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STRUCTURAL INVESTIGATION OF ZNO NANOSTRUCTURES

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Abstract- The study of nanostructures with controlled morphology, shapes and size is essential for developing materials with novel properties. One of the versatile advantages of nanoparticles is the large surface to volume ratio. Nanoparticles exhibit dramatic optical, physical and magnetic behavior due to their size. In this paper, the structural study of ZnO nanoparticles fabricated through Solid state chemical reaction rout has been highlighted. XRD study confirms the wurtzite structure of ZnO nanoparticles, it also reveals the formation of nanoparticles with average size about 15.9 nm. TEM analysis confirmed the formation of ZnO nanorods having average aspect ratio ~3.7.
Keywords – Nanoparticles (NPs), ZnO, Nanorod

1. INTRODUCTION

Different types of semiconducting nanomaterials have attracted a large group of scientific community because of their exceptional properties, which are different from bulk materials [1,2]. Zinc oxide (ZnO), one of the very important and versatile semiconductors with direct band gap of gap of ~3.37 eV and a large exciton binding energy of ~60 meV at room temperature (RT) is a promising candidate for functional components of devices. Selective doping with transition metal ions into ZnO lattice host is capable of tailoring its physical properties. In this paper, the structural properties of bare ZnO are highlighted. I have fabricated TM doped ZnO and bare ZnO by adopting solid state chemical reaction route which has been described earlier works [3-10]. In this paper the structural investigations of bare ZnO nanoparticles is discussed.

2. EXPERIMENTAL DETAILS

During synthesis, as synthesized samples were obtained in the form of powder. Structural investigations of the as fabricated samples were carried out by utilizing tools like XRD, HRTEM, SAED etc. The phase and purity of the as prepared samples were determined by X-ray powder diffraction pattern. For identification of structural phase and crystallographic orientation, Rigaku Miniflex diffractometer employing Cu-Kα radiation at 1.54 Å with a scanning rate of 0.02 deg/s has been utilized. XRD measurements have showed that the undoped and Mn doped ZnO crystallize into hexagonal wurtzite structures. The XRD pattern for ZnO NPs as presented in figure:1(A) shows prominent diffraction peaks which can be perfectly indexed to the hexagonal wurtzite structure of ZnO according to JCPDS data card no.36-145. The XRD data have ensured wurtzite structure of ZnO with a high degree of crystallinity. The comparative X-ray diffraction pattern for bare ZnO and Mn:ZnO system is shown in figure:1.

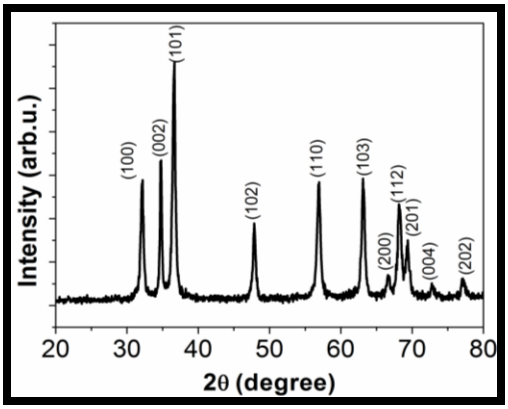

Figure 1. XRD pattern for the ZnO NPs

The most intense (101) peak for bare ZnO sample was observed at a Bragg angle (2θ) of ~36.60. The experimental results of 'a' and 'c' estimated for the sample were compared with the theoretical values for wurtzite phase of bulk ZnO (a = 3.250 A0, c = 5.265 A0). In the study, the calculated lattice parameters for the synthesized ZnO NPs are shown in table 1, which corresponds to the theoretical values. Table: 2 shows 'd' spacing values for the planes (001) and (002) as estimated for the sample.

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(hkl)	ZnO (A0)
(100)	2.786
(002)	2,576

Table 1. Values of lattice parameters for ZnO NPs,

Lattice parameter	ZnO
a (A0)	3.2173
c(A0)	5.152

Table 2. Values of lattice lattice spacing 'd' for the planes (100) and (002) for ZnO NPs.

