

Consequence of Cobalt Incorporation on Structural and Optical Properties of Transparent Nano-Crystalline ZnO Thin Film

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Abstract: We have investigated the effect of Co(4%) doping on structural and optical properties of the zinc oxides thin film deposited on glass substrate by spin coating techniques. The structural analysis and surface morphology have been carried out with the help of XRD and Atomic Force Microscopy (AFM) characterisation respectively. UV-Vis spectroscopy and Photoluminescence spectroscopy has been employed to obtain information about absorption and luminescence properties of Pure and Co-doped ZnO thin film. The XRD patterns confirm the crystalline nature and hexagonal wurtzite structure formation in the samples. The thickness of the film is measured by MProbe Thin Film Measurement System. AFM observations indicate a smooth surface morphology with small grains. AFM results suggest that cobalt doping decreases the average grain size and roughness of ZnO thin film. UV-Vis analysis indicates that absorption edge of cobalt doped ZnO thin film lie in the visible region and energy band gap of $\text{Zn}_{0.96}\text{Co}_{0.04}\text{O}$ (3.05eV) is less than pure ZnO thin film (3.2eV). The defect generated absorption in the visible region is present due to the incorporation of cobalt in ZnO thin film. Photoluminescence study shows the broad emission in the visible region in all samples. The Co doping causes an increase in broad emission in the visible region.

Keywords: Co-doped ZnO, Sol-gel method, Optical properties, Spin coating.

1. Introduction

The transition metal and rare earth doped ZnO has been extensively studied in last few decades due to its wide application in optoelectronic

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devices, solar cell, spintronics devices, ultraviolet luminescence devices, optical coatings, light emitting diodes (LED), gas sensors, optical limiting applications, photo catalysts, antibacterial activity, piezoelectric devices and transparent electrodes etc.¹⁴. ZnO has wide band gap (3.36 eV), high excitation binding energy (60 MeV) semiconductor and belongs to space group $P6_3mc$ ⁵⁻⁶. ZnO is an n-type semiconductor and exhibits hexagonal wurtzite crystal structure. Diluted magnetic semiconductors (DMS) have attracted the considerable attention of scientific fraternity due to its unique spintronics (spin-based electronics) properties. Transition metal doping significantly affects optical and magnetic properties of zinc oxide⁷⁻⁸. The room temperature ferromagnetism (RTFM) in transition metal doped ZnO has been observed by different group. The Co-doped ZnO nanoparticles emerged as one of the most prospective material in spintronics devices due to its RTFM behaviour. The existence of RTFM in pure and doped ZnO is still a topic of discussion. The magnetic properties of DMS can be tuned by controlling type of carrier, their density and mobility. ZnO has absorption in the UV region and emission in visible region with intense peak centred at violet colour of spectrum. Our earlier study on Mn and Co-doped ZnO nanoparticles ascertain that doping of transition metal causes shift in absorption edge, intense emission peak position and influence the ferromagnetic behaviour of ZnO nanoparticles⁹⁻¹⁰.

The thin film of ZnO/doped ZnO shows slightly less variation in optical and magnetic properties as compared to nanoparticles of same materials. Transition metal doped ZnO thin film have been reported for different applications such as visible light photo catalyst, gas sensor and UV photo detector¹¹⁻¹³. The ZnO thin film can be prepared with different method such as sputtering, pulsed laser deposition (PLD), chemical vapour deposition (CVD), spin coating, thermal evaporation, dip coating. The preparation method affects the quality of film, which influences the optical and magnetic properties of thin film. The sol-gel spin coating method has some merits, such as easy control of chemical components and fabrication of thin film at low cost to investigate structure and optical property of ZnO thin films. In this paper, we have used the spin coating method for fabrication of thin film and focussed on maintaining crystalline structure to investigate its structural and optical properties.

2. Experimental Procedure

2.1 Synthesis of ZnO: Co Thin film

Materials used: Zinc acetate dehydrate, Cobalt acetate tetra hydrate ; Solvent -Ethanol ; Stabilizer -Mono-ethanolamine, Substrate- Micro Slide Glass.

