Structural and Optical properties of Mn doped ZnO Nanoparticles

Teny Theresa John, K. R. Priolkar* and P. R. Sarode
Department of Physics, Goa University, Taleigao Plateau, Goa - 403206

**Email: krp@unigoa.ac.in*

Abstract

Mn-doped ZnO nanoparticles prepared by Chemical Bath Deposition (CBD) with substituent fraction ranging from x= 0.01 to x=0.05 are characterized structurally and optically using X-Ray Diffraction (XRD), UV-Vis Absorption and Fourier Transform Infrared Spectroscopy (FTIR). The unique feature of the sample preparation is the low temperature processing. The band edge shows a red shift on higher doping concentration. FTIR spectra reveal a transition of Mn^{4+} state to Mn^{2+} state on increasing doping concentration.

INTRODUCTION

Recently there has been intense searching for ferromagnetic ordering in doped, dilute magnetic semiconductors focusing on possible spin-transport properties, which has many potentially interesting device applications. One natural way of incorporating magnetism into a non magnetic semiconductor of II-VI or III-V type is to substitute transition metal ions for the nonmagnetic ions of the semiconductor.

One material which shows particular promise for yielding a suitable ferromagnetic semiconductor is ZnO. Stimulated by the theoretical predictions of room temperature ferromagnetism in DMSs by Dietl et al [1] many systems of ZnO:TM (TM = Mn, Co, Ni, V, Cr etc) have been synthesized by different methods and extensively studied, but controversial results are reported. The first observation of ferromagnetism above room temperature for dilute (< 4%) Mn doped ZnO was reported by P. Sharma et al [2]. In light of all controversies, we have undertaken a detailed study of $Zn_{1-x}Mn_xO$ samples. In this paper, we combine XRD, UV-Vis absorption and FTIR for structural and optical properties of Mn doped ZnO.

EXPERIMENT

For synthesis CBD method has been chosen because it is cost effective, requires only low temperature processing and allows homogeneous dispersion of dopants. The ammonium zincate bath used for the deposition of ZnO is prepared by adding ammonium hydroxide (30% ammonia solution) to an aqueous solution of zinc acetate ($(CH_3COO)_2Zn.2H_2O$) with constant stirring. At first a white precipitate of zinc hydroxide ($Zn(OH)_2$) appears. On further addition of ammonia, the precipitate dissolves forming the $(NH_4)_2ZnO_2$ bath. The final reaction that leads to the formation of ZnO from ammonium zincate bath is

$$(NH_4)_2ZnO_2 + H_2O \longrightarrow ZnO + 2\,NH_4OH \quad \ldots \quad (1)$$

An excess of alkali is required to have a stable ammonium zincate bath. The bath was kept at 70°C. The precipitate which formed was separated from the solution by filtration and dried in the oven at 50°C. It was then pressed into pellets and annealed at 160°C for 1 hr on hot plate prior to structural characterization. For $Zn_{1-x}Mn_xO$ required quantity of aqueous solution of manganese acetate is added with stirring to the zinc acetate solution prior to the addition of ammonia so that the x value varies as 0.01, 0.02, 0.03 and 0.05. The samples thus prepared are named as Mn_0 (undoped), Mn_01, Mn_02, Mn_03 and Mn_05 respectively.

XRD patterns were recorded on a Rigaku D-Max IIC diffractometer with CuK_α radiation. The collected data were subject to Rietveld profile analysis using Fullprof suite. Optical absorption and FTIR studies were done using UV-Vis2401PC and FTIR-8900 (Shimadzu) spectrophotometers respectively.

RESULTS AND DISCUSSION

The x-ray diffractogram of the synthesized powder with Rietveld refinement is shown in Fig.1.

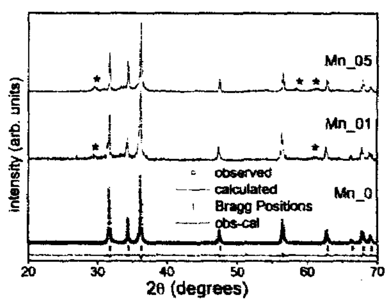

Figure 1 XRD pattern of undoped and Mn doped ZnO nanoparticles. Rietveld refinement of undoped sample is also shown.
*denotes impurity peaks

XRD pattern of nanosized undoped ZnO shows reflections of pure hexagonal wurtzite structure (space group

P6₃mc).The lattice parameters obtained (a = b = 3.251(1) Å and c = 5.208(8) Å) match well with the reported values [3]. The unit cell volume was calculated to be 47.68 $Å^3$. A few impurity peaks have grown on doping Mn, which correspond to different phases of zinc manganese oxide. As the amount of Mn increases, the x-ray peak width increases upto Mn_02 and then decreases. Evolution of lattice parameters and cell volume, as obtained from Rietveld refinement, with x is shown in Fig. 2. The cell parameters and volume decreases linearly with x from x = 0 to x = 0.02 and then increases. Grain size as obtained from Williamson-Hall plot also shows similar variation. The value decreases from 47 nm (Mn_0) to 28 nm (Mn_02) and then increases (51 nm for Mn_05) on further doping.

