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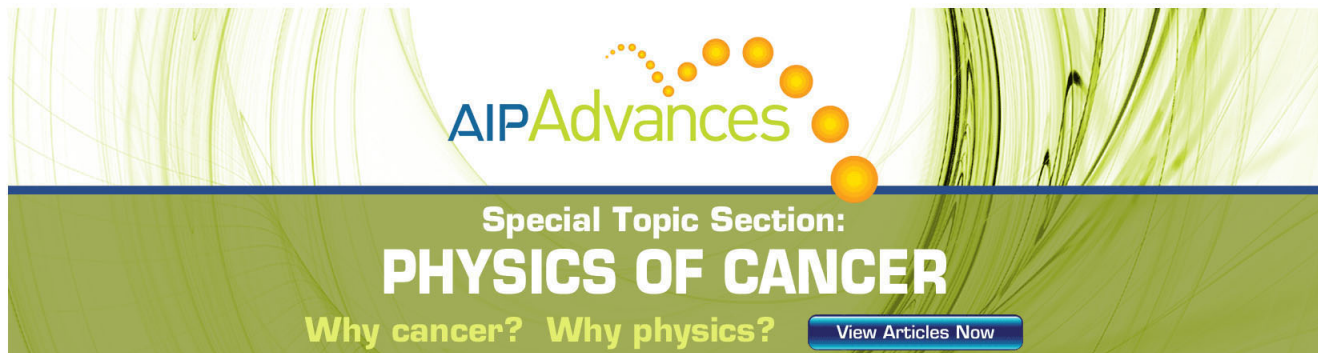
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Charge-carrier mediated ferromagnetism in Mo-doped In_2O_3 films

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We investigated the correlation between the ferromagnetism and electric resistivity of Mo-doped (3–10 at. %) In_2O_3 films. We find that the saturation magnetization increases with the Mo concentration until it reaches its maximum at 7 at. % Mo doping (7.1 emu/cm^3), after which it rapidly decreases upon higher doping concentration. Interestingly, the resistivity reveals opposite behavior with the Mo concentration, showing a minimum value at 7 at. % Mo doping. According to the temperature-dependent resistivity and the Hall effect measurements, we find that the samples with higher magnetization show metallic behavior with higher electron concentration. Notably, the samples show a linear relationship between the carrier concentration and the degree of magnetization. We believe the ferromagnetism in Mo-doped In_2O_3 is ascribed to the indirect exchange interaction mediated by the charge carriers. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4722928>]

Since the theoretical predictions of ferromagnetism in Mn-doped GaAs, considerable research has been carried out to find a new ferromagnetic semiconductor for spintronic applications.^{1–8} Particularly, a report of magnetism in Co-doped TiO_2 triggered growing interest in the room-temperature ferromagnetism of wide-band gap oxide semiconductors doped by 3d transition metals such as Fe, Co, and Mn.^{9–11} However, much debate regarding the existence of magnetism in 3d transition metal-doped oxide semiconductors has ensued, especially on the topic of the cluster problem. Thus, additional work is required in these areas.^{12–16} Recently, theoretical predictions have suggested the existence of ferromagnetism in 4d transition metal-doped oxide materials.^{17–19} Motivated by these predictions, we found and published evidence of room-temperature ferromagnetism in Mo-doped In_2O_3 films,²⁰ reporting that the magnetization of 5 at. % Mo-doped In_2O_3 and undoped In_2O_3 was controlled by the quantity of oxygen vacancies. In both films, the magnetization of the samples depends on detailed fabrication conditions, including the oxygen pressure. Interestingly, the films were free from the cluster problem because the bulk Mo itself is not ferromagnetic; only Mo ions which occupy In(1) or In(2) sites in In_2O_3 are known to be magnetic.^{17,19}

To reveal the origin of the ferromagnetism in Mo-doped In_2O_3 , the series of samples were fabricated on MgO (100) substrates at 450 °C using a PLD (pulsed laser deposition) technique in a high vacuum chamber with a base pressure of 1.5 μTorr . We purchased all targets (Plasmaterials inc.). The purity of an undoped target was 99.99% and the purity levels of the 3, 5, 7, and 10 at. % Mo-doped In_2O_3 targets were 99.95%. It should be mentioned that the nonexistence of 3d transition metal impurities in each target was confirmed using EDS (energy dispersive spectroscopy). This was done because the most important point of this study is to find the ferromagnetic property in nonmagnetic elements. The targets were ablated by means of a KrF excimer laser ($\lambda = 248 \text{ nm}$) operating at 2 Hz with an integrated intensity of 0.3 J/cm^2 .

