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# The role of Cu codoping on the Fe metal clustering and ferromagnetism in Fe-doped $In_2O_3$ films

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ABSTRACT

We have grown room temperature ferromagnetic Fe, and Fe,Cu-codoped $In_2O_3$ films on sapphire substrates by pulsed laser deposition. The magnetization of the Fe-doped $In_2O_3$ films was independent of the thickness and the observed ferromagnetism was almost homogeneous. The addition of Cu caused the films to exhibit obvious thickness dependent magnetization and the ferromagnetism became inhomogeneous. The temperature dependence of the magnetization, X-ray absorption fine structure and magnetic circular dichroism data, clearly established the presence of Fe metal clusters in Fe,Cu-codoped $In_2O_3$ films, which contribute to the inhomogeneous ferromagnetism.



## 1. Introduction

Diluted magnetic semiconductors (DMSs) have attracted much attention for their potential applications in spintronic devices [1–3]. Fe-doped $In_2O_3$ DMSs are regarded as a promising candidate for future spintronic device application because a homogeneous material can be realized due to the high solubility of Fe in the $In_2O_3$ host lattice (~20%) [4,5], therefore many research groups, including ourselves, have paid more attention to the Fe-doped $In_2O_3$ system [6–9]. Moreover, Cu has been used as a dopant or codopants in DMSs because neither metallic Cu nor its oxides (CuO and $Cu_2O$) are ferromagnetic and hence could exclude the possibility that the ferromagnetism originates from the magnetic impurities brought by Cu itself [10,11].

Recently, it has been reported that adding Cu into Fe-doped $In_2O_3$ DMSs can influence their magnetic and transport properties significantly. For example, Yoo and co-workers [4,5] obtained room temperature (RT) ferromagnetism in Fe-doped $In_2O_3$ bulk and film samples by co-doping a small amount of Cu (2 at.%), which creates the mixed valence cations, i.e., $Fe^{2+}$, $Fe^{3+}$, necessary for the ferromagnetism and charge transport. Ho et al. [12] found that the RT ferromagnetism of Fe-doped $In_2O_3$ bulk was reduced by additional Cu doping. Although few attempts have been made to explain the role of Cu on ferromagnetism in Fe-doped $In_2O_3$ [13], the fundamental mechanism regarding the contributions of Cu codopant toward the magnetic ordering of $In_2O_3$-based DMSs is far from clearly understood.

In this letter we report measurements on the effects on the RT ferromagnetism of adding 3% of Cu into Fe-doped $In_2O_3$ films prepared by pulsed laser deposition (PLD). In order to explore the origin of ferromagnetism in this specific system further, we studied the dependence of the magnetism on the film thickness. Interestingly, we find that the magnetization of Fe-doped $In_2O_3$ films was independent of thickness and the observed ferromagnetism was almost homogeneous [9]; however the films showed obvious thickness dependent magnetization after adding Cu. The temperature dependence of the magnetization, X-ray absorption fine structure (XAFS) and magnetic circular dichroism (MCD) results demonstrate that adding Cu causes Fe metal clusters to be formed in the doped $In_2O_3$ films leading to the inhomogeneous ferromagnetism. The role of adding Cu on the formation of Fe clusters in Fe-doped $In_2O_3$ DMSs is also discussed.

## 2. Experiments

The $(In_{0.95}Fe_{0.05})_2O_3$ and $(In_{0.92}Fe_{0.05}Cu_{0.03})_2O_3$ films were grown on *c*-cut sapphire substrates by a PLD technique from their corresponding targets with thickness varying from 100 to 400 nm

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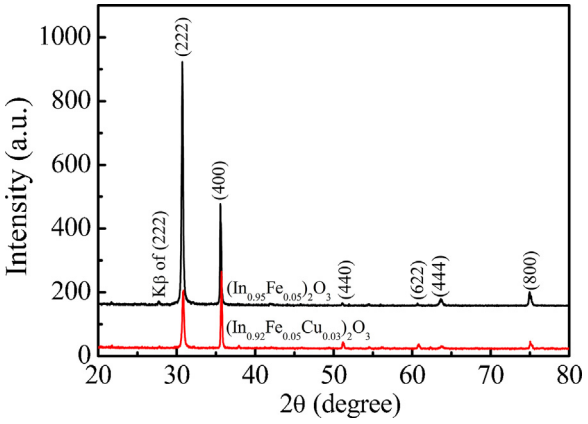


**Fig. 1.** The XRD patterns of $(In_{0.95}Fe_{0.05})_2O_3$ and $(In_{0.92}Fe_{0.05}Cu_{0.03})_2O_3$ films.

[9]. The film deposition was performed using a substrate temperature of 600 °C and with an oxygen pressure of $5 \times 10^{-3}$ mTorr. The films were characterized using X-ray diffraction (XRD), X-ray absorption fine structure (XAFS), and magneto-optical techniques. The magnetic measurements were carried out in a Quantum Design SQUID magnetometer.

## 3. Results and discussion

Fig. 1 shows the XRD patterns of $(In_{0.95}Fe_{0.05})_2O_3$ and $(In_{0.92}Fe_{0.05}Cu_{0.03})_2O_3$ films. The results indicated that the films were polycrystalline with mostly (2 2 2) or (4 0 0) orientations and all the diffraction peaks could be indexed assuming the same cubic bixbyite structure as pure $In_2O_3$. No other peaks related to Fe metal clusters or Fe oxide secondary phases were observed in the spectra within the limit of XRD.

