Physica B 404 (2009) 2117–2121

Contents lists available at ScienceDirect

Physica B

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

Anomalous Hall effect in Cu and Fe codoped In_2O_3 and ITO thin films

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ARTICLE INFO

Article history:
Received 4 August 2008
Accepted 19 January 2009

PACS:
75.50.Pp
74.62.Dh

Keywords:
Magnetic semiconductors
Anomalous Hall effect

ABSTRACT

We present a systematic study of the structure, magnetization, resistivity, and Hall effect properties of pulsed laser deposited Fe- and Cu-codoped In_2O_3 and indium-tin-oxide (ITO) thin films. Both the films show a clear ferromagnetism and anomalous Hall effect at 300 K. The saturated magnetic moments are almost the same for the two samples, but their remanent moments M_r and coercive fields H_C are quite different. M_r and H_C values of ITO film are much smaller than that of In_2O_3. The ITO sample shows a typical semiconducting behavior in whole studied temperature range, while the In_2O_3 thin film is metallic in the temperature range between 147 and 285 K. Analysis of different conduction mechanisms suggest that charge carriers are not localized in the present films. The profile of the anomalous Hall effect vs. magnetic field was found to be identical to the magnetic hysteresis loops, indicating the possible intrinsic nature of ferromagnetism in the present samples.

1. Introduction

Since the theoretical prediction by Dietl et al. [1] that ferromagnetism (FM) could be achieved above room temperature in manganese doped semiconductors, much effort has been put into studying diluted magnetic semiconductors due to their potential for applications in spintronics [2]. Many promising materials like TiO_2, ZnO, and SnO_2 and III–V group compound GaN doped with transition-metal ions have been reported to exhibit FM with Curie temperature near or above 300 K [3–10], but the origin of FM in these systems is poorly understood. Oxide systems based on host semiconductor with high solubility of magnetic ions are especially important to form thermodynamically stable magnetic semiconductors. Two possible mechanisms are suggested to explain the FM in these compounds, carrier-mediated model and superexchange model [11]. In carrier-mediated models, the magnetic coupling between different magnetic ions can be achieved through electrons in the conduction bands or holes in the valence band. In such a system, the charge carrier is mobile. In superexchange models, the magnetic coupling is considered to be achieved through anions between the magnetic ions, where carrier is suggested to be localized.

For the development of a ferromagnetic oxide material, In_2O_3 and Fe are one of the most promising candidates as a host material and as a magnetic dopant, respectively. In_2O_3 is a transparent wide band gap (3.75 eV) semiconductor [12]. It crystallizes in the cubic bixbyite structure with the lattice parameter $a = 10.12$ Å and can be prepared as an n-type semiconductor with a high electrical conductivity by introducing oxygen deficiencies or by Sn doping [13]. The magnetic moment of Fe^{3+} is the largest among those of 3d transition metal ions. It is of great interest to study the doping effects using ions with such a large magnetic moment into the wide band gap host In_2O_3. Previous report suggested that Fe ions can substitute indium in In_2O_3 host lattice with a very high solubility [13]. Magnetic properties of Fe-doped indium oxide have been explored by several groups, different magnetic state such as paramagnetic [14], spin-glass [15], and ferromagnetic [13,16] were observed. In order to achieve multi-valence and thus FM, Yoo et al. [17] and He et al. [13] codoped some Cu along with Fe into In_2O_3. Their samples show clear room-temperature FM and the FM disappears if it is not codoped with Cu or subjected to annealing in oxygen atmosphere. From the analysis of the possible contribution of magnetic impurities to the FM by the authors, the FM in their samples is considered to be intrinsic. In addition, FM was also observed in indium-tin-oxide (ITO) thin film, where FM is suggested to originate from nanosized Fe clusters in the highest oxidation state Fe_2O_3 [18]. In this work, we performed a comparing study of the magnetization, resistivity, and Hall effects of Fe- and Cu-codoped indium oxide and ITO. In both samples, FM and anomalous Hall effects have been observed.

