Hydrothermal Synthesis, Structural and Optical Investigations of Undoped and Mg doped ZnO nanorods

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Abstract. Undoped and Mg doped ZnO nanorods were synthesized by sol gel and hydrothermal method.Vertically aligned ZnO nanorods were sequentially characterized for structure(XRD), morphology(FESEM), Optical properties(UV-Vis) and electrical properties (I-V).XRD studies indicates a significant c-axis compression and reduced crystallite size for the Mg doped sample as compared to undoped ZnO nanorods, which was further confirmed by FESEM images. Decrease in optical band gap (3.14 eV) and enhancement in photocurrent density (6.67 mA/cm^2)was observed incase of the doped sample. All these results indicates that 5 % Mg doped ZnO can be suitably used for applications in optoelectronic devices.

INTRODUCTION

The demand of clean and green energy has been extensively increased in the last few decades. Among several other materials, zinc oxide (ZnO) is arguably one of the most popular material due to its properties like wide bandgap, large exciton binding energy, high electron mobility, cost effectiveness, low toxicity, easy fabrication, environmental stability etc. But being a UV active material there remains constraints in use of the full solar spectrum. This causes reduction in efficiency. Thus in order to enhance the absorption of visible light of the solar spectrum, various dopants are chosen that create defect levels within the band gap or shift band-edge positions, narrowing the optical band gap[1]. Among these doping of cations into the host lattice with keeping the structural phase unaltered is a possible solution.

One of the promising ways to achieve the extended use of spectrum is by varying the morphology of the nanostructures. In order to achieve this 1D semiconductors have got immense attention of research community due to its amazing chemical as well as physical properties.Among all the 1D nanostructures, nanorods stands out to be the best for applications in optoelectronic devices since it provides long diffusion length and large surface to volume ratio.

Due to similar ionic radii of Mg^{2+}(0.57 ´) and Zn^{2+}(0.60 ´), Mg doping can significantly enhance the physical properties of ZnO. Exciton binding energy of ZnO is large (60 meV), thus doped ZnO is expected to exhibit extreme stability of excitons at room temperature even with a low concentration of Mg. Mg doped ZnO nanostructures have been fabricated by various techniques like pulsed layer deposition, molecular beam epitaxy and chemical vapor deposition. However, these fabrication technologies are vacuum based that comes at a very high cost and are not easy to scale up for mass production. Among the solution processed techniques like spray coating, dip coating, sol-gel method, chemical bath deposition; sol-gel stands to be the most useful and easy method of production where precursors are homogeneously mixed in solvent to form an integrated network of liquid phase i.e. gel. This gel is then heat treated to form nanostructures, controlling its shape, size and morphology. In this report, we have fabricated undoped and 5% Mg doped ZnO nanorods and also investigated the effect of this cation doping on the physical properties of ZnO nanorods.

EXPERIMENTAL DETAILS

Undoped and 5% Mg doped ZnO nanorods were grown on cleaned glass substrates by simple low cost spin coating technique followed by a low temperature hydrothermal methodas reported earlier[2]. Magnesium Chloride hexahydrate [$MgCl_2.6H_2O$ 99% purity (Merck)] was used as doping precursor for growth of Mg doped ZnO nanorods. An equimolar solution of 0.025 M Zinc Nitrate Hexahydrate and Hexamethylenetetramine in DI water was prepared. Two different molar solutions were prepared by varying doping percentage of Mg from 0% and 5%.Then the seeded glass substrates were put in this growth solution in top down manner at 90 °C for 5 hours. The as prepared nanorods were immediately taken out of the oven and rinsed with DI water to remove organic residuals from the surface. The undoped ZnO and Mg doped ZnO nanorods sample were identified as ZnO and Mg_ZnO respectively.

Characterization

Hydrothermally grown nanorods were characterized for their structural properties by XRD using PanalyticalXpert Pro MPDmodel using monochromatic $CuK_{\alpha 1}$ radiation (λ= 1.5405 Å) at TIFR, Mumbai. The surface morphology of the samples wereobserved by FESEM (ZEISS Supra 55 model). Optical properties of the nanorods were studied by using Agilent carry 5000 UV-vis-NIR double beam spectrophotometer. Current-voltage characteristics were recorded by Keithley 2450 source meter.