To reduce the degree of particulate formation, each target was rotated at 20 rpm during fabrication. The typical deposition rate was $\sim 0.5 \text{ \AA/s}$. Each film with a nominal thickness of 100-nm was prepared under a low oxygen pressure of $P_{\text{O}_2} = 3 \mu\text{Torr}$ in a PLD chamber. The structures of the series were characterized by XRD (x-ray diffraction) with a 12 kW Rigaku diffractometer. RBS (Rutherford back scattering) and EDS measurements were carried out to confirm the composition ratio in the samples. The ferromagnetic properties were characterized using AGM (alternating gradient magnetometer). We carried out R-T (resistivity versus temperature) and Hall effect measurements to investigate the correlation between the magnetism and electric resistivity. We confirmed the reproducibility of our results via repeated measurements of more than 10 samples for each composition. It should also be mentioned that we used Teflon tweezers cleaned with ethanol to prevent possible Fe contamination during the all processes of growth and measurements.²¹

Figure 1(a) shows M-H curves of the 3, 5, 7, and 10 at. % Mo-doped In_2O_3 and undoped In_2O_3 films measured at 300 K. It is noted that the saturation magnetic moments of the films are on order of 10^{-6} – 10^{-5} emu , which are obtained by subtracting the diamagnetic signal of the MgO substrate from the total magnetic moment of the samples.²¹ Every sample clearly reveals hysteric behavior, demonstrating the existence of ferromagnetism. Interestingly, the ferromagnetic property observed in the undoped In_2O_3 film (Fig. 1(a)) is similar to the experimental data previously reported by Hong *et al.*²²

Figure 1(b) shows the saturation magnetization and resistivity versus the Mo concentration in Mo-doped In_2O_3 films at 300 K. In this figure, one can see that the saturation magnetization increases with the Mo concentration up to 7 at. % Mo-doping, but it decreases in the 10 at. % Mo-doped film. According to the theoretical predictions,^{17,19} only Mo^{3+} ions which substitute into In(1) or In(2) sites in the In_2O_3 matrix have a finite magnetic moment at room

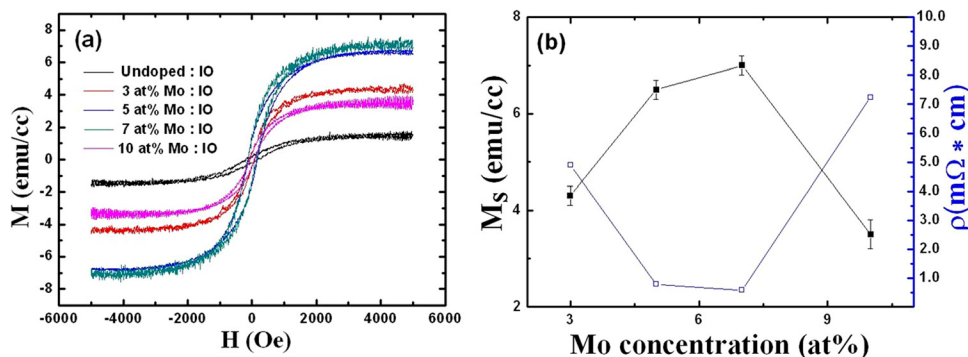


FIG. 1. (a) Magnetic hysteresis loops of 100-nm thick 3, 5, 7, and 10 at. % Mo-doped In_2O_3 , and undoped In_2O_3 films at 300 K. (b) The saturation magnetization and resistivity as a function of the Mo concentration at 300 K.

temperature. The Mo^{3+} ion substituted into the In(1) site has a magnetic moment of $1.85 \mu_B$, whereas that into the In(2) site has a magnetic moment of $1.32 \mu_B$.¹⁷ Interestingly, the resistivity shows opposite behavior with the Mo concentration, showing the lowest value at 7 at. % Mo doping. This result is consistent with the theoretical predictions¹⁷⁻¹⁹ that Mo^{3+} ions substituted into In(1) and In(2) sites are the source of charge carriers.

