Materials Research Bulletin 47 (2012) 1417–1422

Contents lists available at SciVerse ScienceDirect

Materials Research Bulletin

journal homepage: www.elsevier.com/locate/matresbu

Room temperature ferromagnetism in Co doped ZnO within an optimal doping level of 5%

J. Mohapatra [a], D.K. Mishra [b,*], Debabrata Mishra [c], A. Perumal [c], V.R.R. Medicherla [a], D.M. Phase [d], S.K. Singh [b]

[a] Department of Physics, Institute of Technical Education and Research, Siksha 'O' Anusandhana University, Bhubaneswar 751030, Orissa, India
[b] Advanced Materials Technology Department, Institute of Minerals and Materials Technology (CSIR), Bhubaneswar 751013, Orissa, India
[c] Department of Physics, Indian Institute of Technology, Guwahati 781039, India
[d] UGC-DAE, CSR, University Campus, Khandwa Road, Indore 452001, India

ARTICLE INFO

Article history:
Received 24 September 2011
Received in revised form 29 December 2011
Accepted 29 February 2012
Available online 7 March 2012

Keywords:
A. Semiconductors
A. Magnetic materials
C. Raman Spectroscopy
C. X-ray diffractions
D. Magnetic properties

ABSTRACT

We report on the structural, micro-structural and magnetic properties of $Zn_{1-x}Co_xO$ ($0 \le x \le 0.1$) system. Electron probe micro-structural analysis on 5% Co doped ZnO indicates the presence of segregated cobalt oxide which is also confirmed from the Co 2p core level X-ray photoelectron spectrum. The presence of oxygen defects in lower percentage of Co doped ZnO (≤5%) enhances the carrier mediated exchange interaction and thereby enhancing the room-temperature ferromagnetic behaviour. Higher doping percentage of cobalt (>5%) creates weak link between the grains and suppresses the carrier mediated exchange interaction. This is the reason why room temperature ferromagnetism is not observed in 7% and 10% Co doped ZnO.

1. Introduction

Transition metal ions doped zinc oxide system finds application in optoelectronics, solid state light emitting diodes, photonics and also in data storage systems [1–3]. There is a great enhancement of atomic spin effect when transitional metallic elements such as Fe, Co, Ni and Mn along with some rare earth elements are present in oxide systems and this enhancement may be due to the cooperative interactions of large number of these atomic spins producing a region where all atomic spins within it are aligned parallel [4–6].

Among all transition metals doped ZnO system, Co-doped ZnO has attracted considerable interest [7]. There have been a number of reports about the observation of room-temperature ferromagnetism (RTFM) in thin films of $Zn_{1-x}Co_xO$ [5,8–10]. However, recent works on well-characterized polycrystalline $Zn_{1-x}Co_xO$ samples indicate that they are not ferromagnetic at room temperature [11–17], except for the samples in an isolated report by Deka et al. [18]. A number of groups observed no ferromagnetism (FM) in $Zn_{1-x}Co_xO$ [11–13], while Ueda et al. [5] and Peng et al. [19] reported FM in Co-doped ZnO thin films. Many studies reported that presence of additional carriers apart from the doped magnetic ions is essential [20–24] for the appearance of ferromagnetism in TM doped ZnO bulk and nanocrystalline samples. This can be generated either by additional carrier doping or by development of defects. Only hole doping promotes RTFM in Co-doped ZnO has been predicted from the computational study done by Spaldin [25]. This is in contrast to RTFM observed by Schwartz and Gamelin [26] in electron-doped and Co-doped ZnO. Through an analysis of density functional calculations, Sluiter et al. [27] showed that both electron doped with zinc interstitials and hole doped with zinc vacancies make the Co:ZnO samples strongly FM. Kittilstved et al. [28] and Rubi et al. [29] demonstrated that the FM of n-type ZnO:Co thin films and powders could be switched on or off by chemical manipulation using nitrogen or oxygen, respectively. Zhu et al. reported RTFM in two-step-prepared Co doped ZnO bulks by Zn treatment [30]. The origin of observed FM in these samples is still a debatable.