RESULTS AND DISCUSSION

Structural Studies

Figure 1 depicts the X-ray diffraction patterns of undoped and Mg doped ZnO nanorods. We observed that all the samples are crystalline having hexagonal wurtzite structure (JCPDS no. 36-1451). No impurity peaks were observed after doping Mg into ZnO lattice. The high intensity diffraction peak of (002) plane indicates that the nanorods exhibit c-axis orientation. A higher angle shift was observed in (002) peak for the doped sample as compared to undoped ZnO nanorods. This shift indicates shrinkage of unit cell which may be due to the effective doping of Mg atoms into ZnO lattice because of smaller ionic radius of Mg^{2+}(0.57 ˊ) as compared to Zn^{2+} (0.60 ˊ)[3]. Crystallite size was calculated by Debye-Scherer's formula,

$$D = \frac{K\lambda}{\beta_{hkl} \cos\theta} \quad (1)$$

Where K is the shape factor, β is FWHM of (002) peak, λ is the wavelength of X-ray used and θ is the Bragg angle.The average crystallite size, values of β and 2θ forboth thesamples are listed in Table1.

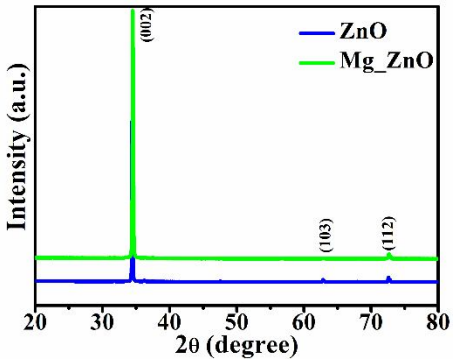

Figure 1. XRD patterns of undoped and Mg doped ZnO nanorods

Morphological Studies

Figure 2 shows the top view FESEM images of undoped and Mg doped ZnO nanorods. Top view confirms hexagonal structure of nanorods uniformly grown on the substrates. We observed that diameter of doped sample (113 nm) gradually decreases as compared to that of pristine ZnO (182 nm). This decrease in diameter may be because of reduced crystallite size of doped ZnO as observed from XRD results.

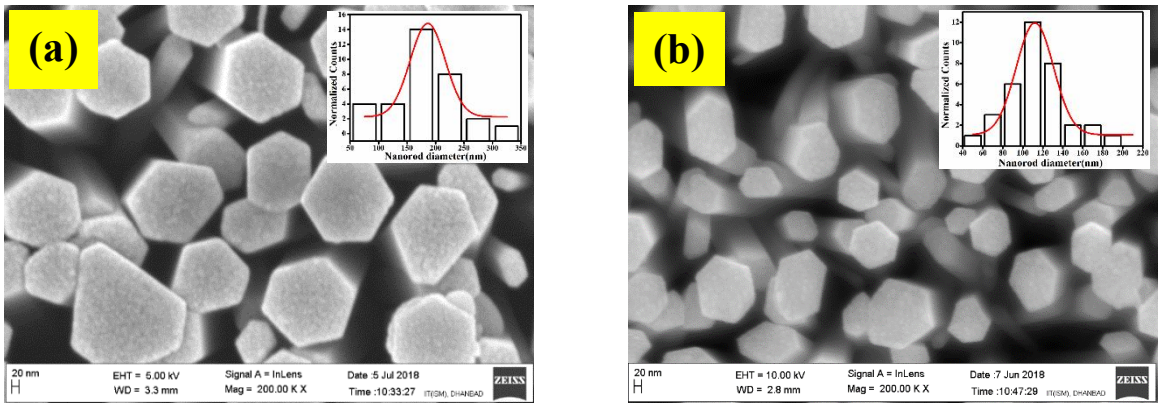

Figure 2. Top view FESEM images of (a) undoped ZnO and (b) 5% Mg doped ZnO nanorods

