

Effect of Tin Codoping on Transport and Magnetic Properties of Chromium-doped Indium Oxide Films

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This study examined the effect of Sn co-doping on the transport and magnetic properties of Cr-doped In₂O₃ thin films grown on (100) silicon substrates by pulsed laser deposition. The experimental results showed that Sn co-doping enhances the magnetization and appearance of the anomalous Hall effect, and increases the carrier (electron) concentration. These results suggest that the conduction carrier plays an important role in enhancing the ferromagnetism of a laser-deposited Cr-doped In₂O₃ film, which may have applications in transparent oxide semiconductor spin electronics devices.

Keywords : diluted magnetic semiconductors, indium tin oxide, ferromagnetism, magnetotransport

1. Introduction

Oxide based diluted magnetic semiconductors (DMS) have attracted considerable attention on account of their promising potential in spintronics. In particular, there have been some reports on the discovery of room temperature ferromagnetism in several oxide DMS [1-3]. Among these systems, ZnO- and TiO₂-based DMS have been studied extensively as the most promising candidates with Curie temperatures well in excess of 300 K, which are essential for realizing room temperature practical spintronic devices. However, the real origin of the ferromagnetism observed in these systems is not completely understood, and the possibility of an extrinsic origin of ferromagnetism, such as ferromagnetic clustering, cannot be excluded. The experimental results reported are not even reproducible, with different preparation methods yielding different magnetic phenomena. On the other hand, it has been suggested that crystal defects in oxide DMSs play a major role in inducing high temperature ferromagnetism [4-6].

Both theoretical and experimental studies suggest that

wide bandgap oxide semiconductors with a high carrier density are one of the most favorable host compounds for ferromagnetic DMS with a higher Curie temperature [2, 3]. Indium oxide, In₂O₃, is an excellent base material for a transparent conducting oxide with a tunable carrier density and high mobility as well as a wide band gap > 3.5 eV [7]. The *n*-type conductivity in In₂O₃-based system is due to the electrons generated by oxygen deficiencies. Recently, In₂O₃-based DMSs have been found to exhibit both ferromagnetism and an anomalous Hall effect at room temperature [6, 8, 9]. In particular, Cr-doped In₂O₃ is a unique system in that the magnetic doping and carrier concentration can be controlled independently to possibly show a high Curie temperature [6]. In this study, an attempt was made to vary the electron concentration by doping with Sn, which acts as a donor in In₂O₃.

This paper reports the effect of Sn co-doping on the transport and magnetic properties of Cr-doped In₂O₃ in order to demonstrate the enhancement of carrier-mediated ferromagnetism in Cr-doped In₂O₃ by electron doping through Sn co-doping.

2. Experiments

All Cr + Sn co-doped In₂O₃ [(In_{0.95-x}Cr_{0.05}Sn_x)₂O₃] films

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were prepared using a conventional pulsed laser deposition (PLD) method with a KrF excimer laser operating at 248 nm and an intensity of 5 J/cm². The ceramic targets were prepared from high-purity In₂O₃, Cr₂O₃ and SnO₂ powders at certain molar ratios using standard solid-state reaction procedures. The mixed powders were cold pressed and sintered at 1300°C for 96 hr in air. The substrates were 10×10 mm² SiO₂ (200 nm)/Si (100) that maintained at 400°C at a fixed oxygen pressure of 100 mtorr during deposition. The film thickness ranged from 800-1000 nm. The film composition was determined by energy-dispersive X-ray (EDX) spectroscopy.

3. Results and Discussion

Conventional X-ray diffraction (XRD) using Cu K α radiation and secondary ion mass spectroscopy (SIMS) were used for structure analysis and phase identification of the synthesized films. Fig. 1 shows the XRD patterns of the Cr + Sn co-doped In₂O₃ [(In_{0.95-x}Cr_{0.05}Sn_x)₂O₃] films with a fixed Cr concentration of 5 at.% for 0 ≤ x ≤ 0.12, where x denotes the Sn concentration. The peak positions for In₂O₃ of a cubic bixbyite structure [10] are shown in the bottom panel of Fig. 1. All diffraction lines from the films were indexed assuming a bixbyite structure with no detectable secondary phases, indicating homogeneous single-phase growth without phase segregation. Furthermore, as shown in the insets of Fig. 1, the results of SIMS analysis for x = 0.05 and 0.12 demonstrate a uniform distribution of Cr and Sn ions at different film depths, indicating no surface or interface segregation of the doped ions.

