Magnetooptical Faraday effect in Cobalt-doped SnO$_2$ transparent semi-conducting films prepared by spray pyrolysis technique

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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.

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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
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 TiO₂: 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 SnO₂, In₂O₃, TiO₂ 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 TiO₂-based thin films, some researchers have looked at other matrices having the same rutile type structure [3, 11]. Moreover, SnO₂ has an n-type conduction which is potentially interesting for spintronic devices [12]. Ogale and his co-workers [11] have deposited Co-doped SnO₂ 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 SnO₂: Co DMS structure which has not been seen in any DMS systems, thus far.

In the present paper SnO₂: 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 SnO₂ thin film have deposited using an aqueous-ethanol solution including SnCl₂·2H₂O, H₂O and CH₃CH₂OH with the same weight percentage (1: 1: 1) and a few ml of hydrochloric acid by the spray pyrolysis technique. Also, Co doped SnO₂ films have been prepared using certain amounts of CoCl₂·6H₂O 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>
<thead>
<tr>
<th>CoCl₂·6H₂O (wt% in solution)</th>
<th>SnCl₂·2H₂O (mole in solution)</th>
<th>CoCl₂·6H₂O (mole in solution)</th>
<th>[Co] / [Sn] (at.% in solution)</th>
<th>[Co] / [Sn] (at.% in film)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.146</td>
<td>0.000</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>2</td>
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<td>0.007</td>
<td>4.8</td>
<td>5.22</td>
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<td>4</td>
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<td>0.0146</td>
<td>10.0</td>
<td>6.80</td>
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<tr>
<td>6</td>
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<td>15.0</td>
<td>8.91</td>
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<tr>
<td>8</td>
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<td>0.029</td>
<td>19.8</td>
<td>11.41</td>
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<td>0.036</td>
<td>24.6</td>
<td>16.65</td>
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<tr>
<td>12.5</td>
<td>0.146</td>
<td>0.045</td>
<td>30.8</td>
<td>18.67</td>
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<td>15</td>
<td>0.146</td>
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<td>0.073</td>
<td>50.0</td>
<td>30.50</td>
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<tr>
<td>25</td>
<td>0.146</td>
<td>0.091</td>
<td>62.3</td>
<td>38.10</td>
</tr>
</tbody>
</table>

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 SnO₂ films. After reaching 500 °C, the solution was sprayed on the hot glass substrate in the following condition: carrier-gas, O₂, 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 SnO₂ (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\textsubscript{2} films were recorded utilizing D8 advance Bruker system using Cu-K\textalpha\ (\(\lambda=0.1540560\) 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), \(\lambda\) is the X-ray wavelength, \(\delta w\) is the full width at half maximum (FWHM) of XRD peaks and \(\theta\) is the Bragg’s angle.

Magnetooptical properties of SnO\textsubscript{2}: Co thin films with different concentration of Co-doped SnO\textsubscript{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.](image)

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\textsubscript{2}: Co films deposited at \(T_e=480\) °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\textsubscript{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\textsubscript{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. In 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\textsubscript{2}: Co films, for Co-doping from 0 at. % to 38.1 at. %.](image)
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 SnO$_2$: 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