2. Experimental

Thin films of $(In_{0.83}Fe_{0.15}Cu_{0.02})_2O_3$ (IFCO) and $(In_{0.78}Sn_{0.05}Fe_{0.15}Cu_{0.02})_2O_3$ (ISFCO) were grown on $(1\bar{1}02)$ sapphire substrates by pulsed-laser deposition (PLD) technique using

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0921-4526/$ - see front matter © 2009 Published by Elsevier B.V.
doi:10.1016/j.physb.2009.01.028

corresponding stoichiometric targets. The ceramic targets were synthesized from stoichiometric amounts of high purity In_2O_3, SnO_2, Fe_2O_3, and CuO powders. The oxide powders were thoroughly ground and sintered at 900, 1000, and 1100 °C for 24 h, respectively. The detailed structural, magnetic, and transport properties of the targets will be reported elsewhere. A KrF excimer laser ($\lambda = 248$ nm) with a beam energy density of 1.8 J cm^{-2} was used at a repetition rate of 10 Hz. During deposition, the substrate temperature was 550 °C and the oxygen partial pressure was kept as 10^{-6} Torr. The thickness of the films is estimated to be 300 nm.

The structure and phase purity of the films were checked by means of X-ray diffraction using Cu K_α radiation at room temperature. The ac resistivity and Hall coefficient were measured using the standard 4-probe method on a quantum design physical properties measurement system (PPMS). The magnetic measurements were carried out with a vibrating sample magnetometer (VSM) attached to the PPMS system in the temperature range of 5–320 K.

3. Results and discussion

Fig. 1 shows the X-ray diffraction (XRD) pattern for the $(In_{0.83}Fe_{0.15}Cu_{0.02})_2O_3$ and $(In_{0.78}Sn_{0.05}Fe_{0.15}Cu_{0.02})_2O_3$ thin films. One can see from Fig. 1 that both the films are polycrystalline and only cubic In_2O_3 peaks are present in the spectrum. No hints of either Fe_3O_4 or $CuFe_2O_4$ clustering or phase separation were observed in these patterns. However, those peaks are rather broad and have no strong intensity, indicating that the films likely do not have a very good crystallinity. By comparing the spectra in Fig. 1(a) and (b), one can see clearly that after Sn doping, the peaks of the XRD patterns move toward to a higher degree and the ratio of intensity of the peak [2 2 2] and [4 0 0] increases, which may indicate that the orientation along the [1 1 1] direction is more dominant with the adding of Sn^{4+}. The calculated lattice constant of IFC and ISFC thin films from [2 2 2] peaks are 10.4596 and 10.4575 Å, respectively. The result is consistent with that the Sn^{4+} ion has a much smaller radius than In^{3+} ion.

The temperature dependence of the dc magnetization (M) of the two films is shown in Fig. 2 in the temperature range of 5–320 K. The data were collected in a 0.1 T applied field with zero field cooling (ZFC) and field cooling (FC) modes. As can be seen from the figure, the two films show obviously distinct M vs. T behavior. A weak magnetization peak in the vicinity of T_1 (~250 K) in both the ZFC and FC curves of IFCO film, followed by a

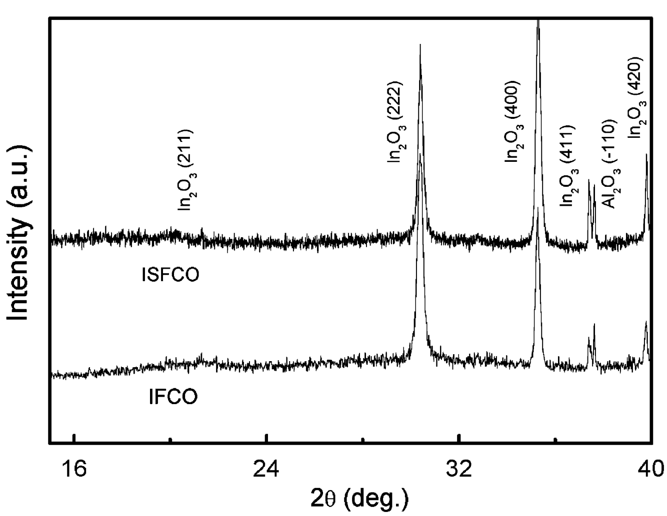

Fig. 1. X-ray diffraction patterns for IFCO and ISFCO thin films.