After structural characterization, the influence of Sn co-doping on the transport properties of the Cr-doped In₂O₃

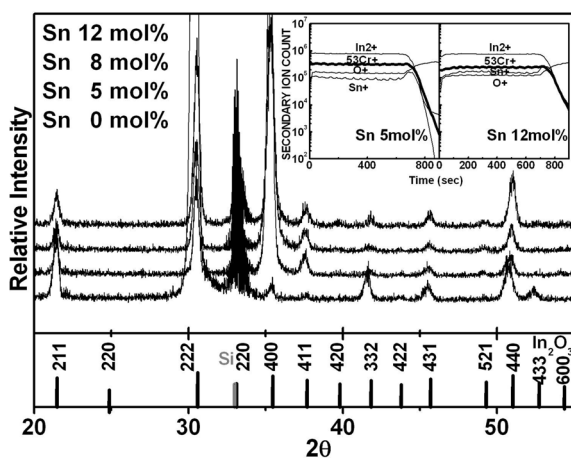


Fig. 1. X-ray diffraction patterns of the laser-deposited (In_{0.95-x}Cr_{0.05}Sn_x)₂O₃ (0 ≤ x ≤ 0.12) films. The insets show the results of SIMS analysis for x = 0.05 and 0.12.

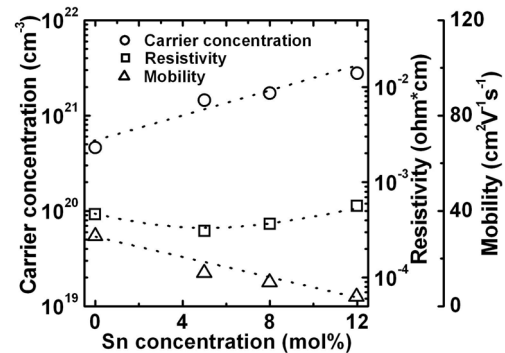


Fig. 2. Electron concentration, mobility and resistivity of the (In_{0.95-x}Cr_{0.05}Sn_x)₂O₃ (0 ≤ x ≤ 0.12) films, obtained from Hall effect measurements.

samples was examined by Hall measurements using the van der Pauw configuration at room temperature. Fig. 2 shows the change in carrier concentration, mobility and electrical resistivity as a function of the Sn concentration for the (In_{0.95-x}Cr_{0.05}Sn_x)₂O₃ films. All the samples showed *n*-type conductivity and the electron concentration increased from 4.61×10²⁰ cm⁻³ for x = 0 to 2.78×10²¹ cm⁻³ for x = 0.12 with Sn co-doping. This suggests that the Sn ion acts as a donor. On the other hand, there was a linear decrease in the mobility with increasing Sn codoping, which was attributed to an increase in alloy scattering caused by the presence of Sn ions. As a result, the films maintained a low resistivity of approximately 4×10⁻⁴ Ω cm.

The effect of Sn co-doping to the magnetic properties

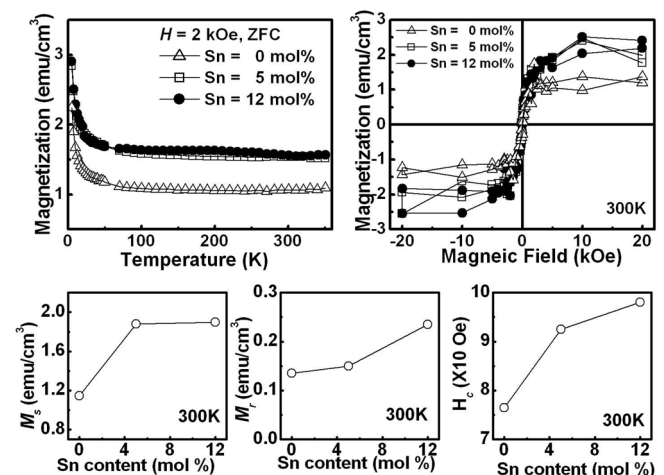


Fig. 3. (a) Magnetization versus temperature curves measured in a field of 2 kOe; (b) The magnetization versus magnetic field curves measured at 300 K; (c) Saturation magnetization (M_s); (d) Remnant magnetization (M_r); (e) Coercive field (H_c) for the laser-deposited (In_{0.95-x}Cr_{0.05}Sn_x)₂O₃ (x = 0, 0.05 and 0.12) films.