In the present study, room temperature ferromagnetism has been observed for 3% and 5% Co doped ZnO. The presence of oxygen vacancies increases with the increase in Co percentages and the carrier mediated exchange interaction is forbidden due to the weak

* Corresponding author at: Advanced Materials Technology Department, Institute of Minerals and Materials Technology (CSIR), Bhubaneswar 751013, India. Tel.: +91 674 2379456; fax: +91 674 2581637.
E-mail address: dilipiuac@gmail.com (D.K. Mishra).

0025-5408/$ – see front matter © 2012 Elsevier Ltd. All rights reserved.
doi:10.1016/j.materresbull.2012.02.046

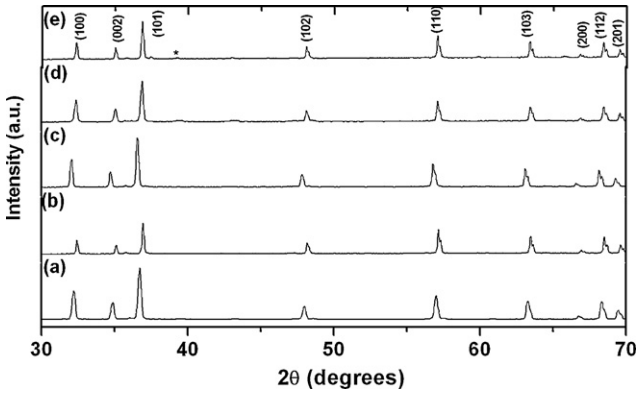

Fig. 1. XRD Patterns of polycrystalline $Zn_{1-x}Co_xO$ system ((a) $x = 0.00$; (b) $x = 0.03$; (c) $x = 0.05$; (d) $x = 0.07$; and (e) $x = 0.1$) (* indicated the impurity peak of Cobalt oxide).

links between the grains. This is the reason why the ferromagnetic ordering in higher percentage of Co doped ZnO is suppressed and paramagnetic behaviour is enhanced.

2. Experimental details

Commercial grade oxide powders of Zn and Co (99.9%) were taken to prepare samples of different compositions. The compositions of the $Zn_{1-x}Co_xO$ oxides were taken with different x ($x = 0$, 0.03, 0.05, 0.07, 0.1) values and the respective powders were mixed thoroughly and heated at 500 °C for 5 h following several times quenching and grinding. The powders were mixed with polyvinyl alcohol (PVA, 1 wt %) and pressed into pellets at a pressure of 6 t/cm^2. The pellets thus prepared were slowly heated at 500 °C to remove the PVA binder and other low temperature volatiles (if present) and then were used for sintering at 700 °C for seven hours. X-ray diffraction (XRD) using Philips diffractometer (Model 1715) and Fourier transform infrared (FTIR) characterizations were carried out for structural analysis. Micro-Raman and Scanning electron microscopic studies were carried out for the defect and micro-structural analysis using Renishaw in-Via micro-Raman spectrometer and Philips FEG Xl'30 respectively. Elemental distribution and compositional mapping were carried out using electron probe microstructure analyzer (EPMA) and the elemental qualitative analysis has been carried out using EDX attached to EPMA. X-ray Photoelectron Spectroscopy (XPS) measurements were performed using a VG ESCA system. This system is equipped with dual Mg–Al anode and has a base pressure of 1.0×10^{-10} Torr. The system resolution is 0.9 eV. XPS measurements of surfaces were carried out using the Mg Kα X-ray source with pass energy of 20 eV. Magnetic field dependent magnetization measurements of all the samples were recorded at room temperatures (300 K) using Vibration Sample Magnetometer (VSM) at maximum field of 15 000 Oe.