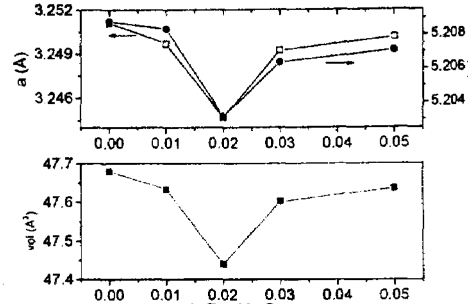

Figure 2 Evolution of a and c cell parameters and cell volume with increasing x in $Zn_{1-x}Mn_xO$

Optical absorption spectra are recorded in the wavelength region 300-900 nm. The band gap of sample Mn_0 is found to be 3.2(4) eV.

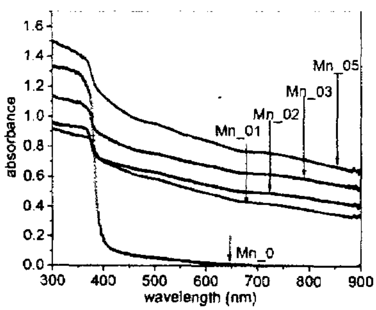

Figure 3 Optical absorption of undoped and Mn doped samples

From the spectra it is clear that there is almost no absorption in the visible region for this sample. But for doped samples, the absorption edge is not sharp and there is absorption in this region. This may be due to the introduction of defect states due to doping of Mn. The shoulders in the absorption edge at thresholds lower than the energy gap might be transition between an impurity and a band. The absorption edge of the Mn_05 sample clearly shifted towards longer wavelength side. Figure 4 shows FTIR spectra of undoped and doped ZnO nanoparticles in the range 350 to 1000 cm^{-1}. The bonding between Zn-O (468 cm^{-1}) is clearly seen. [4].

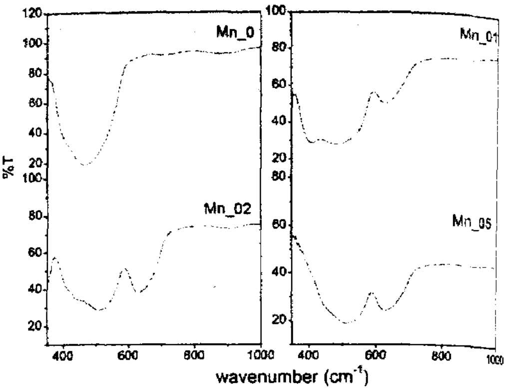

Figure 4 FTIR spectra of undoped and Mn doped samples

Two new bands appear at around 625 cm^{-1} (for all Mn doped samples) and 450 cm^{-1} (for Mn_01 and Mn_02 only). From the spectra recorded for pure MnO_2, it is seen that the band at around 450 cm^{-1} corresponds to MnO_2 phase. On increasing Mn concentration (Mn_03 and Mn_05) this band disappears. This is perhaps because of transition from Mn^{4+} to Mn^{2+} state with increasing Mn doping. Such a transition is also seen in the behaviour of cell parameters and cell volume. An abrupt increase in cell parameters and volume beyond 2% Mn doping can be attributed to ionic sizes of Zn^{2+}(0.60 Å), Mn^{4+}(0.39 Å) and Mn^{2+} (0.66 Å). Substitution of Mn in 4+ state at lower Mn doping results in a decrease while nearly equal cell volumes of Mn_03, Mn_05 and undoped ZnO indicate Mn to be in 2+ state.

CONCLUSION

Undoped and Mn-doped ZnO nanoparticles were prepared using chemical bath depositon with lattice parameters varying with the extent of doping. Incorporation of Mn into ZnO lattice is obvious from the optical absorption and FTIR studies. FTIR measurements predict a possible Mn^{4+} to Mn^{2+} transition in the doped samples which is supported by the variation in lattice parameters and cell volume. Further confirmation studies are going on.

REFERENCES

[1] T. Dietl, et al Science **287** (2000) 1019.
[2] P. Sharma et al Nature Materials **2** (2003) 873.
[3] S. Kolesnik, et al J. Appl. Phys. **95** **(5)** (2004) 2582.
[4] Y. J. Kwon, et al Ceramic Processing Research 3 (3) (2002) 146.

ACKNOWLEDGEMENTS

Authors thank DST, Govt. of India for funding under the project.