Optical Studies

Figure 3(a) represents the absorbance spectra of undoped and Mg doped ZnO nanorods recorded in wavelength range between 300-800 nm. We observed high absorbance for Mg doped ZnO nanorods as compared to pristine ZnO. Both the samples exhibited strong optical absorption at 369 nm. Band gap of both the nanorod samples were calculated by using Tauc's relation,

$$(\alpha h\nu)^2 = A(h\nu - E_g) \qquad (2)$$

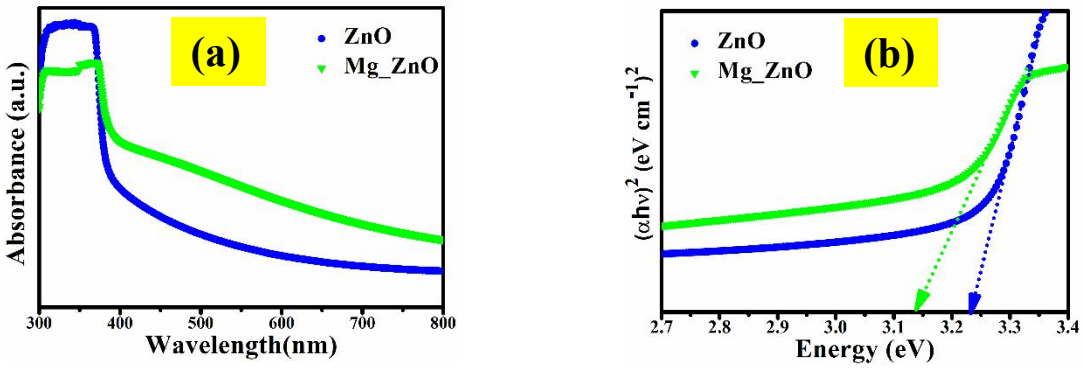

Figure 3.

Figure 3(b) represents Tauc's plot of the as grown nanorod samples. We observed a decrease in band gap for Mg doped sample as compared to undoped ZnO nanorods. This steady decrease in band gap might be associated with number of defects such as oxygen vacancy in the film[4]. Similar trend of narrowing of the energy band has been reported earlier [5]. Values of optical band gap and refractive index are listed in Table1.

Electrical Studies

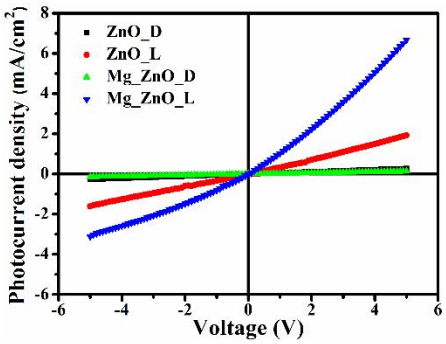

Figure 4. I-V curve representing photocurrent density of undoped and Mg doped ZnO nanorods

Figure 4 shows the current-voltage characteristics curve of pristine ZnO and Mg doped ZnO nanorods measured at room temperature within voltage range of -5 to +5V. These I-V curves were recorded under both dark as well as under UV illumination. Values of photocurrent density are listed in Table 1. We observed a remarkable increase in photocurrent density of Mg doped ZnO (6.67 mA/cm^2) in contrast with the undoped ZnO (1.92 mA/cm^2). This may be because of the generation of excess free electrons in the doped sample under illumination.

TABLE 1. Values of structural and optical parameters obtained from XRD and UV-Vis absorption spectra respectively. Values of Photocurrent density is calculated from I-V curves of both the nanorod samples.

Sample	2θ (deg)	FWHM (deg)	Crystallite Size (nm)	Optical Band gap (eV)	Refractive Index	Photocurrent density (mA/cm^2)	
						J_D	J_L
ZnO	34.451	0.143	57.82	3.23	2.40	0.269	1.922
5MgZ	34.531	0.152	54.40	3.14	2.42	0.135	6.672

CONCLUSION

In summary, ZnO nanorods doped with Mg have been successfully fabricated by simple cost effective sol-gel and hydrothermal method.Incorporation of Mg into ZnO indicates c-axis compression of the hexagonal lattice. The doped nanorods have reduced crystallite size (54.40 nm) and smaller diameter (113 nm) as compared to undoped ZnO. The absorbance spectrum exhibits a strong absorption at 369 nm. We observed narrowing of optical band gap (3.23 to 3.14 eV). As a result of high value of photocurrent density and suitable band gap, the as- prepared Mg doped ZnO nanorods may find potential applications in optoelectronic devices.

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