We have prepared thin films of pure and Co-doped ZnO on the glass substrate by the sol-gel spin coating technique. The Zinc acetate dehydrates and Cobalt acetate tetra hydrate have been used as a starting material. Ethanol and monoethanolamine (MEA) have been used as a solvent and stabilizer respectively. For the synthesis of the ZnO thin film, we dissolved appropriate amount of zinc acetate dehydrate in ethanol and start stirring at 1200 rpm at room temperature for 2 hours. Then small amount of MEA is added in the solution to get clear transparent solution of 300 millimole concentration (0.3M) and string continues for 3 hours to get solution for ZnO thin film preparation. For Co(4%) doped ZnO, we have added the appropriate proportion of cobalt acetate tetra hydrate in the solution and the same process was repeated. The glass substrates were cleaned with alenox detergent and water followed by propanol and acetone for 10min. in an ultrasonic cleaner. The substrate was preheated in an oven at 200⁰C for 10min. The obtained solution was coated with the help of spin coater. The spin coater was rotated at 3000 rpm for 60 seconds at room temperature. After depositing each layer, we heated the samples in Hot air oven at 200⁰C for 10min to evaporate the solvent and remove organic residuals. The procedures from coating to drying have been repeated four times, then the film inserted into a furnace and annealed in air at 550⁰C for 1 hours. The final sample obtained after annealing has been used for characterisation purpose.

2.2 Characterisations

We have analysed phase confirmation of thin film samples using Rigaku-MiniFlex-II DESKTOP powder X-ray diffractometer with CuK_α radiation ($\lambda = 1.54 \text{ \AA}$) at 30 kV and 15 mA. All patterns were recorded over the range $20 \leq 2\theta \leq 80$ with a step size of 0.02°. Surface morphology of the thin films has been investigated by Atomic Force Microscopy (AFM) NT-MDT set up. M-Probe thin film measurement system has been employed to measure the thickness of thin film samples. The optical absorption spectra of thin film samples were recorded in the range of 300-800 nm by Lambda-35 UV-Vis spectrophotometer from PerkinElmer. Photoluminescence spectra

have been measured by Horiba Fluorolog-3 spectrophotometer equipped with 450w Xe flash lamp.

3. Results and Discussions

3.1 Structural Analysis

Figure-1 depicts the XRD spectra of pure and Co-doped ZnO thin film deposited on glass substrates. The sharp and intense peaks indicate the crystalline nature of samples. The observed peaks are indexed according to hexagonal wurtzite crystal structure of pure ZnO nanoparticles (PDF: 792205). The prominent peaks of ZnO [(100),(002) and (101)] are present in pure and doped samples, confirms the hexagonal wurtzite type structure of ZnO. All the peaks of pure ZnO thin film are also present in Co-doped ZnO thin film. The XRD analysis confirms that cobalt behaves as a substitutional dopant in the ZnO and does not change the wurtzite crystal structure. The crystalline size of samples has been calculated corresponding to (002) peak using Scherer's formula⁹

$$D = \frac{0.9\lambda}{\beta \cos \theta},$$

where λ is the wavelength of X- rays (1.54 for Cu K_{α}), θ is Bragg's angles & β is the full width at the half maximum. The FWHM has been calculated for (002) peaks of samples.

The calculated crystallite size of ZnO and Co doped ZnO are 24 and 26.5nm respectively. The crystallite size variation is affected by growth of ZnO grains, which depends on movement and diffusion of Zn^{+2} ions. However, in case of cobalt doped ZnO, The cobalt act as electrical doping. The incorporation of cobalt increases the impurity/charge carriers and electrical conductivity because it can diffuse. Thus the grain size increases due to Co doping in the ZnO thin film.

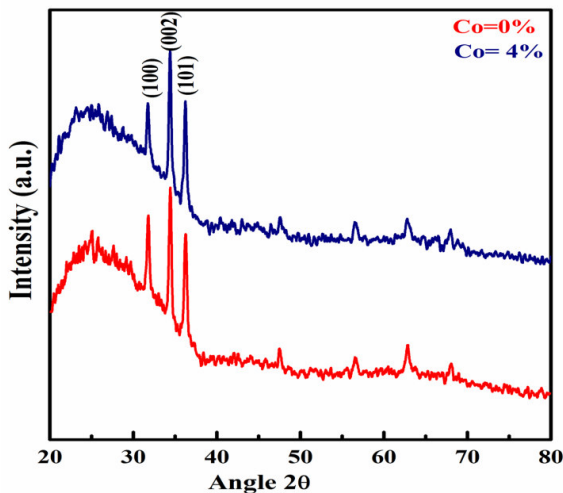


Fig.1: XRD spectra of pure and Co doped ZnO thin film.

