Proceedings of the Third Moscow International Symposium on Magnetism (2005)

Magnetooptical Faraday effect in Cobalt-doped SnO_2 transparent semi-conducting films prepared by spray pyrolysis technique

M. R. Alinejad[a], M. Ghanaatshoar[b], M. M. Tehranchi[b], M. M. Bagheri Mohagheghi[a], S.M. Mohseni[b,*]

[a]*Dept. of Physics, Faculty of Science, Ferdowsi Univ., Mashhad, Iran*
[b]*Laser Research Institute, Shahid Beheshti University, Evin, 1983963113 Tehran, Iran*

Abstract

In the present work, Magnetooptical and structural properties of Co doped SnO_2 transparent semi-conducting films deposited by spray pyrolysis technique are studied. The SnO_2: Co diluted magnetic semiconductors were deposited on the glass substrate at substrate temperature of 480 °C using an aqueous- ethanol solution consisting of tin and cobalt chloride. Doping level of cobalt chloride is changed from 0 to 25 at wt. % in solution. The X-ray diffraction (XRD) patterns show that the SnO_2: Co deposited films are polycrystalline tin-oxide single phase with the average grain size of 30 nm. Magnetooptic Faraday rotation and consequently the magnetization of films reduce by increasing Co dopant in the structure.

PACS: 75.50.Pp; 81.15.Rs; 78.20.Ls

Keywords: Diluted magnetic semiconductors; Faraday rotation; Spray pyrolysis technique

1. Introduction

Nowadays, modern information technology in new nano-electronic and photonic devices utilizes the spin degree of freedom in magnetic materials to store information and make useful them for sensor application. Magnetoelectronics is a novel interesting and fast developing field where combines both feature: the charge and the spin of electrons, which is called spintronics. Spintronic devices such as spin-valves, spin light-emitting diodes, non-volatile memory, logic devices, optical isolators and ultrafast optical switches are some of the areas of interest for introducing the ferromagnetic properties at room temperature in a semiconductor [1]. Development of new ferromagnetic semiconductors with appreciable spontaneous magnetization and coupling between semiconducting and magnetic degrees of freedom at room temperature has become an important challenge of material science [2].

Doping non-magnetic semiconductors with impurities to change their properties, usually to p- or n-type using magnetic elements make them magnetic. This category of semiconductors, called Diluted Magnetic Semiconductors (DMSs). They exhibit both semiconducting and magnetic properties and they offer unprecedented opportunities for spintronic devices [2-5]. DMSs have attracted considerable attention in the past few years in view of their projected potential for the development of novel

* Corresponding author. Tel.: +98 21 2413350; fax: +98 21 2418698.
E-mail address: m-mohseni@cc.sbu.ac.ir.

magneto-opto-electronics. These materials exhibit a spin-dependent coupling between localized states and those in the valence and conducting bands. The report of room temperature ferromagnetism in TiO_2: Co oxide film [6] has obviously encouraged experimental studies and intensive experimental works has begun in condensed matter community on oxide-type DMS [3]. Toward this end, one approach is to introduce magnetic dopant into non-magnetic solids, and expectation that they not only remain magnetically active but also couple with the electronic states of the solid. Considerable success has been achieved in inducing ferromagnetism by transition elements doping in compound semiconductor system [3, 5] although the Curie temperature are much lower than room temperature. Early attempts at the manufacture of DMS oxide used ZnO as the host and yielded mixed results [7-10]. Currently, DMSs have been found for SnO_2, In_2O_3, TiO_2 and ZnO transparent thin films with magnetic dopant such as Co, Mn and Fe [1-11]. They stay in their magnetization states in the more than room temperature. With respect to TiO_2-based thin films, some researchers have looked at other matrices having the same rutile type structure [3, 11]. Moreover, SnO_2 has an n-type conduction which is potentially interesting for spintronic devices [12]. Ogale and his co-workers [11] have deposited Co-doped SnO_2 thin films using pulsed laser deposition (PLD) technique. They concluded room temperature ferromagnetism with Curie temperature (T_c) as high as 650 K. Moreover, they have observed giant magnetic moment in SnO_2: Co DMS structure which has not been seen in any DMS systems, thus far.