of Cr-doped In_2O_3 films was examined. Figure 3(a) shows the temperature dependence of the magnetization (M - T curves) of the $(\text{In}_{0.95-x}\text{Cr}_{0.05}\text{Sn}_x)_2\text{O}_3$ films at three Sn concentrations ($x = 0, 0.05$ and 0.12), which were measured using a superconducting quantum interference device (SQUID) magnetometer during warming from 5 to 350 K in an applied magnetic field (H) of 2 kOe parallel to the film surface. The diamagnetic contribution due to the substrate was subtracted. It should be noted that all three films have large magnetization values $> \sim 1$ emu/cm³ and show similar magnetization at temperatures > 50 K. This indicates the presence of a ferromagnetic ordering in the films. From the field dependence of the magnetization (M - H curves) at 300 K for the three samples, shown in Fig. 3(b), clear ferromagnetic hysteresis loops were observed, showing further evidence for the ferromagnetism in the films. This is consistent with the discovery of ferromagnetism in Cr-doped In_2O_3 films with an electron concentration above 2×10^{19} cm⁻³ [6], considering that the electron concentrations of the samples in the present study ranged from 0.4 - 3×10^{21} cm⁻³. There was no noticeable difference in the M - T curves between the zero-field-cooled and field-cooled ones, indicating the absence of spin-glass-like behavior or magnetic cluster formation. The observed upturn in the M - T curves at very low temperatures can be attributed to the paramagnetic Cr moments. Consequently, the characteristics of the M - T curves can be well understood by the coexistence of the ferromagnetic and paramagnetic components, as observed in the Mn-doped ZnO [11], Co-doped Cu_2O [12] and Mn-doped GaN [13].

Fig. 3(c), (d) and (e) show the changes in saturation magnetization (M_S), remnant magnetization (M_r) and the coercive field (H_C) with Sn co-doping, respectively, which were obtained from the M - H curves in Fig. 3(b). The increase in M_r and H_C as well as M_S demonstrates the enhancement of ferromagnetism in Cr-doped In_2O_3 films co-doped with Sn. This highlights the electron-doping-driven enhancement of carrier-controlled ferromagnetism in Cr-doped In_2O_3 as reported by Philip *et al.* [6].

One of the important criteria for intrinsic ferromagnetism caused by spin-polarized carriers in magnetic semiconductors is the observation of an anomalous Hall effect (AHE). The Hall resistivity (ρ_{xy}) in ferromagnets is customarily expressed as a sum of the ordinary and anomalous Hall term, $\rho_{xy} = R_0 B + R_S M$, where R_0 is the ordinary Hall coefficient, B is the magnetic induction and R_S is the anomalous Hall coefficient [14]. The AHE, which is proportional to the magnetization (M), is dominant at low magnetic fields and has a positive slope. Fig. 4 shows the magnetic field dependence of the Hall resistivity, ρ_{xy} , of

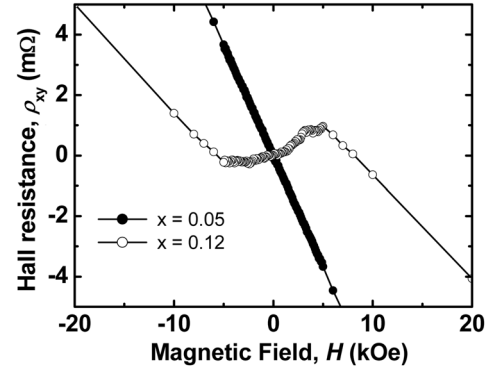


Fig. 4. Hall resistivity ρ_{xy} as a function of the magnetic field for the laser-deposited $(\text{In}_{0.95-x}\text{Cr}_{0.05}\text{Sn}_x)_2\text{O}_3$ ($x = 0.05$ and 0.12) films.

the $(\text{In}_{0.95-x}\text{Cr}_{0.05}\text{Sn}_x)_2\text{O}_3$ films at $x = 0.05$ and 0.12 at room temperature. For the $x = 0.12$ film with an electron density of 2.78×10^{21} cm⁻³, the Hall resistivity ρ_{xy} increases linearly with increasing magnetic field at fields $< \sim 5$ kOe, i.e. the AHE. At higher fields ($> \sim 5$ kOe), ρ_{xy} had a negative slope, indicating that n -type conduction and an ordinary Hall effect (OHE) were dominant at higher magnetic fields. It is well known that the anomalous part decreases, and the OHE becomes stronger with decreasing carrier concentration. It should be noted that R_0 is inversely proportional to the carrier concentration, which is illustrated in Fig. 4 for the $x = 0.05$ film.

4. Conclusion

In conclusion, this study examined the magnetic and transport properties of Cr and Sn co-doped In_2O_3 films grown on SiO_2/Si substrates by pulsed laser deposition. The results showed a clear enhancement of ferromagnetism and the appearance of an anomalous Hall effect as a result of electron-doping in Cr-doped In_2O_3 . These results suggest that the high temperature ferromagnetism and transport properties of Cr and Sn codoped In_2O_3 films are reproducible. These features indicate that Cr-doped In_2O_3 is a promising material for transparent oxide semiconductor spintronic devices operable at room temperature.

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