3. Results and discussions

The XRD patterns of $Zn_{1-x}Co_xO$ system for $x = 0.00$; 0.03; 0.05; 0.07 and 0.1 are shown in Fig. 1. The diffraction pattern of $Zn_{1-x}Co_xO$ system for $x = 0.03$; 0.05; 0.07 and 0.1 shows the similar reflection peaks of ZnO which indicates that wurtzite structure is not disturbed a lot by Co substitution. No additional peaks are observed for $x = 0.03$ and 0.05 in Co doped ZnO system due to absence of any impurities. However, the secondary phases of cobalt oxides are clearly seen in the XRD pattern of 7% and 10% Co doped ZnO system. It is known that tetrahedral Co ions have slightly lower ionic radii of 0.72 Å as compared to the tetrahedral Zn ions (0.74 Å). Substituting of Co ion in the Zn site will show the XRD peak shift towards the higher 2θ angle. It is clearly evidenced in 3% Co doped ZnO whereas higher percentage of Co above 3% does not substitute Zn site of the ZnO matrix. Even there is no signature

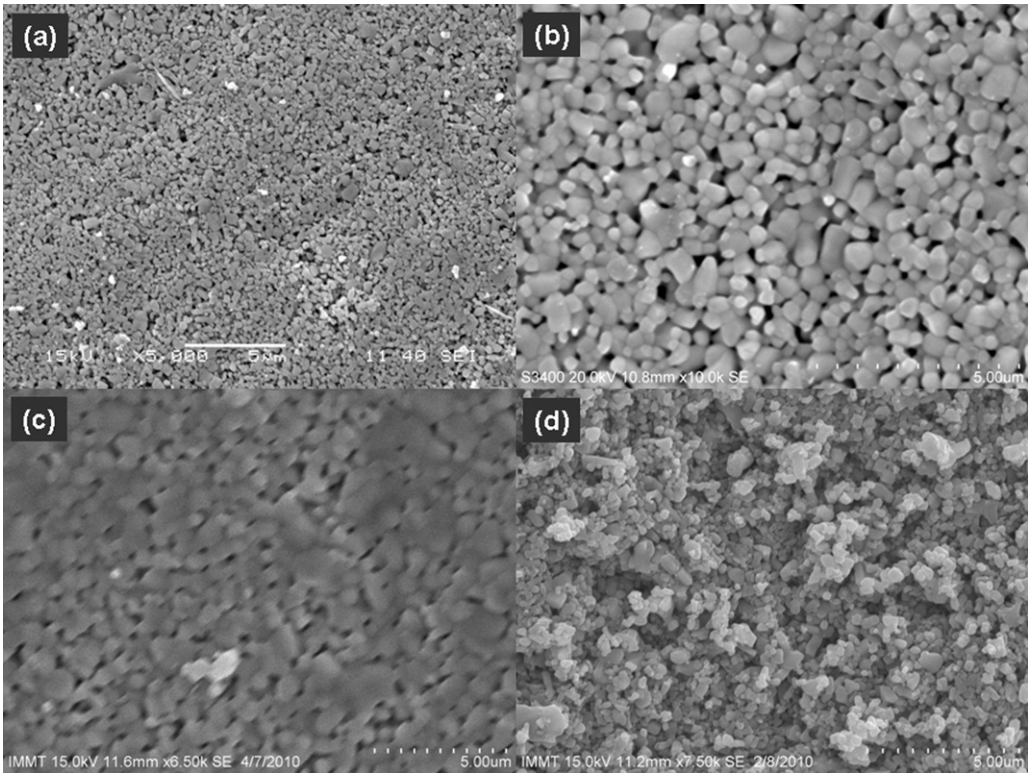

Fig. 2. SEM pictures of $Zn_{1-x}Co_xO$ system ((a) $x = 0.03$; (b) $x = 0.05$; (c) $x = 0.07$; and (d) $x = 0.1$).