Co²⁺ doped ZnO nanoflowers grown by hydrothermal method

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Undoped zinc oxide (ZnO) and cobalt doped ZnO nanostructures without any surfactant were grown by hydrothermal method by varying the process parameters such as molarity of precursors and time of growth. X-ray diffraction spectra of the sample show wurtzite ZnO without any secondary Co phases. SEM image confirms the formation of hexagonal shaped rods and these rods assembled like a flower. Inductively coupled plasma atomic emission spectroscopic (ICP AES) studies confirm the incorporation of cobalt in the ZnO nanostructures. The electronic structure as well as the optical properties of ZnO:Co²⁺ have been characterized. In the energy range below the band gap, the optical absorption spectra show the internal d–d transitions related to Co²⁺ incorporated on the Zn site in ZnO lattice. The g-values of ZnO:Co samples obtained from electron paramagnetic resonance confirms the incorporation of Co²⁺ in ZnO. Photoluminescence (PL) studies shows that these nanostructures exhibit a blue luminescence on excitation with wavelength 350 nm due to the Zn interstitial related defects.

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1. Introduction

Dilute magnetic semiconductor (DMS) have become a new area of research interest due to its potential applications in the field of spintronics.^{1)–4)} The basic requirement for practical applications is to achieve Curie temperature (T_c) well above the room temperature.⁵⁾ Transition metal doped semiconductors, namely ZnO, SnO₂ etc., have attracted a great research interest due to the prediction of room temperature ferromagnetism (RTFM) in them.^{6)–9)} However the origin of RTFM is not yet clearly understood. The preparation method and growth conditions play an important role in determining the magnetic behaviour of ZnO based DMS materials. Zinc oxide (ZnO) is a wide band gap (3.3 eV) II–VI compound semiconductor and having an exciton binding energy of 60 meV. Hydrothermal method is one of the most cost effective methods and flexible in terms nature of substrates due to its significantly low growth temperature employed. The low growth temperature prevents the diffusion of dopants to form metal clusters.

In this paper we report the synthesis of undoped and Co²⁺ doped ZnO nanostructures by hydrothermal method and their structural, morphological and optical properties by X-ray diffraction (XRD), scanning electron microscopy (SEM), photoluminescence (PL) and diffuse reflectance (DRS) measurements.

2. Experimental

Undoped ZnO and cobalt doped ZnO nanostructures were grown by hydrothermal method. An appropriate quantity of ammonium hydroxide was added to the mixture of zinc acetate (1 M–0.3 M) and cobalt nitrate (0.01 M–0.001 M) solution to adjust the pH value between 9–11. The Co content was changed by altering the molar ratio of zinc acetate and cobalt nitrate. The mixture was stirred vigorously for 20 min to form a homogeneous solution with the colour changing from pink to brown.

The resulting solution was then transferred into a teflon-lined autoclave, which was sealed and maintained at 100°C for 3–6 hrs, before being left to cool to room temperature naturally. A light green precipitate was obtained. After washing with distilled water several times, these samples were finally dried at 60°C for 2 hrs for further characterization. The experiment is repeated by varying process parameters such as duration of growth, molar concentration of precursors and growth temperature. The undoped ZnO nanoparticles were also synthesized in a similar manner described above but without adding Co(NO₃)₂.

The synthesized nanostructures were structurally characterized by X-ray diffraction technique using Rigaku D max-C X-ray diffractometer with Cu K α radiation (1.5418 Å). Morphology of the samples was analyzed using scanning electron microscopy (SEM) technique using JEOL Model JSM-6390LV. The exact amount of cobalt that is incorporated in the ZnO nanostructures was determined using inductively coupled plasma-atomic emission spectroscopic (ICP-AES) data using thermo electron IRIS INTREPID II XSP DUO. The optical band gap E_g was estimated from the UV–Vis–NIR diffuse reflectance spectroscopic (DRS) studies with JASCO V-570 spectrophotometer. The samples for this study were used in the form of powder and pure BaSO₄ used as the reference. Room temperature photoluminescence (PL) of the samples was measured on Horiba Jobin Yvon Fluoromax-3 spectrofluorimeter using Xe lamp as the excitation source.