3.2 Surface Morphology

The surface morphology of the thin film has been obtained by AFM image analysis with the help of Nova PX software. The morphology of sample does not significantly affect by Co doping. Fig.2(a) and (b) shows the 2d and 3d AFM image of pure ZnO thin film and indicate that deposited films are indeed continuous and of polycrystalline nature. The 2D AFM image of Co-doped ZnO thin film used for grain size calculation are depicted in Fig.3 AFM observations indicate a smooth surface morphology with small grains. Average grain size and roughness of cobalt doped thin film is 20.3 nm and 2.66 nm, while ZnO thin film has average grain size 30.7 nm and roughness 3.84 which indicate that cobalt doping decrease the average grain size and roughness of ZnO thin film. The small value of roughness indicates smooth surface morphology of samples.

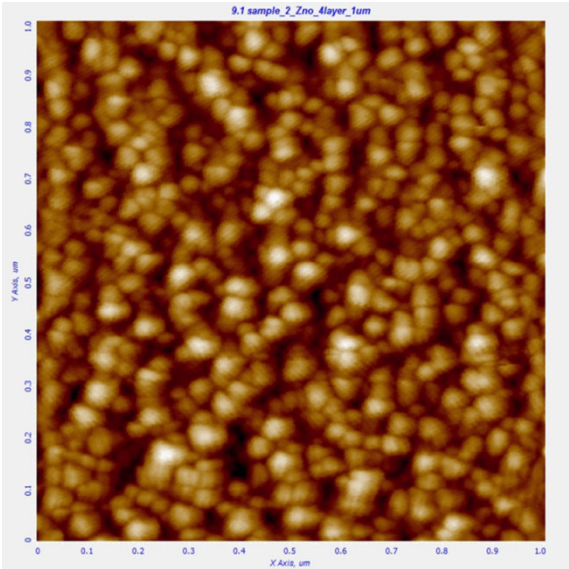


Fig.2(a): 2DAFM image of ZnO thin film.

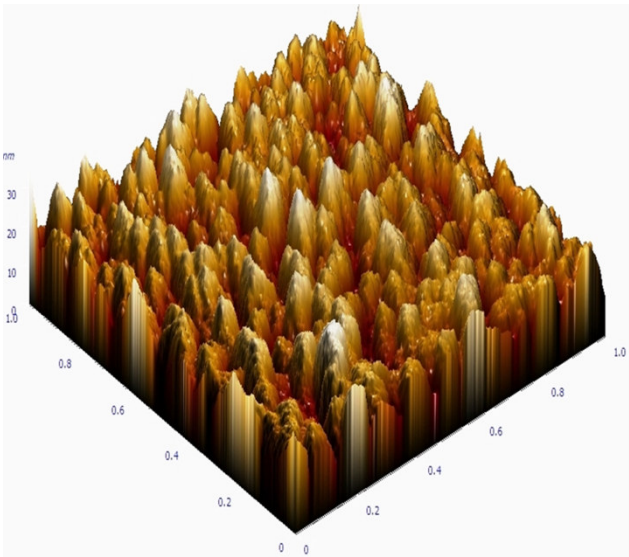


Fig.2(b): 3D AFM image of ZnO thin film.

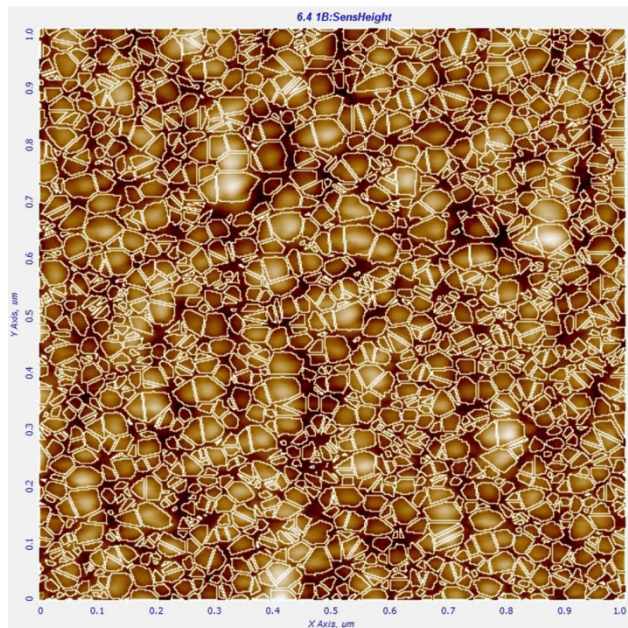


Fig.3: 2DAFM image of Co doped ZnO thin film.