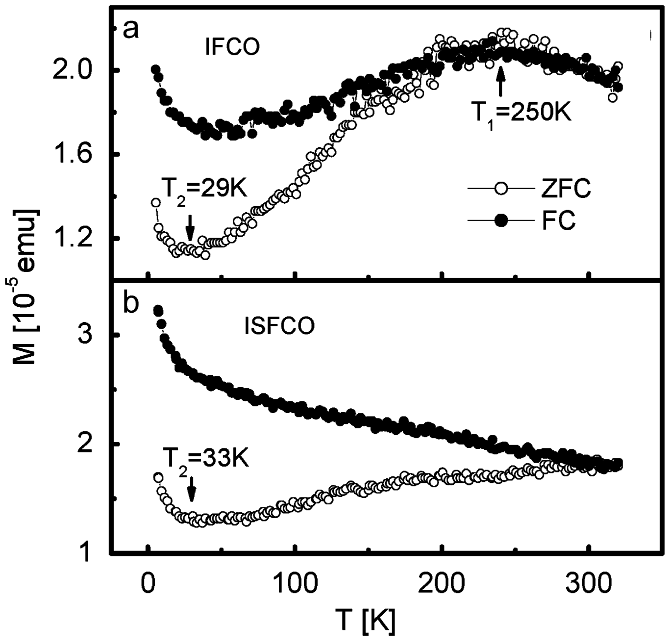

Fig. 2. Temperature dependence of magnetic moment for IFCO (a) and ISFCO (b) thin films measured at magnetic fields of 0.1 T with $H//ab$ configuration.

subsequent decrease in M at lower T except for a M upturn below T_2~30 K. In general, such a broad maxima observed in the M vs. T curve can be attributed to the collective modes of spin fluctuations which saturate at the peak temperature [19–21]. With decreasing temperature from 250 K, magnetization decreases much more quickly than that of FC, resulting in an obvious bifurcation of the ZFC and FC magnetizations at low temperatures. As to the Sn-doped film ISFCO, the FC magnetization increases linearly with decreasing temperature from 320 to ~30 K, whereas ZFC magnetization decreases in the same temperature range with a little hump near 200 K. It is noteworthy that ZFC curve already deviates from the FC one at temperature above 320 K as shown in Fig. 2(b), similar behavior was also observed in Fe-doped powder In_2O_3 oxides [22]. These behaviors are not expected for a ferromagnet and suggest the presence of magnetic cluster in the film or the spin-glass nature of the system [23,24].

The magnetization as a function of applied field is also measured at a series of temperature and the representative curves at 5 and 300 K are shown in Fig. 3 and its inset, respectively. The applied magnetic field is parallel to the film plane. Hysteresis loops for both two films in the whole studied temperature range (5–300 K) show obvious FM behavior with the Curie temperature higher than 300 K, in addition to a component of the magnetization related to the sapphire substrate, where the interactions are diamagnetic. A simple method to separate the FM contribution from the diamagnetic matrix is to recognize that the high-filed magnetization is given by $M_F + \chi_{DF}\mu_0 H$, where M_F is the FM component and χ_{DF} is the slope of the M vs. $\mu_0 H$ at high field. Extrapolation of this high-field behavior back to $\mu_0 H = 0$ therefore gives the FM component only. The obtained results are indicated in Fig. 4. From the corrected magnetic curves, we find that both the saturation magnetic moments and coercive field decreases with increasing temperature as presented in Table 1. The room temperature saturation magnetic moments and coercive field are 1.189×10^{-4} emu, 320 Oe and 1.188×10^{-4} emu, 292 Oe for IFCO and ISFCO samples, respectively. The saturated magnetic moments of the two films are almost the same, consistent with the same concentration of the magnetic ions in the sample. Both the films have large coercive fields even at room temperature,