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Citation: J. Appl. Phys. 101, 09H121 (2007); doi: 10.1063/1.2714192
View online: http://dx.doi.org/10.1063/1.2714192
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Large positive magneto resistance effect below Curie temperature in In$_{1.90-x}$Mn$_{0.1}$Sn$_x$O$_3$

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(Submitted on 11 January 2007; received 29 October 2006; accepted 23 January 2007; published online 11 May 2007)

We report on the magnetoresistance (MR) and magnetic properties of In$_{1.90-x}$Mn$_{0.1}$Sn$_x$O$_3$ (0 ≤ x ≤ 0.06) oxide. All samples were found to be ferromagnetic below $T_C$=46 K. Sn doping changed In$_{1.90}$Mn$_{0.1}$O$_3$ from an insulator to a highly conducting phase at 300 K. A positive MR effect was observed over a wide temperature range just below $T_C$. Calculated MR values reached a maximum of 20% at 5 K. A change in the MR effect, from positive to negative, occurred under magnetic field $H > 4$ T at 5 K. The results of x-ray absorption near-edge spectroscopy indicated that Mn ions are present both as Mn$^{2+}$ and Mn$^{4+}$. © 2007 American Institute of Physics. [DOI: 10.1063/1.2714192]

In recent years, extensive research in the field of diluted magnetic semiconductors (DMSs) has been carried out to discover materials that could exhibit ferromagnetism at room temperature or well above it, because they potentially could be used in optoelectronic, magnetoelectronic, or other devices. The substitution of the cations in III-V and II-VI nonmagnetic semiconductors with magnetic transition metal (TM) ions, such as Mn, Cr, Ni, or Co, leads to a number of magnetic, optical, magnetooptical, and magnetotransport phenomena. The presence of transition metal ions in the system leads to an exchange interaction between itinerant sp band electrons or holes and the d electron moments localized on the magnetic ions, resulting in various magnetic field-induced functionalities. Theoretical predictions by Dietl et al. have boosted the search for ferromagnetism in transition metal doped ZnO. Other well known semiconductors (SnO$_2$ and TiO$_2$) are also being widely investigated. Recently, high temperature ferromagnetism was observed in Co doped SnO$_2$ thin films with large magnetic moment, ~7.5μB/Co.\textsuperscript{4} while ferromagnetism in Co–TiO$_2$ thin films was found to originate from the formation of Co clusters.\textsuperscript{5} Poor reproducibility and controversy over the published results strongly suggest that alternative host semiconductors must be researched and used.

In$_2$O$_3$ is a very promising candidate for this task. It is a well known semiconducting oxide already in practical use worldwide in batteries, transparent infrared reflectors, and photovoltaics. When In$_2$O$_3$ is doped with SnO$_2$, a so-called indium tin oxide (ITO) is formed. The high conductivity of ITO is attributed to the high carrier concentration, which is caused by the incorporation of Sn ions into the In$_2$O$_3$ host lattice and by oxygen nonstoichiometry. Recently Philip et al.\textsuperscript{6} have reported high temperature ferromagnetism in Mn doped ITO thin films. In addition, other groups have observed room temperature ferromagnetism in Fe, Co, and Ni doped In$_2$O$_3$ oxide bulk and thin film samples.\textsuperscript{7–9} Analysis of the films showed that transition metal ions are well distributed through the whole body of the film,\textsuperscript{9} which is in contrast to what happens in Co doped ZnO thin films, where the Co is mainly situated close to the surface of the films.\textsuperscript{10} Since laser ablation or other commonly used thin film preparation techniques are techniques with nonequilibrium conditions, the preparation and investigation of samples prepared under equilibrium conditions are very important and interesting. Recently, we have observed that the Mn doped In$_2$O$_3$ polycrystalline samples prepared by solid state reaction exhibited ferromagnetism with a Curie temperature of only 46 K, in contrast to that of Mn doped ITO films having a $T_C$ of above room temperature.\textsuperscript{11} However, we noted that our Mn doped In$_2$O$_3$ samples showed a very poor conductivity. Diluted magnets should have good conductivity and exhibit spin dependent magnetoresistance in order to be considered as a component in spintronic devices. In this letter, we report on our observations on the enhancement of conductivity and giant magnetoresistance in bulk In$_{1.90-x}$Mn$_{0.1}$Sn$_x$O$_3$ samples.