3.3 Thickness Measurement of the thin film

We have measured the thickness of thin film with the help of M-Probe measurement system. We have taken the observation at the different position of the film and average thickness has been calculated using these data. It has been observed that average thickness of samples lies in the range of 25-30 nm.

3.4 UV-Vis Spectroscopy

The absorption study of thin films have been carried out using UV-Vis analysis. The absorption spectra measured in the range of 300-800 nm are shown in Fig.4. It can be pointed out that cobalt doping results in encroachment in the visible region with a red shift in band edge. The additional peaks in the range of 550 to 720 nm have been observed in Co-doped ZnO thin film. Inset of Fig.4 indicates close inspection in that range. Three additional peaks of Co-doped ZnO have been observed at 565, 610 and 655 nm, which can be attributed to the d-d transition of tetrahedral coordinated Co^{+2} ions in ZnO hexagonal wurtzite crystal structure. These peaks correspond to $^4\text{A}_2(^4\text{F}) \rightarrow ^4\text{A}_1(^4\text{G})$, $^4\text{A}_2(^4\text{F}) \rightarrow ^4\text{T}_1(^4\text{P})$ and $^4\text{A}_2(^4\text{F}) \rightarrow ^2\text{E}(^2\text{G})$ transitions¹⁴⁻¹⁵. These peaks have been observed with significant intensity in Co-doped ZnO nanoparticles¹⁰. The additional peaks indicate the presence of Co in the

ZnO host lattice. The Tauc relationship has been used to calculate the band gap of samples⁹

$$\alpha h\nu = B(h\nu - E_g)^n,$$

where α represent absorption coefficient given by $\alpha = -A/d$, (d is the thickness of sample cell and A is the absorbance), $h\nu$ is photon energy, B is a constant and E_g is the energy band gap of the material. The value of 'n' depends on the type of the transitions.

We have used Tauc plot [$(\alpha h\nu)^2$ versus $h\nu$] for band gap calculation. The extrapolation of the linear part that meets the abscissa indicates band gap energy (E_g) of the sample. Tauc plot for Pure and Co-doped ZnO thin film is shown in Fig. 5(a) and (b) respectively. We found the decrease in band gap due to Co doping. The band gap of pure ZnO thin film is 3.25eV, while for Co-doped ZnO it is 3.21eV. The observed small red shift in the band gap energy may be due to sp-d exchange interaction between ZnO band and electrons and localised d electron (moments) of doped Co ions. The cobalt doping causes an increase in charge carriers that affect the sp-d exchange interaction and results a red shift in the band gap. The band gap decrease due to cobalt doping has been observed in Co-doped ZnO nanoparticles¹⁰.

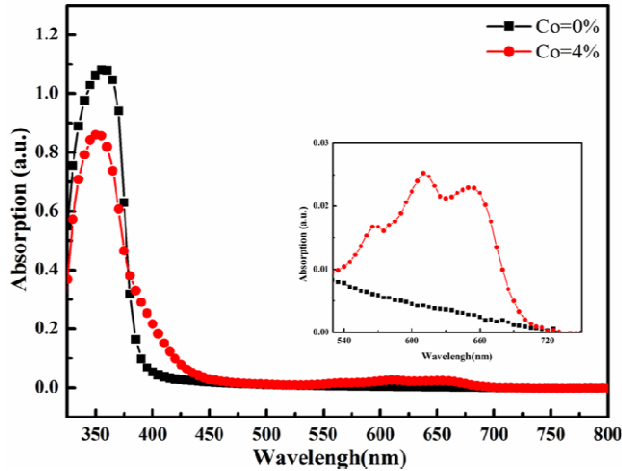


Fig.4: Absorption spectra of pure and Co doped ZnO thin film. Inset shows close inspection in the visible region.

