

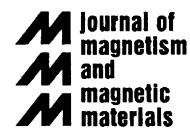


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A study of room-temperature ferromagnetism in transition metal and fluorine-doped spray-pyrolyzed SnO_2 thin films

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Abstract

Room-temperature ferromagnetism has been observed in Co- or Mn-doped SnO_2 and Co- and F-co-doped SnO_2 thin films. A maximum magnetic moment of $0.80\mu_{\text{B}}/\text{Co}$ ion has been observed for $\text{Sn}_{0.90}\text{Co}_{0.10}\text{O}_{1.925-\delta}\text{F}_{0.075}$ thin films, whereas in the case of $\text{Sn}_{1-x}\text{Mn}_x\text{O}_{2-\delta}$ it was $0.18\mu_{\text{B}}/\text{Mn}$ ion for $x = 0.10$. The magnetization of both $\text{Sn}_{1-x}\text{Co}_x\text{O}_{2-\delta}$ and $\text{Sn}_{1-x}\text{Co}_x\text{O}_{2-y-\delta}\text{F}_y$ thin films depends on the free carrier concentration. An anomalous Hall effect has been observed in the case of Co-doped SnO_2 films. However, the same was not observed in the case of Mn-doped SnO_2 thin films. Carrier-mediated interaction is convincingly proved to be the cause of ferromagnetism in the case of Co: SnO_2 . It is, however, proposed that no carrier-mediated interaction exists in the case of Mn: SnO_2 . Present studies indicate that dopants and hence electronic cloud–lattice interaction plays an important role in inducing ferromagnetism. © 2008 Elsevier B.V. All rights reserved.

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1. Introduction

The thrust for miniaturization in the electronic industry and bringing in multifunctionality in a material has resulted in spintronics, which combines the two important degrees of freedom of a charged particle, i.e., the spin and charge in a single material. To achieve this, the semiconductor that forms the backbone of the IC industry should be able to store the information at room temperature (RT) and this is predicted to be achieved by introducing transitional metal dopants such as Co, Fe, Mn, Ni, Cr, V, etc. into conventional semiconductors. Realizing room temperature ferromagnetism (RTFM) with reproducible results is a challenge, posing the scientific community. For any practical applications, the Curie temperature (T_{c}) should be well above the RT. After the theoretical prediction of RTFM in p-doped Mn-doped GaP and ZnO by Dietl et al. [1] and the discovery of RTFM in Co-doped TiO_2 by Matsumoto

et al. [2], much attention has been paid to wide band gap semiconductors. RTFM has been reported in many TM-doped TiO_2 [3–5], ZnO [6–8], CuO [9], SnO_2 [10–14], In_2O_3 [15–18] and GaN [19,20] systems. These wide band gap semiconductors combine semiconductivity and transparency with ferromagnetism, which may result in novel devices.

In the present work, an SnO_2 semiconductor has been doped with Co, Mn and F to induce RTFM, owing to its metal-like conductivity, easy tunability of conductivity by using dopants like F, high visible transparency [21] and an already existing widespread industry. Though the observation of RTFM has been reported in TM-doped SnO_2 degenerate semiconductors, the results are not in complete agreement and also the mechanism responsible for ferromagnetism is not well understood. At this point, we strongly feel that RTFM in this system has to be reinvestigated, with an aim to understand the mechanism responsible for ferromagnetism.

In this paper, we present our studies on structural, magnetic, electrical and optical properties of Co: SnO_2 and Mn: SnO_2 thin films as well as of F- and Co-co-doped and F- and Mn-co-doped SnO_2 thin films. The analysis of various properties indicates that a carrier-mediated indirect

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exchange interaction is responsible for the observed ferromagnetism in Co-doped SnO_2 thin films, whereas this mechanism is not operative in Mn: SnO_2 systems.

2. Experimental procedure

The basic precursors used for the deposition of Co: SnO_2 and Mn: SnO_2 thin films are $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ for Sn, $(\text{CH}_3\text{COO})_2\text{Co} \cdot 4\text{H}_2\text{O}$ for Co and $(\text{CH}_3\text{COO})_2\text{Mn} \cdot 4\text{H}_2\text{O}$ for Mn and NH_4F for F-doping. In the case of Co: SnO_2 , the constituent precursors have been spray pyrolyzed at 450°C one after another, rather than first mixing in the solution. To get the films of Mn: SnO_2 , the constituent precursors have been mixed in the solution, and the resultant solution has been spray decomposed at 450°C on quartz substrates. The films have been then air annealed at a temperature of 500°C for 30–60 min. The spray depositions have been carried out in an ambient atmosphere using nitrogen as carrier gas at a pressure of $\sim 0.4 \text{ kg/cm}^2$.

