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Research Paper

Effect On Particle Size And Microstrain Due To Iron Doping On Zno Nanoparticle Prepared By Wet Chemical Method

Physics

KEYWORDS : Microstrain, Particle size, Scherrer's equation, Chemical bath deposition.

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ABSTRACT

Iron (Fe) deposited Zinc oxide (ZnO) thin films were successfully deposited by Chemical Bath Deposition (CBD) method with Zinc Acetate Dihydrate as inorganic precursor and Iron Chloride (FeCl3) as dopant. Thin films are prepared for 0.1M, 0.05M and 0.025M doping concentration at room temperature (RT). The films were analyzed by X-Ray Diffraction (XRD). Using XRD microstrain and particle sizes are calculated at different doping concentration at RT. It is found that as doping concentration increases particle size as well as microstrain increases.

Introduction

Studies of ultra fine particles in the size range from a few to several nano meters [1] are increasing worldwide. The nano meter sized particles exhibit structure and properties which are quite different from those of the corresponding bulk materials [2]. Zinc Oxide (ZnO) is a very extensively studied semiconductor for its primary and industrial importance. ZnO shows properties like transparency in the visible range, direct band gap, high electrochemical stability, toxic absorbance and plenty in nature [3]. Among oxides of transition metal, ZnO is considered to be one of the most important multifunctional semiconductor material for technological application such as light emitting diodes, gas sensors, drug delivery, transparent field effect transistors, photodiodes and optoelectronic devices due to the wide band gap (3.3eV), high transmission coefficient in the visible and near infrared spectral range and large excitation binding energy (60meV) at room temperature [4,5]. There are wide varieties of synthetic methods for the preparation of ultrafine oxide nanoparticles such as sol- gel, hydrothermal, microwave, Chemical Bath Deposition etc. Out of these methods we prepared Fe doped ZnO nanostructures by using CBD technique which is robust and reliable without requiring the expensive and complex equipments. Less consumption of energy and less pollution occurs in this method. Doping of various metals (e.g. Cr, Co, Ni and Fe), due to its unique chemical stability, is recognized as one of the most efficient doping element to improve and tune the structural and optical properties of ZnO nanomaterials.

Therefore in the present work, we report the effect of doping on the structural properties of ZnO nanocrystals synthesized by CBD technique at different doping concentration prepared at room temperature (RT).

2 Materials and Methods

All materials are purchased from the commercial market with highest purity(99.99%). Zinc Acetate Dihydrate (CH_3COO_2Zn-$2H_2O$) and Sodium Hydroxide (NaOH) as the starting materials, Polyvinyl Alcohol (PVA) as capping agent Ferric Chloride ($FeCl_3$) as doping agent and double distilled water as dispersing solvent are used to prepare the ZnO thin film. Zinc Acetate Dihydrate ($CH_3COO_2Zn2H_2O$) is stirred constantly for 1hour at 70°C(solution1) . 2gm PVA is stirred constantly at 70°C (solution2). Now NaOH is slowly added drop by drop into the solution 1 and stirred at room temperature for half an hour and a white solution is obtained (solution3). Ferric Chloride ($FeCl_3$) solution at different concentration (0.1M, .05M and .025M) is prepared (solution 4). The final mixture (solution2 , solution3 and solution 4) is constantly stirred for 1hr at 343K. Glass substrates are washed with some acid and then with distilled water and allowed to dry. Now the substrate is dipped into the final solution and allowed to dry at room temperature.

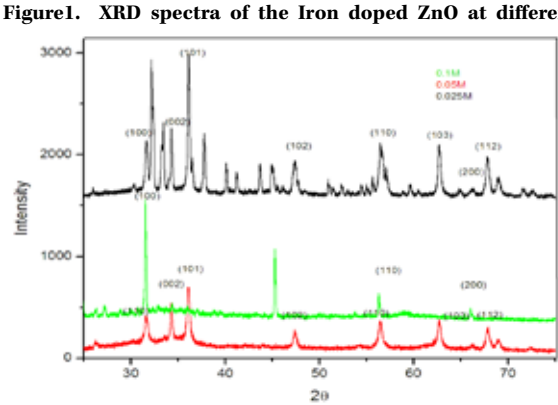
3. Results and Discussions:

3.1 XRD study:

XRD is widely used to determine the particle size of nanoparticle. In order to identify the phase and to know the structure of ZnO nanoparticles X-ray Diffractometer (X' Pert Pro) is employed with generator setting of 30mA and 40kV with CuKα1(λ=1.54056A°) radiation. The XRD is calibrated with a standard silicon sample. The broadening of peaks are also corrected with Warren rule [6] that arises due to instrumental effect. Continuous scanning is applied in the range from 25-75° (2θ) at a scanning rate of 1sec/ step and step size is 0.02° 2θ .

The XRD pattern of the thin film of Iron doped ZnO for different Iron concentration 0.1M, 0.05M and 0.025M.