For the structural characterization, we performed XRD measurements of the samples. As shown in Fig. 2(a), the samples show distinct diffraction peaks, revealing the high degree of texture. Importantly, we did not observe the XRD peaks corresponding to Mo_xO_y phases with up to 7 at. % Mo doping in Fig. 2(a). This implies that the most of the Mo atoms properly substitute into In sites (up to the 7 at. % Mo doping) within the resolution of 0.01° of the XRD (note that Mo nanoclusters would not be detected to x-ray under a certain size). Figure 2(a) also shows that the peak positions of the 3, 5, and 7 at. % Mo-doped In_2O_3 films are at higher angles than that of undoped In_2O_3 film. This indicates that the lattice constant is smaller in 3, 5, and 7 at. % Mo-doped In_2O_3 film as compared to undoped In_2O_3 film: $a = 10.103$, 10.087 , and 10.073 \AA in the 3, 5, and 7 at. % Mo-doped In_2O_3 samples, respectively, and $a = 10.141 \text{ \AA}$ in the undoped In_2O_3 sample. Considering the fact that the radii of the Mo ions ($R_{\text{Mo}^{3+}} = 0.83 \text{ \AA}$ and $R_{\text{Mo}^{6+}} = 0.73 \text{ \AA}$) are smaller than that of an In ion ($R_{\text{In}^{3+}} = 0.94 \text{ \AA}$), the change in the lattice constant upon Mo-doping can be ascribed to the substitution of Mo in In(1) or In(2) sites. It provides the important evidence for that the most of the Mo atoms properly substitute into In sites.

From the EDS measurements, we can rule out the possible existence of magnetic impurities and confirm the uni-

formity of the composition ratio in the films: we observed each sample three times at different positions. Moreover, RBS measurements were also carried out for more accurate analysis because it offers higher resolution of 0.01%, which is 10 times better than that of EDS. The results of both measurements were identical. These indicate that the ferromagnetic properties in our system did not arise from magnetic impurities but from Mo-doping, which was theoretically predicted to have a ferromagnetic property.^{17,18} The substituted Mo ions are believed to provide the magnetic moment and to generate carriers. However, the 10 at. % Mo-doped In_2O_3 shows less magnetization and greater resistivity than the samples with lower Mo concentrations, as shown in Fig. 1(b). This deviation is closely related to the extra formation of $\text{Mo}_{17}\text{O}_{45}$ and Mo_4O_{11} phases in Fig. 2(b), which will be discussed later.

We measured the resistivity (ρ) with the temperature (T) for the series of samples. Figure 3 shows the ρ - T curves of the 3, 5, 7, and 10 at. % Mo-doped samples of In_2O_3 . As shown in the figure, metallic behavior was noted in the 5 at. % and 7 at. % Mo-doped In_2O_3 samples, whereas semiconducting behavior arose in the samples with the other concentrations. It is important to note that the metallic samples have relatively large magnetizations as compared to the other semiconducting samples.

To confirm the substituted Mo ion as the source of carrier generation, we measured the Hall effect of the samples at 300 K. Figure 4 shows the carrier concentrations of the 7.5×10^{19} , 1.9×10^{21} , 2.8×10^{21} , and $5.1 \times 10^{19}/\text{cc}$ for 3, 5, 7, and 10 at. % Mo-doped In_2O_3 samples, respectively. Here, the 5 and 7 at. % Mo-doped In_2O_3 samples, which show metallic behavior, reveal higher carrier concentrations, whereas the 3 and 10 at. % samples, showing the semiconducting