Polycrystalline samples of In$_{1.90-x}$Mn$_{0.1}$Sn$_x$O$_3$ (0 ≤ x ≤ 0.06) were prepared by a conventional solid state synthesis technique. High purity (99.99%; Aldrich) In$_2$O$_3$, SnO$_2$, and MnCO$_3$ were weighed and mixed in a mortar in corresponding ratios to obtain nominal chemical compositions for the final products. Mixed powders were calcined in an argon atmosphere at 850 °C for 12 h. After the calcination, the reacted powders were reground, pressed into pellets, and fired at 950 °C for 12 h in an argon atmosphere. The crystallographic structures of the prepared samples were characterized by the x-ray diffraction (XRD) technique using Cu Kα irradiation (Philips PW-1730). X-ray diffraction pat-
terns of the pulverized pellets of $\text{In}_{1.90-x}\text{Mn}_0.1\text{Sn}_x\text{O}_3$ samples are shown in Fig. 1. All samples were $\text{In}_2\text{O}_3$ of the cubic bixbyite crystal structure, showing no presence of any secondary phases or residues of unreacted materials. A slight increase in lattice parameter $a$ with increasing Sn content was observed, i.e., $a(\text{In}_{1.90}\text{Mn}_0.1\text{O}_3)=10.109(\pm0.004) \text{Å}$ and $a(\text{In}_{1.84}\text{Mn}_0.1\text{Sn}_{0.06}\text{O}_3)=10.119(\pm0.006) \text{Å}$.

Magnetic properties of the samples were investigated using a magnetic property measurement system (MPMS XL, Quantum Design). Figure 2 shows the field cooled and the zero field cooled molar magnetic susceptibility ($\chi$) as a function of temperature ($T$) measured under 2000 Oe from 10 to 340 K. All samples were found to be ferromagnetic below $T_C=46$ K. Although our samples are ferromagnetic this result is significantly different from reported data for Mn doped ITO thin films, where the samples were ferromagnetic at room temperature. The inset of Fig. 2 represents magnetization ($M$) versus applied magnetic field ($H$) at 10 K. A high coercive field $H_c\approx5000$ Oe was observed for the sample with $x=0$. With increasing Sn content in the samples the extent of this coercive field is strongly suppressed, i.e., the coercive field in the sample with $x=0.06$ has disappeared. Furthermore, with increased $x$, $M$-$H$ loops tend to accommodate their shape to that typical of paramagnetic materials. This feature suggests that introduction of Sn into the system caused a larger amount of magnetic ions to be coupled antiferromagnetically. This, though, is consistent with the $\chi$-$T$ curves (Fig. 2), where samples with higher Sn content have lower absolute susceptibility and significantly changed anisotropy in the $\chi$-$T$ curve below $T_C$.

In order to determine the valence of Mn ions, x-ray absorption near-edge spectroscopy (XANES) analysis was carried out at the Synchrotron Radiation Research Centre (SRRC, Taiwan). Figure 3 shows a spectrum of the Mn $L$-edge x-ray absorption structure for $\text{In}_{1.9}\text{Mn}_0.1\text{O}_3$ topmost curve, as well as spectra for $\text{MnO}$, $\text{Mn}_3\text{O}_4$, and $\text{MnO}_2$ reference samples having Mn$^{2+}$, Mn$^{3+}$, and Mn$^{4+}$ ions. As we can see, the observed peaks at 639.2, 640.4, and 642.6 eV in the XANES spectra correspond to those of Mn$^{2+}$ and Mn$^{4+}$. This shows that multivalent species of Mn coexist in our sample, leading to a possible double exchange interaction between Mn$^{2+}$ and Mn$^{4+}$. This interaction is very common among Mn-based magnetic materials and could be the origin of ferromagnetism in our samples.

The Curie temperature of our Mn doped ITO samples is much lower than Mn doped ITO thin films (above 300 K), as presented in Ref. 6. It should be noted that our samples were made by the conventional solid state reaction which is an equilibrium sintering process. However, the reported Mn-ITO thin films were fabricated using pulsed laser deposition which is a nonequilibrium process. Therefore, it is highly possible that the distributions and valences of Mn ion should be different in the samples made by the equilibrium and non-equilibrium processes. This would result in the different magnetic interactions between carriers and Mn ions and lead to the huge difference in the Curie temperatures. This have...