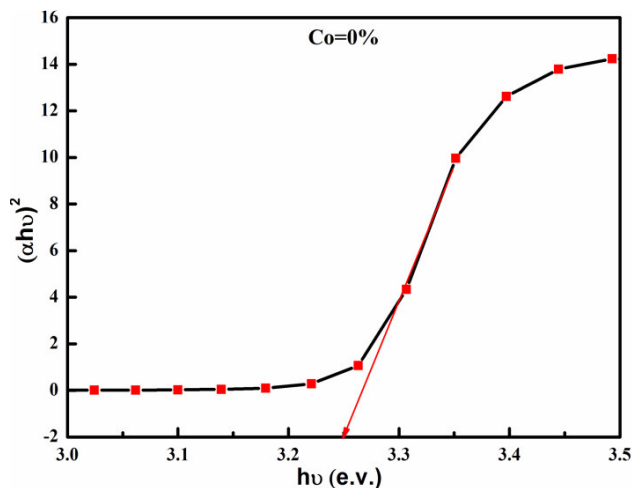


Fig.5(a): Tauc plot of ZnO thin film.

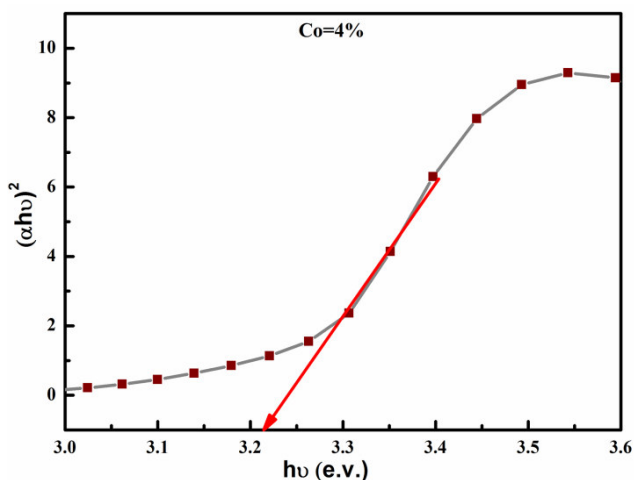


Fig.5(b): Tauc plot of Co doped ZnO thin film.

3.5 Photoluminescence Spectroscopy

The room temperature photoluminescence (PL) spectra of pure and cobalt doped ZnO thin film are shown in fig. ZnO shows emission in the visible region (370-425nm) with a prominent peak in violet colour (389 nm), while cobalt doped ZnO samples have intense peaks around 400nm with emission range 370-470nm. The observation indicates that Co doping slightly shifts the intense peak position of ZnO. We have also observed a small peak at 525nm (green colour). The peaks observed at 389, 400nm can be attributed to near band edge emission (NBE). The recombination of the excited electron from a localised level below the conduction band with the

hole in the valence band is responsible for NBE emission¹⁶. The intensity of NBE emission increases due to Co doping. This intensity enhancement can be attributed to increase in charge carriers in the system due to Co doping which favour the charge recombination process. The observed weak intensity green emission at 525 nm can be attributed to recombination of the electron with hole trapped in singly ionised oxygen vacancies¹⁰.

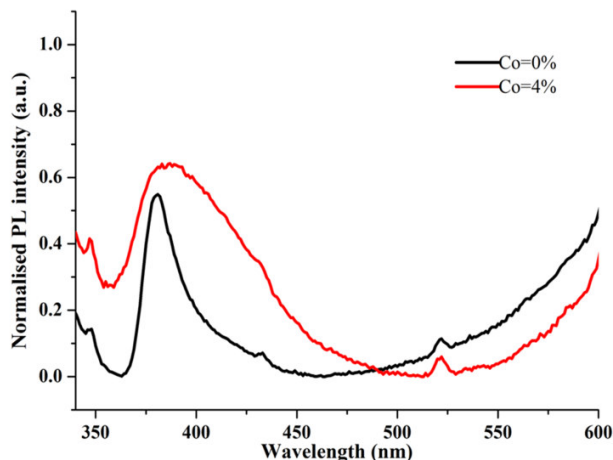


Fig.6: Photoluminescence spectra of pure and Co doped ZnO thin film.

4. Conclusion

In this work, we have prepared pure and Co-doped ZnO thin film with an easier route of synthesis. We are focussed on maintaining the crystalline quality of samples. The results of XRD indicate that all samples exhibit hexagonal crystalline structure. The AFM analysis ascertains smooth surface and formation of grains of approximately uniform size. The absorption study shows that Co concentration causes the occurrence of visible light absorption in the range 540-700 nm and encroachment of band edge in the visible region. The red shift in the band gap of samples has been observed due to Co doping. The photoluminescence study confirms the wide absorption visible range. The obtained modification in optical properties of ZnO can be useful for ZnO based optoelectronics devices.

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