In the present paper SnO_2: Co films with various doping level using spray Pyrolysis technique have been deposited. Structural and Magnetooptical properties of fabricated materials have been studied.

2. Experiments

2.1. Material preparation and deposition of films

The undoped SnO_2 thin film have deposited using an aqueous-ethanol solution including $SnCl_2*2H_2O$, H_2O and CH_3CH_2OH with the same weight percentage (1: 1: 1) and a few ml of hydrochloric acid by the spray pyrolysis technique. Also, Co doped SnO_2 films have been prepared using certain amounts of $CoCl_2.6H_2O$ that added to the initial solution from 0 to 25 wt. % {2 wt. %, 4 wt. %, 6 wt. %, 8 wt. %, 10 wt. %, 12.5 wt. %, 20 wt. %, 25 wt. %}, without any changes in the clarity of the solution. The spray solution compositions, atomic concentration ratio of [Co/Sn] in solution and films are shown in Table 1.

Table 1 Co-concentration doped in SnO_2, before and after deposition.

$CoCl_2.6H_2O$ (wt% in solution)	$SnCl_{2,2}H_2O$ (mole in solution)	$CoCl_2.6H_2O$ (mole in solution)	[Co] / [Sn] (at.% in solution)	[Co] / [Sn] (at.% in film)
0	0.146	0.000	0.0	0.00
2	0.146	0.007	4.8	5.22
4	0.146	0.0146	10.0	6.80
6	0.146	0.022	15.0	8.91
8	0.146	0.029	19.8	11.41
10	0.146	0.036	24.6	16.65
12.5	0.146	0.045	30.8	18.67
15	0.146	0.054	36.9	22.36
20	0.146	0.073	50.0	30.50
25	0.146	0.091	62.3	38.10

Firstly, for preparing films, the glass substrates were cleaned and placed on the hot plate. The hot plate temperature was kept in the rage of 480 to 500 °C which is known to be the optimal range for the formation of SnO_2 films. After reaching 500 °C, the solution was sprayed on the hot glass substrate in the following condition: carrier-gas, O_2, pressure: 1.7 - 2 atm., flow rate of solution: 10 ml/min., solution volume: 12 cc, substrate-to-nozzle distance: 45 cm. For preventing rapid reduction in hot plate temperature, spraying was done in short time intervals. All experiments have been carried out approximately at the same conditions. The metallic salt solution, when sprayed onto a hot substrate, pyrolitically decomposes and a chemical reaction takes place on the heated substrate and at last a thin layer of SnO_2 (undoped and doped) is deposited. Thin layers with about 0.5 μm thickness are prepared in this manner, as estimated by SEM micrographs.

2.2. Structures and Magnetooptics measurements

For investigating the structural properties, the X-ray diffraction (XRD) pattern of the undoped and Co-

doped SnO_2 films were recorded utilizing D8 advance Bruker system using Cu-Kα (λ= 0.1540560 nm) radiation. Also, atomic concentration in films (at. %) has been determined by SEM analysis using EDAX-Oxford system, whose results are presented in Table 1. The average crystalline grain size was calculated using familiar Sherrer's approximation based on the XRD patterns, $D=K\lambda/\delta w \cos\theta$, where D is the average crystalline size, K is a constant parameter (~1), λ is the X-ray wavelength, δw is the full width at half maximum (FWHM) of XRD peaks and θ is the Bragg's angle.

Magnetooptical properties of SnO_2: Co thin films with different concentration of Co-doped SnO_2 are studied in order to elucidate the origin of ferromagnetism as well as to explore the possibility of application of these materials as Faraday isolators.