Size determination of the nanostructures so formed was performed by utilizing three methods (i) Scherrer formula, (ii) Williamson-Hall Plot and (iii) TEM analysis. It is the simplest approach to calculate size from XRD line broadening. For size determination of the nanocrystals, usually, the most intense peak has been selected from the XRD spectra. In my case the most intense peak is obtained from the reflection of (101) plane for the sample.

Sample NPs	FWHM	2 θ value (In degree)	Crystalline size (nm)
ZnO	0.482	36.59	17.15

Table 3. Size of the ZnO NPs as calculated from the XRD data

The variation of Full width half maxima (FWHM) corresponding to different peak positions with crystallite sizes is given in the table: 3. The average crystallite size as obtained from individual XRD line broadening and using Scherrer formula for the ZnO NPs is 17.15nm .

By plotting $\beta\cos\theta$ versus $4\sin\theta$, the strain component from the slope ($C\varepsilon$) and the size component from the intercept ($K\lambda/L$) are calculated. The Williumson-Hall plot for pure ZnO sample is shown in figure 2. The values for ß and θ were taken from four different peaks of the respective XRD pattern of the sample. From the slope of the graph, the strain was obtained as 14.46 x 10-2 and from the intercept of the straight line the particle size (L) was estimated as 12.82 nm by considering $K = 0.9$ and $\lambda = 1.54$ Å. The strain and particle size of other nanostructures so fabricated were calculated from the analysis of Williamson-Hall plot. There is a linear increase in strain with increasing particle size. An anomaly regarding the particle size was observed in this case. This may be due to the fact that, Scherrer approach is based upon the assumption where strains and faulting are ignored for a small cubic crystal and the peak broadening is only due to the small size. The strain exhibited by the ZnO NPs with average size 12.82 nm is obtained as 14.46x102.

However the Williamson-Hall method has many assumptions: its absolute values should not be taken too seriously but it can be a useful method if used in the relative sense; for example a study of many powder patterns of the same chemical compound, but synthesized under different conditions, might reveal trends in the crystallite size/strain which in turn can be related to the properties of the product.

One-dimensional (1D) ZnO nanostructures have been studied intensively and extensively over the last decade not only for their remarkable chemical and physical properties, but also for their current and future diverse technological applications. Wurtzite structured ZnO grown along the c axis has high energy polar surfaces such as ± (0001) surfaces with alternating Zn2+-terminated and O2−-terminated surfaces [11]. So when a ZnO nucleus is newly formed, owing to the high energy of the polar surfaces, the incoming precursor molecules tend to favorably adsorb on the polar surfaces. However, after adsorption of one layer of precursor molecules, the polar surface transforms into another polar surface with inverted polarity. For instance, a Zn2+-terminated surface changes into an O2−-terminated surface, or vice versa. Such a process is repeated over time, leading to a fast growth along the ± [0001] directions, exposing the non-polar {1100} and {2110} surfaces to the solution. This is essentially how a 1D nanostructure is formed [12]. In my study, it has been observed the formation of one dimensional nanostructures of as synthesized bare ZnO samples synthesized via solid state chemical reaction route. The elongated nanostructure was confirmed through transmission electron microscope (TEM) study. For TEM study we have utilised JEM-2100 model with resolution 1.9Å to 1.4Å, accelerating voltage 60-200 KV in 50 steps having magnification 50 to 1500000 times.

During TEM observations, focusing the electron beam on the ZnO cluster, the presence of one dimensional ZnO nanostructures was confirmed. Various TEM images for the bare ZnO sample are presented in figure:3.