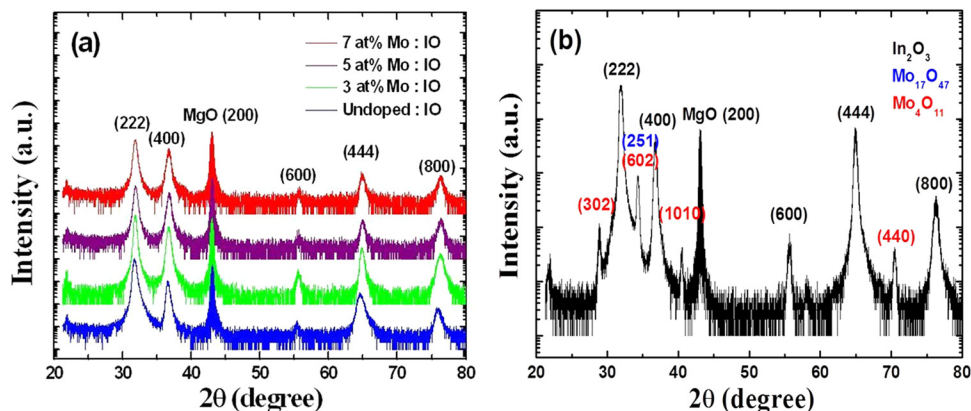


FIG. 2. (a) θ - 2θ x-ray diffraction patterns of 100-nm thick 3, 5, and 7 at. % Mo-doped In_2O_3 and undoped In_2O_3 . (b) θ - 2θ x-ray diffraction patterns of 100-nm thick 10 at. % Mo-doped In_2O_3 .

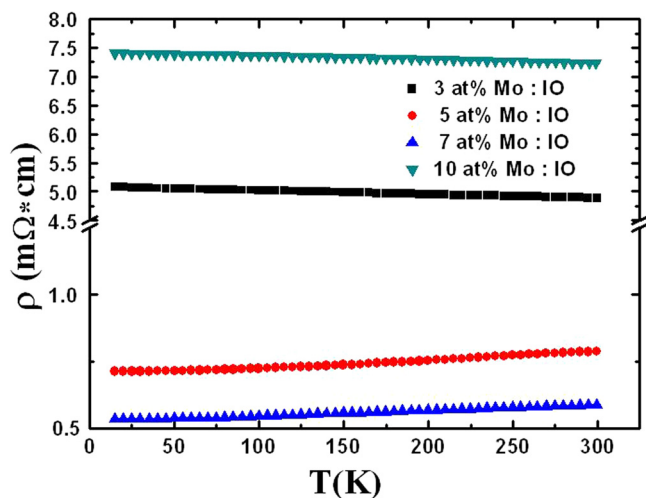


FIG. 3. Temperature-dependence of the resistivity of the 100-nm thick 3, 5, 7, and 10 at. % Mo-doped In_2O_3 samples. There is a break between 1.25 and 4.50 $\text{m}\Omega\cdot\text{cm}$.

phase, reveal lower carrier concentrations. From the comparison of the saturation magnetization (Fig. 1(b)) and carrier concentration (Fig. 4) for each Mo concentration, we found a strong correlation between the saturation magnetization (M_s) and the carrier concentration. Figure 5 shows a plot of the saturation magnetization vs. the carrier concentration, exhibiting an intriguing linear relationship between the two physical quantities. Although the 10 at. % Mo-doped In_2O_3 sample shows weak deviation from the linear relationship, the datum (for the 10 at. % Mo-doped In_2O_3) still supports a linear relationship.

It is well-known that ferromagnetic exchange coupling in Mn-doped III-V semiconductor is mediated by charge carriers, revealing the strong relationship between the ferromagnetism and the charge carrier concentration.⁶ According to a recent report, there is a finite possibility that a small amount of magnetic moment can come from the interstitial In atom.¹⁸ However, we believe that the interstitial In atom plays a minor role in the ferromagnetism of Mo-doped In_2O_3 system based on following reason. The lattice constants of