Faraday rotation of the samples has been measured using Magnetooptic modulator technique at the wavelength of 632 nm [13]. Required magnetic fields have been produced using electromagnets, while the sample was placed between electromagnet poles. Magnetic field of order of 8 kOe which has been sufficient for saturating the samples, has been applied perpendicular to the samples surface. Polarized light source of He-Ne laser with 632 nm wavelength has been modulated using shielded Magnetooptic modulator. Scheme of the experimental set up for magnetooptical measurements is shown in figure 1.

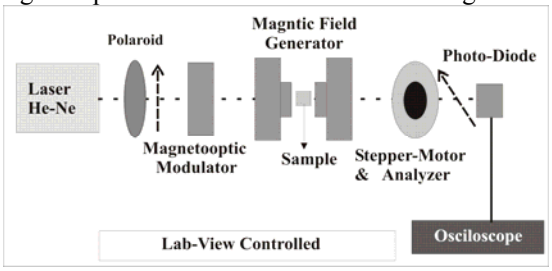

Fig. 1. Scheme of the experimental setup for measuring Faraday rotation.

In this system, a stepper-motor is used for accurate measuring magnitude of the Faraday rotation. Also, output signals are detected by a photo-diode in an oscilloscope (model HM 1507 Analog-Digital Scope). System is controlled via a Lab-View programmable setup. At first, the analyzer is aligned in a direction where double frequency of initially modulated signals obtained. After applying fields, the Faraday's effect deforms the signal. Then, magnitude of the Faraday rotation is determined by applying required rotation of the analyzer to get another double frequency. The accuracy of these measurements is in order of 0.003 degrees.

3. Results and discussion

The XRD patterns of the SnO_2: Co films deposited at T_s= 480 °C, for Co-doping ranges from 0 at.% to 38.1 at.% in films, are shown in figures 2(a) to 2(f). It is quite clear that the films are SnO_2 single phase polycrystalline samples, irrespective of the Co-doping level. The average size of crystallites estimated to be about 30 nm corresponding to the Scherrer's formula. By increasing Co-doping level up to 25 wt. %, no lines corresponding to the Cobalt or its oxides can be detected. However, relative intensity of the SnO_2 peaks gradually decreases and their width broadened by increasing Co content. Thus, one may say that the crystallinity of the sample decreases by increasing Co content. This Co-induced crystal size refinement is too small to be evaluated using Sherrer's approximation. This indicates that the substitution of Co for Sn introduces relatively large strains into the lattice. I addition, gradual increase of the background of the XRD patterns by increasing Co-content in figure 2(a) to 2(f), show that the crystal size refinement is accompanied by increasing amorphous phase content.

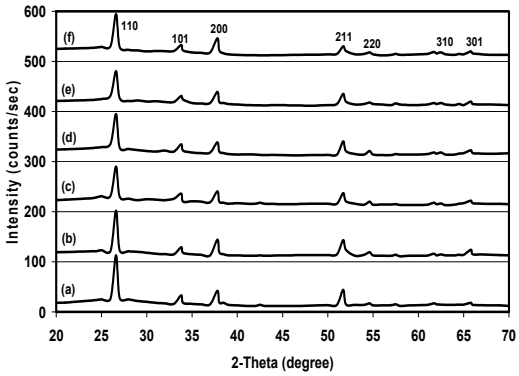

Fig. 2. XRD patterns of the SnO_2: Co films, for Co-doping from 0 at. % to 38.1 at. %.

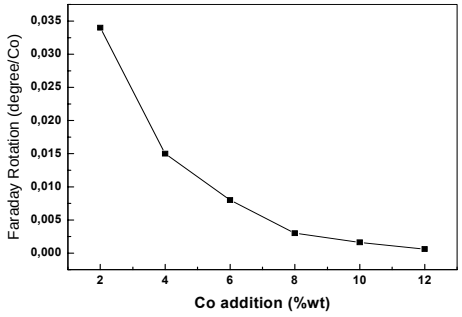

Fig. 3. Saturated Faraday rotation of Co-doped SnO_2 transparent semi magnetic semi-conducting films measured at 632 nm.