3. Results and discussion

Figure 1 shows the powder X-ray diffraction patterns of cobalt doped ZnO nanostructures prepared at different molarity of zinc acetate and a growth temperature of 100°C for 3 hrs with a fixed cobalt nitrate concentration of 0.01 M. **Figure 2** shows the XRD pattern of cobalt doped ZnO nanostructures prepared at different molarity of cobalt nitrate, the zinc acetate was fixed at 1 M and the growth temperature being 100°C for 3 hrs. All the peaks in the X-ray diffraction profile could be assigned to the typical wurtzite structure of ZnO.¹⁰⁾ There are no characteristic

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Fig. 1. XRD patterns of Co doped ZnO nanostructures grown by hydrothermal method with different concentration of $\text{Zn}(\text{Ac})_2$, the $\text{Co}(\text{NO}_3)_2$ concentration fixed at 0.01 M and the growth temperature as 100°C for 3 hrs.

Fig. 2. XRD patterns of Co doped ZnO nanostructures grown by hydrothermal method with different concentration of $\text{Co}(\text{NO}_3)_2$, $\text{Zn}(\text{Ac})_2$ concentration fixed at 1 M and the growth temperature is 100°C for 3 hrs.

peaks of impurity phases regardless of the dopant concentrations. Thus the wurtzite structure is not modified by the addition of Co into the ZnO matrix. The wurtzite structure of the ZnO is not obtained as the concentration of the $\text{Co}(\text{NO}_3)_2$ precursor increases beyond 0.1 M. With increase of dopant concentration, the peak positions of cobalt doped ZnO shift towards high angles because Co ions have the smaller ionic radius ($0.72 \text{ \AA}$) than Zn ions ($0.74 \text{ \AA}$).¹¹⁾ It is found that the lattice parameters of Co doped ZnO nanostructures increases with molar concentration of cobalt nitrate. The increase in the lattice parameters is attributed to the cobalt substitution in zinc site of zinc oxide nanostructures.

Figure 3 shows the SEM image of the cobalt doped ZnO nanostructures synthesized at 100°C for 6 hrs from 0.3 M zinc acetate and 0.01 M cobalt nitrate. SEM image confirms the formation of hexagonal shaped rods and the rods assemble like a flower. The cobalt doped ZnO structures has an average diameter of about $0.56 \mu\text{m}$ and a length of about $13 \mu\text{m}$. **Figure 4** shows the SEM image of the cobalt doped ZnO nanostructures synthesized at 100°C , but for a duration of 3 hrs from 0.3 M zinc acetate and 0.001 M cobalt nitrate. It confirms that the width

Fig. 3. SEM image of the cobalt doped ZnO nanorods grown by hydrothermal method at a growth temperature of 100°C for 6 hrs.

Fig. 4. SEM image of the cobalt doped ZnO nanorods grown by hydrothermal method at a growth temperature of 100°C for 3 hrs.

Fig. 5. SEM image of the undoped ZnO nanorods grown at a temperature of 100°C for 6 hrs by hydrothermal method.

of the nanorods decreases as the time of growth decreases from 6 to 3 hrs, however there is not much change in the length of these rods which is about $13 \mu\text{m}$. **Figure 5** shows the SEM image of the pure ZnO nanorods synthesized at 100°C for 6 hrs from 0.3 M zinc acetate as precursor. Thus the doping of cobalt in ZnO matrix may generate some active sites around the circumference of ZnO nuclei, so that ZnO will preferentially grow on the active sites. Flower like ZnO nanostructures can be grown by varying the process parameters such as time of growth, temperature, pH etc.¹²⁾

Fig. 6. EPR spectra of Co doped ZnO nanostructures grown at 100°C for 6 hrs by hydrothermal method.

Fig. 7. Room temperature photoluminescence emission spectra of ZnO and Co doped ZnO nanostructures grown at 100°C for 6 hrs by hydrothermal method.

The exact amount of cobalt that is incorporated in the ZnO nanostructures was determined using ICP-AES data. The ICP-AES shows that cobalt incorporated into the nanostructures is about 0.11 atomic % for lower concentration of cobalt nitrate (0.001 M) and about 1.06 atomic % for higher concentration (0.01 M) of cobalt nitrate in the precursor solution. It is found that the Co content in the ZnO nanostructures increases with cobalt nitrate concentration.

