particles in de-ionised water were recorded using Perkin Elmer Lambda -45 spectrophotometer in the wavelength range 200-800nm.

RESULTS AND DISCUSSION

3.1: Structural Study

A typical XRD pattern of the prepared nano rods is shown in fig.1. The pattern obtained is indexed with hexagonal unit cell structure with wurtzite structure (JCPDS Card no.36-1451). The observed relative peak intensities and interplaner spacing has been compared to that of their standard values which is given in table 1. All peaks of the obtained product correspond to the hexagonal wurtzite structure of Zn which is studied by many researchers. In fig.1, the detected peaks are at 2θ values of 31.8384°, 34.4937, 36.40840, 47.57920, and 56.65420 corresponding to the following lattice planes [100], [002], [101], [102], [110]. It has been observed that there is a small difference in the relative peak intensities of the lattice planes [100] to [002] and in the d spacing of different peaks. Also, it has been seen that the XRD patterns of the nano rods are considerably broad because the crystals are randomly arranged or have low degree of periodicity. Furthermore no impurities were found in XRD pattern. This result shows that high purity hexagonal ZnO nano rods could be obtained by this chemical method.

Table 1: X-Ray Diffraction peak intensities and d-spacing

XRD Peak (hkl)	2θ (degree) observed	2θ (degree) from JCPDS	Intensity observed	Intensity from JCPDS	d-spacing observed	d-spacing from JCPDS
100	31.8384	31.770	61.64	57	2.80842	2.81430
002	34.4937	34.422	76.20	44	2.60022	2.60332
101	36.4084	36.253	100	100	2.46775	2.47592
102	47.5792	47.539	21	23	1.91120	1.91114
110	56.6542	56.603	30.60	32	1.62337	1.62472

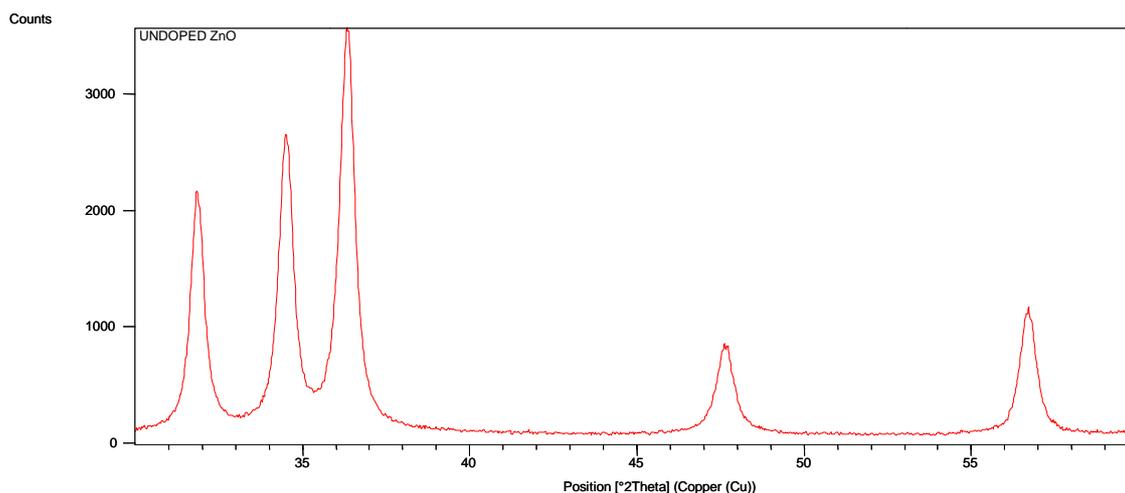


Fig. 1 XRD pattern of undoped ZnO nanorods.

3.2: Morphological Study

Fig.2 shows the morphology of prepared ZnO nano rods. The SEM image clearly shows that the product obtained is ZnO micro rods. The powder contains ZnO micro rods of diameter 1.61 μm and of length 4.89 μm . In this work, the two main reactants used to fabricate ZnO are NaOH and $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$, their solubility in water (109 and 30) are much higher than other solvent. The high solubility is the main factor which decreases the number of nucleation sites [26]. So the size of this rod is in micro range.