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**FIG. 1.** X-ray powder diffraction patterns of pulverized $\text{In}_{1.90-x}\text{Mn}_0.1\text{Sn}_x\text{O}_3$ pellets. Bottom curve shows reference peaks for $\text{In}_2\text{O}_3$ phase.

**FIG. 2.** (Color online) Molar magnetic susceptibility ($\chi$) vs temperature ($T$) for $\text{In}_{1.90-x}\text{Mn}_0.1\text{Sn}_x\text{O}_3$ samples measured in 2000 Oe. Inset: Magnetization ($M$) vs applied magnetic field ($H$) at 10 K.

**FIG. 3.** Mn $L$-edge x-ray absorption spectra for $\text{In}_{1.9}\text{Mn}_0.1\text{O}_3$ and reference materials: MnO, Mn$_3$O$_4$, and MnO$_2$. 

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been commonly observed in transition metal doped ZnO DMSs.

Transport properties of our samples were analyzed using the four probe technique, employing a physical property measurement system (PPMS, Quantum Design). Measurements were performed in a temperature range from 350 down to 5 K. Figure 4(a) presents the dependence of the electrical resistivity ($\rho$) on temperature ($T$) for the samples with $x=0.02$ and 0.06. We were unable to measure the $\rho$-$T$ dependence of the sample with $x=0$, because it was insulating. As we can see, a $2\%$ increase in Sn content greatly improved the electrical conductivity of the material. The absolute values of electrical resistivity ($\rho$) at 300 K show a difference of two orders of magnitude, i.e., $\rho_{300}$ =461 $\Omega$ cm and $\rho_{300}$ =2.54 $\Omega$ cm. Both samples measured showed typical semiconducting behavior, although due to the large increase in $\rho$, the sample with $x=0.02$ could not be measured over the whole temperature range.

Figure 4(b) shows the magnetoresistance (MR) effect measured at different temperatures for the In$_{1.84}$Mn$_{0.1}$Sn$_{0.06}$O$_{3}$ sample. The absolute values of MR were calculated using the relation $\text{MR} = (\rho_H - \rho_0)/\rho_0$. The MR effect, although very small $\sim 0.15\%$, can be seen right after the ferromagnetic transition temperature ($T_C=46$ K, Fig. 2) and increases with decreasing temperature. The maximum MR value was observed at 5 K and reached $20\%$. It is important to note that with increasing magnetic field at 5 K ($H > 4$ T) a change in the sign of MR occurred (from positive to negative). Jeon et al.\textsuperscript{12} claimed that such MR behavior could be induced by a formation of oxygen-vacancy-induced magnetic clusters, which might be possible in this case, because our samples were prepared in a reducing atmosphere. The strong $s$-$d$ exchange interaction at low temperatures stabilizes such clusters. However, when magnetic field is applied, ferromagnetic ordering of the spins is induced and charge carriers do not need to be trapped in order to align the localized spins. Hence, the change to negative MR effect at high fields is most likely induced by these free charge carriers.

The behavior of our MR curve at 5 K [Fig. 4(b)] is very much comparable to that observed by Jeon et al.\textsuperscript{12} for Mn doped ZnO thin films. Thus, we can state that the mechanism behind the MR effect in both systems is very similar. These results indicate that Mn doping is responsible for the localized spin interaction of conducting carriers in both ITO and ZnO.

In summary, polycrystalline samples of In$_{1.90-x}$Mn$_{0.1}$Sn$_{0.02}$O$_{3}$ (0 $\leqslant x \leqslant 0.06$) were prepared. All samples were ferromagnetic below $T_C=46$ K. A large coercive field ($H_C \sim 5000$ Oe) was observed in the sample with $x=0$, while an increase in Sn content eliminates this feature. Furthermore, the introduction of Sn into the insulating ($x=0$) system made it highly conductive. Sample with the richest Sn content showed a large positive MR effect, reaching a maximum of $20\%$ at a temperature of 5 K. A change in the MR sign, from positive to negative, was observed at 5 K when $H > 4$ T. Valence state assessment showed that Mn is present in a multivalent state as Mn$^{2+}$ and Mn$^{4+}$.

One of the authors (X.L.W.) is grateful for the support from the Australian Research Council under Discovery Grant No. DP0558753. Another author (G.P.) thanks the Australian government and the University of Wollongong for providing IPRS and UPA scholarships for his Ph.D. studies.

\textsuperscript{1}H. Ohno, Science 281, 951 (1998).