The successful incorporation of Co^{2+} on Zn sites in the ZnO nanostructures is further confirmed by electron paramagnetic resonance (EPR) studies. A broad spectrum observed for these nanostructures due to their random orientation with respect to the magnetic field. The measured spectrum is broader for several reasons. First, Co^{2+} located near the surface of the nanostructures will see a different crystal field compared to Co^{2+} core of the nanostructures. Furthermore Co-Co interactions can also cause a broadening of the spectrum. The g value of Co^{2+} doped ZnO nanostructures, $g = 4.6109$ is comparable with reported values.¹³⁾ The EPR spectrum of $\text{ZnO}:\text{Co}^{2+}$ samples are shown in Fig. 6.

Figure 7 shows the room temperature photoluminescence emission spectra of ZnO nanostructures and cobalt doped ZnO nanostructures prepared at 100°C using 0.3 M zinc acetate for 6 hrs. Blue emission at 437 nm was observed for an excitation wavelength of 350 nm in the ZnO nanostructures and it may be due to Zn interstitial related defects.^{14),15)} The dominant transition at 1.876 eV due to the d-d transitions of Co^{2+} in

Fig. 8. Diffuse reflectance spectra of (a) undoped ZnO and cobalt doped ZnO nanostructures grown by hydrothermal method at a growth temperature of 100°C for 3 hrs using $\text{Zn}(\text{Ac})_2$ precursors of various molarity (b) 0.3 M (c), 0.5 M (d) and 1 M.

tetrahedral crystal fields is not seen in the room temperature PL spectra. Low temperature PL studies are necessary to observe the d-d transitions of Co^{2+} ions.¹⁶⁾

Figure 8 shows the diffuse reflectance spectra (DRS) of undoped ZnO and cobalt doped ZnO nanostructures synthesized by hydrothermal method at a growth temperature of 100°C for 3 hrs. Figure 8(a) corresponds to the DRS of undoped ZnO synthesized from 0.3 M $\text{Zn}(\text{Ac})_2$ and Fig. 8(b), (c) and (d) corresponds to that of Co doped ZnO synthesized from 0.3, 0.5, and 1 M $\text{Zn}(\text{Ac})_2$ respectively for a particular concentration of $\text{Co}(\text{NO}_3)_2$ of 0.01 M. Two bands of absorption are observed for the Co doped ZnO samples: an intense absorption peak in the ultraviolet region and a weak band in the visible region (1.8–2.3 eV). The absorption at high energies is due to the band to band transition of ZnO and the visible band is due to the Co^{2+} d-d internal transitions. The three peaks observed at positions 1.89, 2.03, 2.19 eV have been identified as the internal transitions 4A_2 to $^2T_1(\text{G})$, $^4T_1(\text{P})$ and $^2A_1(\text{G})$ of substitution of Co^{2+} on Zn sites in ZnO, respectively.¹⁵⁾ The band gap of the material can be obtained from the plot and it shows that the band gap of the Co doped ZnO nanostructures increases from 3.32 to 3.44 eV as the concentration of zinc acetate precursor decreases from 1 to 0.3 M while other parameters are kept constant. The band gap of undoped ZnO is found to be 3.42 eV. This blue shift in the band gap of undoped ZnO and Co doped ZnO nanostructures are due to the quantum confinement effects.

4. Conclusions

Cobalt doped zinc oxide (ZnO) and undoped ZnO nanostructures were synthesized by low temperature hydrothermal method by varying the process parameters such as molarity of precursors and time of growth. The structural studies of these Co doped ZnO and undoped ZnO nanostructures were characterized by X-ray diffraction techniques. SEM images show that width of the nanorods decreases with decrease in the duration of hydrothermal growth. We observed the blue PL emission at 437 nm from the ZnO nanostructures at an excitation wavelength of 350 nm. It is due to Zn interstitial related defects. Three peaks observed at positions 1.89, 2.03, 2.19 eV in DRS spectrum confirms the presence of substitutional incorporation of Co^{2+} on

the Zn site in the ZnO matrix. The spectrum also shows that the band gap of ZnO nanostructures is blue shifted from that of bulk ZnO powder due to quantum confinement effects. ICP AES studies confirm the incorporation of cobalt in the ZnO nanostructures. The g value obtained from the EPR measurements is comparable with theoretical values which confirm the Co²⁺ incorporation in ZnO matrix.

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