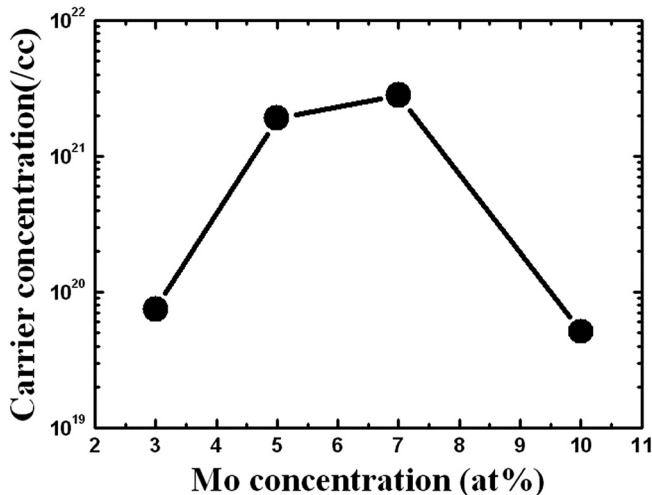


FIG. 4. The charge carrier concentration as a function of the Mo concentration at 300 K.

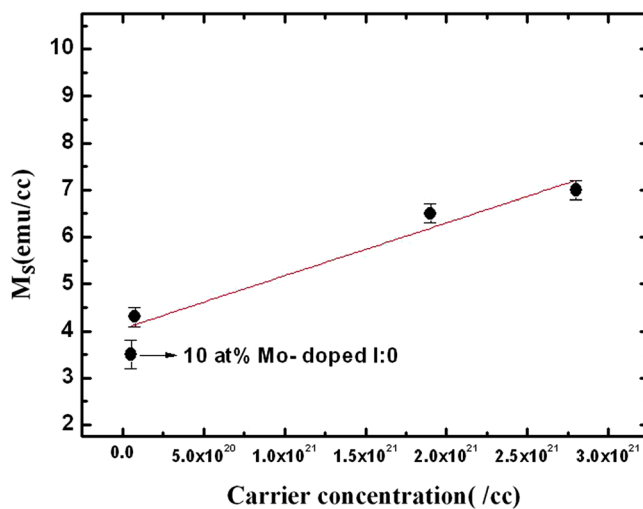


FIG. 5. A plot of the carrier concentration vs. the saturation magnetization.

the Mo-doped In_2O_3 samples reveal smaller values than that of undoped In_2O_3 in Fig. 1(a). Considering that the interstitial In atom induces the larger lattice constant, we can rule out the possibility of the ferromagnetism by interstitial In. Therefore, given to the linear correlation between the ferromagnetic property and the charge carrier concentration in Fig. 5, we believe that the main origin of the ferromagnetism in Mo-doped In_2O_3 is mediated by the charge-carriers.

Before concluding, brief discussion of the details of the 10 at. % Mo-doped In_2O_3 samples is presented. As mentioned earlier, the 10 at. % Mo-doped In_2O_3 sample shows less magnetization (Fig. 1) and a lower carrier concentration (Fig. 5) in spite of the maximum Mo concentration. This behavior can be explained as follows. Generally, the critical limit of the substitution ratio is known to be 5–7 at. % in order not to form clusters by doped ions. Therefore, the most of Mo atoms were substituted into In(1) or In(2) sites below the critical limit, but the formation of Mo_xO_y was energetically favorable beyond the critical one as proven by the XRD analysis in Fig. 2(b). Considering the theoretical prediction,¹⁷ the Mo ion of the Mo_xO_y phase cannot be the source of the magnetic moment and charge carrier. This explains the smaller values of the saturation magnetization and carrier concentration of the 10 at. % Mo-doped film. It should be noticed that, even for the 10 at. % Mo-doped film, the linear relationship between the magnetization and carrier concentration still holds.

In conclusion, we have investigated the correlation between the ferromagnetism and electric resistivity of 3, 5, 7, and 10 at. % Mo-doped In_2O_3 samples. We find that the saturation magnetization and resistivity show the nonmonotonic dependence on the Mo concentrations. From the temperature dependent resistivity and the Hall effect measurements, we find that the higher magnetization samples show metallic behavior and higher charge carrier concentration. Intriguingly, the samples show linear relationship between the carrier concentration and the magnetization. Based on our findings, we conclude that the ferromagnetism in Mo-doped In_2O_3 is mediated by the charge carriers in In_2O_3 systems.

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