Structural characterization of these thin films was carried out by X-ray diffraction (XRD; goniometer resolution = 0.001°) in a glancing angle mode with $\text{Cu K}\alpha$ radiation using a Philips X'pert PRO (Model PW 3040) system. All the diffractograms were recorded under slow scan with a step size of 0.01° and a counting time of 2 s for each step, so that it should be possible to detect the presence of even small quantities of impurities/trace phases. Optical absorption study of these films was carried out at RT by employing Perkin-Elmer double beam spectrophotometer (Model Lambda 900) having a spectral resolution of 0.05 and 0.2 nm in the UV–VIS and NIR ranges, respectively. The magnetization measurement and its temperature dependence were carried out by using an EG&G PAR make vibrating sample magnetometer (VSM, Model 155), having a sensitivity of $5 \times 10^{-5} \text{ emu}$. The calibration and sensitivity of the system were checked (each time a new sample is loaded) with a yttrium iron garnet standard sample (NIST, USA) whose moment falls in the same range as that of the samples under study. Measurement of electrical resistivity of the samples was carried out by using Keithley's source meter (Model 2440) and nanovoltmeter (Model 2182), in van der Pauw geometry at RT. In order to identify the nature of the charge carriers, and to estimate the carrier concentration, Hall measurement of the samples was also performed in the van der Pauw geometry, with the help of Keithley's Hall switch system (Model 7001) at RT. The thickness of the samples was calculated accurately (up to $\pm 1 \text{ nm}$) by simulating the multiple interference pattern obtained from the optical transmittance measurement.

3. Results and discussion

3.1. X-ray diffraction

XRD studies of $\text{Sn}_{1-x}\text{Co}_x\text{O}_{2-\delta}$ thin films ($0 \leq x \leq 0.15$, with a step of 0.025) indicate that upto $x = 0.125$, no peaks

other than that of rutile (cassiterite) phase of SnO_2 are seen, whereas for $x = 0.15$, a peak of Co_3O_4 starts appearing, indicating the solubility limit of Co in SnO_2 to be less than 15 at% (Fig. 1). Lattice constants ' a ' and ' c ' showed a slight decrease when the Co concentration increases up to 0.10. The little change in the lattice constants indicates that thickness of the films is small enough to see any significant variations through XRD. It has been observed that the intensity of certain peaks (101) and (200) shows a systematic evolution when the Co concentration in the film increases. The intensity ratio $I_{(101)}/I_{(200)}$ decreases from 0.221 to 0.076 when the Co concentration increases up to 0.10, indicating the incorporation of Co in the SnO_2 lattice. The observed decrease in the intensity ratio $I_{(101)}/I_{(200)}$ up to $x = 0.10$ is ascribed to the substitution of Sn by Co in the lattice of SnO_2 . It is emphasized here that the atomic scattering factor for Co is almost half the value for Sn, since the atomic number of Co is 27, as against a value of 50 for Sn. Therefore, any substitution of Sn by Co changes the structure factor of the lattice, which, in turn, reflects in the change in the XRD peak intensities on Co-substitution. This systematic evolution of (101) and (200) peaks of SnO_2 , with increase in Co concentration, is therefore linked with the incorporation of Co into the SnO_2 matrix. Park et al. [22] have also reported a systematic evolution of (101) and (200) peaks in Co-doped TiO_2 thin films. The increase in the intensity ratio, $I_{(101)}/I_{(200)}$, above a Co concentration of 10 at% is possibly due to the crossover from substitutional to interstitial site incorporation of Co in the SnO_2 lattice, as this would enhance the structure factor and hence the intensity. The XRD of $\text{Sn}_{1-x}\text{Co}_x\text{O}_{2-\delta}$ thin films also reveals the formation of rutile phase of SnO_2 without any indication of any secondary phases.

The XRD of $\text{Sn}_{1-x}\text{Mn}_x\text{O}_{2-\delta}$ films ($0 \leq x \leq 0.15$, with a step of 0.025) indicates that up to an Mn concentration of

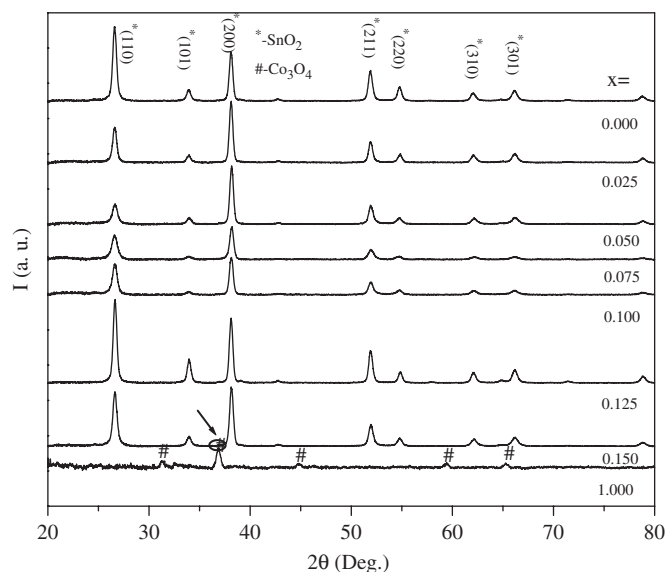


Fig. 1. X-ray diffractograms of $\text{Sn}_{1-x}\text{Co}_x\text{O}_{2-\delta}$ ($0 \leq x \leq 0.15$) thin films.

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