Figure 3 shows saturated Faraday rotation effect in SnO_2 Co-doped layers, measured at 632 nm of wavelength. Reduction of the Faraday rotation by increasing Co content can interpret in terms of decreasing behaviour of average magnetic moment of the Co atoms which has been observed by Ogale, et al. through saturation magnetization measurements [11]. Indeed, at low cobalt concentrations, the orbital contributions in Co-magnetic moment remains unquenched, while enhanced dopant-dopant associations leading to progressive orbital moment quenching by increasing Co content. So, average Co-magnetic moment and saturation magnetization of Co-doped SnO_2 layers decreases by increasing Co concentration. Therefore, Faraday rotation decreases with increasing the Co-concentration as shown in figure 3.

4. Conclusion

Diluted magnetic semi-conducting transparent SnO2: Co thin films with different Co concentration have deposited on the glass substrates, using spray pyrolysis technique. SEM and XRD structural analysis indicate that the samples are single phase polycrystalline layers with about 0.5 μm thickness and the average grain size of 30 nm. Magnetooptic measurements show that Faraday rotation angle decreases by increasing cobalt concentration which is consistence with decreasing behaviour of saturation magnetization of studied layers.

References

[1] P. Sharma, A. Gupta, K.V. Rao, F.J. Owens, R. Sharma, R. Ahuja, J.M. Guillen, B. Johansson and G.A. Gehring, Nature Materials 2 (2003) 673; Ref. 6, 7 therein.
[2] T. Dietl, Nature Materials 2 (2003) 646.
[3] W. Prellier, A. Fouchet and B Mercey, J. Phys :. Condens Matter 15 (2003) R1583; Ref. 54, 55 therein.
[4] F. Matsukura, H. Ohno and T. Dietl, III-V Ferromagnetic Semiconductors, Handbook Of magnetic Materials (Ed. K. H. J. Busschow-Elsevier Science), Vol 14 (2002) Chapter 1.
[5] H. Ohno, Science 281 (1998) 951.
[6] Y. Matsumoto, M. Murakami, T. Shono, T. Hasegawa, T. Fukumura, M. Kawasaki, P. Ahmet, T. Chikyow, S-Y. Koshihara and H. Koinuma, Science 291 (2001) 854.
[7] J.L. Costa-Kramer, F. Briones, J.F. Fernandez, A.C. Caballero, M. Villegas, M. Diaz, M.A. Garcia and A. Hernando, Nanotechnology 16 (2005) 214.
[8] D.C. Kundaliya, S.B. Ogale, S.E. Lofland, S. Dahr, C.J. Metting, S.R. Shinde, Z. Ma, B. Varughese, K.V. Ramanujachary, L. Salamanca-Riba and T. Venkatesan, Nature Materials 3 (2004) 709.
[9] R.C. Budhani, Prita Pant, R.K. Rakshit, K. Senapati, S. Mandal, N.K. Pandey and Jitendra Kumar, J. Phys.: Condens. Matter 17 (2005) 75.
[10] H. Saeki, H. Matsui, T. Kawai and H. Tabata, J. Phys.: Condens. Matter 16 (2004) S5533.
[11] S. B. Ogale, R. J. Choudhary, J. P. Buban, S. E. Lofland, S. R. Shinde, S. N. Kale, V. N. Kulkarni, J. Higgins, C. Lanci, J. R. Simpson, N. D. Browning, S. Das Sarma, H. D. Drew, R. L. Greene, and T. Venkatesan, Phys. Rev. Lett. 91 (2003) 077205-1.
[12] C. Kilic and A. Zuner, Phys. Rev. Lett. 88 (2002) 095501-1.
[13] M. Gaugitsch, H. Hauser, F. Haberl and J. Hochreiter, J. Magn. Magn. Matter. 157/158 (1996) 438.