Fig. 2(a) shows the magnetization versus magnetic field ($M$–$H$) loops for the $(In_{0.92}Fe_{0.05}Cu_{0.03})_2O_3$ films with different thickness at RT. The diamagnetic contribution from the substrate has been subtracted from the loops. It can be seen that the films exhibit distinct ferromagnetic behavior at RT with the magnetic moment at saturation ($M_s$) decreasing with increasing film thickness. As seen in Fig. 2(b), the film with thickness of 100 nm showed a maximum $M_s$ of 0.65 $\mu_B$/Fe. The results suggest that the observed ferromagnetism in the Fe,Cu-codoped $In_2O_3$ films is inhomogeneous. This is very different from our previous results obtained from the Fe-doped $In_2O_3$ films, where the magnetization was essentially independent of thickness as shown in Fig. 2(b) and their ferromagnetism was due to the homogeneous bulk effect [9].

To gain a further insight into the magnetic origin in the Fe and Fe,Cu-codoped $In_2O_3$ films we have performed zero-field-cooled (ZFC) and field-cooled (FC) measurements of the magnetization dependence on temperature under an applied external field of 100 Oe. A distinct bifurcation between the ZFC/FC curves was observed for the $(In_{0.92}Fe_{0.05}Cu_{0.03})_2O_3$ films with different thickness (shown in Fig. 3). The ZFC curves show a gradual increase at low temperatures, and reach a broad peak with a maximum (referred to as the average blocking temperature, $T_B$) [14,15], while FC curves continue to increase with decreasing temperature. This behavior suggests the existence of precipitated ferromagnetic clusters in the $(In_{0.92}Fe_{0.05}Cu_{0.03})_2O_3$ films with blocking temperatures ~32 K. The larger coercivities ($H_c$) at 5 K (insets) further confirm this. However, a different temperature-dependent magnetization behavior was found for the $(In_{0.95}Fe_{0.05})_2O_3$ films; the plots for one such film ZFC/FC are shown in inset of Fig. 2(b). There is no indication of blocking in the whole temperature range of 2–300 K, indicating the absence of ferromagnetic nano-clusters in the $(In_{0.95}Fe_{0.05})_2O_3$ films [16,17].

All the magnetic results presented above demonstrate the presence of hidden ferromagnetic nano-clusters in the Fe,Cu-codoped $In_2O_3$ films, which may also be the major reason for their inhomogeneous ferromagnetism. In order to obtain the specific information on these magnetic clusters in the Fe,Cu-codoped $In_2O_3$ films we have carried out the XAFS experiments of the films at Fe $K$-edge at beamline 20-BM at the Advanced Photon Source. The XAFS technique is highly sensitive to the presence of metallic clusters in doped oxides and has been demonstrated as a powerful probe to determine the local structure of transition metals in DMSs [18,19]. Fig. 4(a) shows the Fe $K$-edge X-ray absorption near-edge structure (XANES) data for the $(In_{0.92}Fe_{0.05}Cu_{0.03})_2O_3$ film compared to data from Fe metal and Fe-doped $In_2O_3$ sample whose extended fine structure (EXAFS) shows the Fe to be entirely substitutional. The spectra have been normalized to the incident intensity $I_o$ and, after subtraction of the pre-edge background, have been scaled to have an edge step of one. The increased pre-edge feature near 7110 eV for the $(In_{0.92}Fe_{0.05}Cu_{0.03})_2O_3$ film is characteristic of metallic Fe. Fitting the near edge data with a linear combination suggests that about 45 ± 5% of the Fe is similar to Fe metal with the rest of the Fe residing in substitutional sites with a valence similar to $Fe^{3+}$. Thus, the near edge data is consistent with a mixture of $Fe^{3+}$ substitutional sites and zero-valent Fe similar to bcc Fe metal. Fig. 4(b) shows the Fourier transforms of the EXAFS for the same samples. Again it is seen that the $(In_{0.92}Fe_{0.05}Cu_{0.03})_2O_3$ film contains features of both Fe metal and substitutional Fe. In this case, the Fe metal signal has to be scaled to about 25% to match the metal peak near $R$ = 2.2 Å. This reduction in amplitude is consistent with the Fe metal particles being small and somewhat disordered. The near edge data is less sensitive to this, and

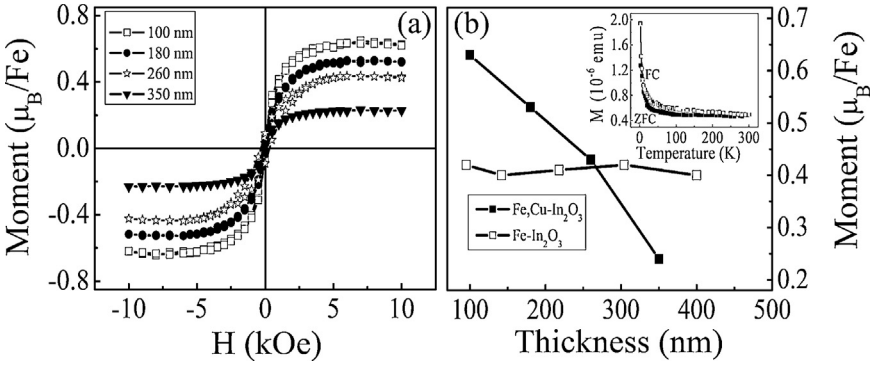


**Fig. 2.** The magnetization versus magnetic field loops for the $(In_{0.92}Fe_{0.05}Cu_{0.03})_2O_3$ films with different thickness at RT (a), and the saturation magnetic moment values dependent on the film thickness for $(In_{0.95}Fe_{0.05})_2O_3$ and $(In_{0.92}Fe_{0.05}Cu_{0.03})_2O_3$ films (b). The inset of (b) shows the ZFC/FC curves for one of the $(In_{0.95}Fe_{0.05})_2O_3$ films (the substrate signal has been subtracted from these plots.).