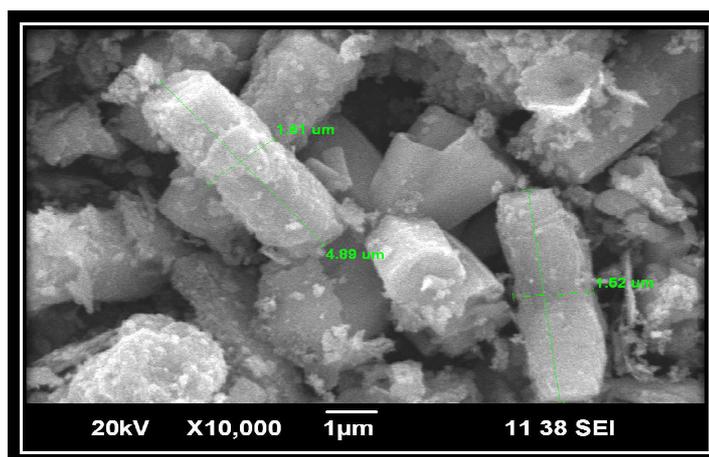


Fig. 2 SEM image of undoped ZnO rods

3.3: Optical Properties

UV-VIS absorption spectra of the ZnO micro rods are shown in fig.3. It is used to evaluate the potential optical properties of ZnO nano rods. These ZnO rods are prepared by chemical precipitation method. The room temperature spectra exhibit strong excitonic absorption peak at 364nm. The absorption spectrum shows a well defined exciton band at 364 nm and significant blue shift relative to the bulk exciton absorption(373nm)[27]. This shift phenomenon is mainly related to the quantum confinement effect of the small size of ZnO [28]. The band gap (E_g) of ZnO was calculated by using the formula $E=hc/\lambda$, where h is plank's constant, c is the velocity of light and λ is the wavelength of the light. The band gap of ZnO was found to be 3.4 eV.

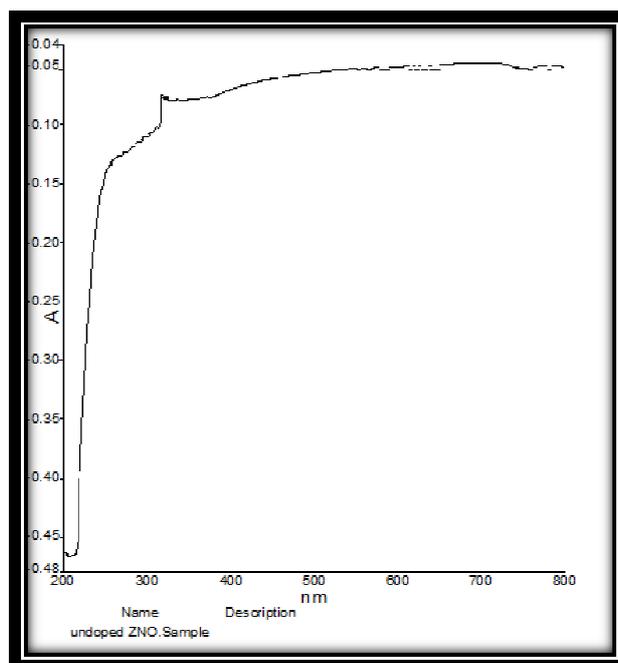


Fig. 3 UV- Visible absorption spectrum of undoped ZnO nanorods

CONCLUSION

ZnO rods with diameter $1.61\mu\text{m}$ and length of $4.89\mu\text{m}$ respectively obtained by SEM have been successfully prepared by a simple chemical precipitation method at room temperature. The XRD patterns obtained confirms the formation of wurtzite hexagonal ZnO nanostructures without any impurities. Also, d-spacing and relative peak intensities have been compared from their standard values and almost negligible difference is observed in these values. Further, the UV absorption at 364 nm is found which is blue shifted; energy band gap of ZnO is calculated as 3.82eV . Hence, it is concluded that in the presence of deionised water as solvent, the size of ZnO rods is in micro range. This study provides new approaches to change the optical properties which can be used as a strong tool for further optoelectronic applications.

Acknowledgements

Authors are thankful to Kochi University of Science and Tech., Kerala for SEM, Panjab University for XRD and UV-Visible absorption spectra.

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