Figure1. XRD spectra of the Iron doped ZnO at different concentration



The diffraction peaks of nanoparticles corresponds to (100), (002), (101), (102), (110), (103), (112), (201) planes are almost matched with standard ZnO powder (ICDD No. 80-0074). The peaks of the standard ZnO powders are found at 31.732°, 34.364°, 36.207° 47.469°, 56.526°, 62.754°, 66.292°, 67.851°, 68.995°, 72.431°, 76.848°2θ corresponds to above mentioned (hkl) planes. No diffraction peaks from other species could be observed which indicates that all the precursor have been completely decomposed and no other crystal products have been retained after the decomposition process. All the peaks indexed to a hexagonal wurtzite structure of ZnO with a dominant peak around 2θ = 31.7°. This proves the strong preferred orientation along a- axis. The diffraction peak for (100) plane shifts towards higher angle as Iron (Fe) concentration increases. Thus due to increase in doping concentration lattice parameters are expanded. The incorporation of Fe^{2+} ions in the prepared sample increases with increasing Fe proportion. With the increase in doping concentration intensity of the XRD peak decreases monotonously. The width of the XRD peaks show a systematic broadening with in-

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creasing doping concentration. These two observations signify the degradation of the crystalline quality. It is probably due to the lattice disorder and strain induced in the ZnO lattice due to the substitution of Zn^{2+} ions of radius. ($0.60A^0$) by reasonably higher ionic radius of Fe^{2+} ions of radius ($0.64A^0$) [7].

The average crystallite size (D) has been calculated from the XRD data using Scherrer's formula [8,9] as

$$D = k\lambda/\beta cos\theta \quad \text{.....(1)}$$

Where D represents the diameter of the crystallites, λ is the X-ray wavelength, β is the Full width at half maximum, K is a constant nearly equal to one and θ is half of diffraction angle.

During deformation, the d- spacing for a given (hkl) plane will change (i.e peak shift) and the associated lattice strain can be calculated. Diffraction peak broaden either because of inhomogenous microstrain induced by dislocation- like defects (strain broadening) or because of shrinkage of coherent scattering volume (size broadening). The observed broadening peak is likely the combined result of both effects.

3.2 Microstrain analysis

The XRD line broadening arises due to small grain size and strain. Grain size causes the radiation to be diffracted individually [10,11]. In the present work Wiiliamson- Hall technique is applied to find out the particle size and microstrain using the following equation: [15-16]. In the present work Williamson-Hall technique is applied to find out the particle size and mequation

$$\beta cos\theta = msin\theta + \lambda/D \quad \text{.....(1)}$$

where m' is the microstrain, D is the particle size and β is the full width at half maximum of the peak measured in radian, 2θ is the diffraction angle and λ is the wavelength of X-ray. The slope of the graph between βcosθ and sinθ gives the microstrain and the intercept on y axis gives λ/D. WH plot of Iron doped ZnO at 0.1M concentration is shown in Figure2.

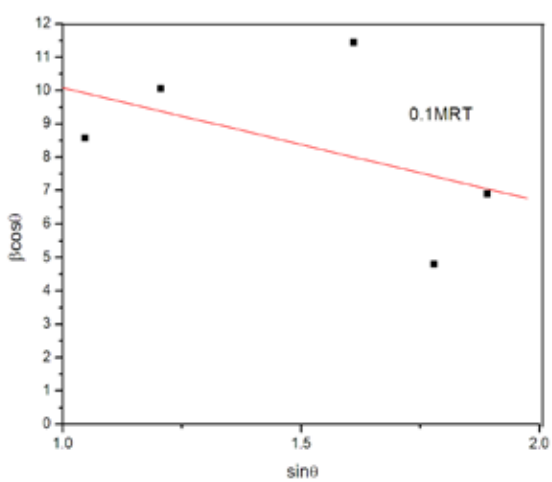

Figure 2. WH plot of Iron doped ZnO at 0.1M dopping concentration.

The particle size obtained from WH plot are similar to that of obtained from Scherrer equation. The microstrain and average crystallite size obtained from Scherrer equation at RT are shown in table 1.

Concentration			0.025M	0.05M	0.1M
Crystallite size (nm) from	Microstrain analysis	RT	3.43	19.4	24.6
	Scherrer's Equation	RT	4.48	20.4	22.6
Microstrain		RT	0.0612	0.0482	0.0357

Table 1. Particle size from Scherrer Equation and microstrain analysis and the microstrain developed.

4.Conclusion

The Iron doped ZnO nanoparticles were successfully synthesized by Wet chemical method at Room Temperature (RT). XRD pattern confirms the hexagonal wurtzite structure of Iron Dopped ZnO and the average particle sizes found to be are 4.48nm, 20.4nm and 22.6nm respectively which are similar to the particle sizes obtained from microstrain analysis. Scherrer's method gives average particle size of all crystallites present in the sample in a direction perpendicular to a particular (hkl) planes. But the WH method gives the average particle size in all directions of all individual particles. As the Scherrer's method and WH method give almost equal average particle size, this is possible only if the shape of the particles are cubical or spherical.

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