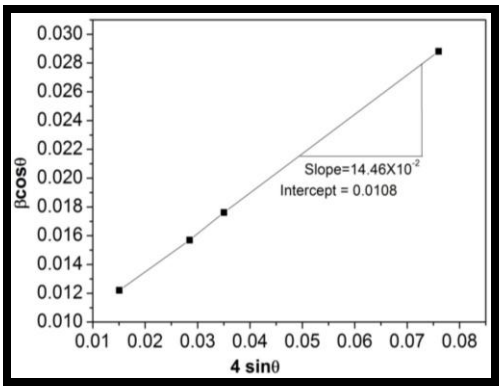

Figure 2. Williumson –Hall plot for the sample ZnO NPs

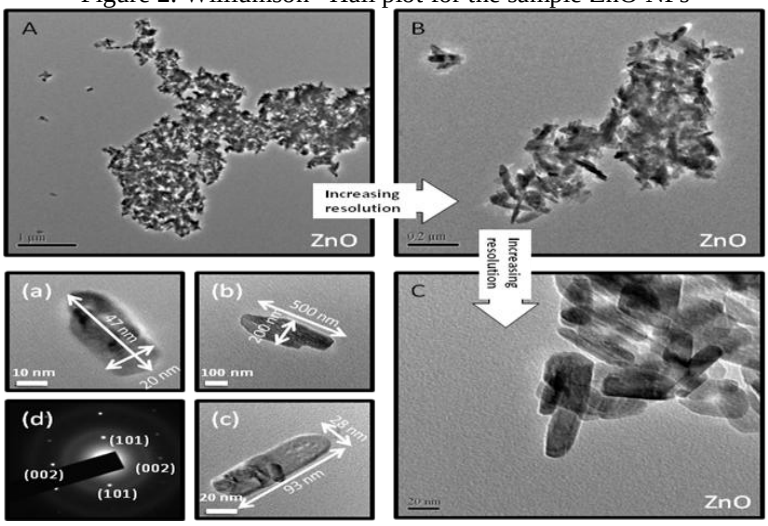

Figure 3. TEM image of the ZnO sample, with increasing resolution from figure: A to C. With high resolution TEM micrograph three isolated elongated nanostructures having different lengths and diameters, (a) 47 nm, 20 nm; (b) 500 nm, 200 nm; and (c) 93 nm, 28 nm; respectively. (d) Selected area electron diffraction pattern (SAED) focussed on the isolated nanorod (c).

During TEM investigation few ZnO nanorods were found to be isolated, three of them are presented in figure: 3(a) - 3(c). Interestingly, a knife like elongated structure with maximum length and diameter ~500 nm and ~200 nm respectively was observed in the TEM micrograph (figure: 3b). Estimated lengths and diameters of other two isolated rods as presented in figure: 3(a) and figure: 3(c) were 47 nm, 20 nm and 93 nm, 28 nm respectively. The average aspect ratio of these elongated nanoparticles is found to be ~3.7. The Uniformly distributed ZnO lattice points are observed in the selected area electron diffraction (SAED) pattern [figure: 3(d)]. All points correspond to the hexagonal wurtzite structure of ZnO. Four points within two inner rings are ascribed for the planes (101) and (002) corresponding to their lattice spacing 2.4Å and 2.6Å.

The HRTEM study was performed on the isolated nanorod. The lattice spacing was estimated to be ~2.1Å at a position where lattice fringes are clear enough, this lattice spacing 'd' corresponds to the plane (102) as calculated from the XRD pattern of the ZnO sample.

Table 1 show the peak signal to noise ratio of performance of our proposed method of watermarked image and original image with various watermark image, where our watermarked images peak signal to noise ratio has a better performance than others.

3. RESULT AND CONCLUSION

It was observed that along with decrease in size, the strain also decreases. Thus, size and strain of the nanostructures can be simultaneously manipulated by changing doping concentration. HRTEM study for all samples exhibited clear fringe patterns; it was attributed due to high crystalline nature of the as-synthesised samples. The growth direction of the bare ZnO was found along (102), while for all TM doped samples it was found along (101) plane. In case of bare ZnO, we have noticed several lattice distortions on the surface of the nanocrystallites, this may play a significant role to influence optical and magnetic properties of the NSs. A significant change in lattice parameters (a and c) has been investigated from the structural study of the as-synthesised NSs. Increasing lattice parameters have been observed as a result of Mn doping. Out of three samples Mn-3 doped ZnO showed highest values of lattice parameters (a and c). Thus, the growth direction of small crystallite is identified to be along (102) plane. It has been noticed that the surface of the small crystallite exposed to the beam consists of several lattice distortion. This structural property may play important role to change the optical, magnetic and other properties of the

sample. A significant change in lattice parameters (a and c) has been investigated from the structural study of the as-synthesised NSs. Thus, the growth direction of small crystallite is identified to be along (102) plane. It has been noticed that the surface of the small crystallite exposed to the beam consists of several lattice distortion. This structural property may play important role to change the optical, magnetic and other properties of the ZnO NPs..

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