The role of Cu codoping on the Fe metal clustering and ferromagnetism in Fe-doped In$_2$O$_3$ films

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**ABSTRACT**

We have grown room temperature ferromagnetic Fe, and Fe,Cu-codoped In$_2$O$_3$ films on sapphire substrates by pulsed laser deposition. The magnetization of the Fe-doped In$_2$O$_3$ 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$_2$O$_3$ films, which contribute to the inhomogeneous ferromagnetism.

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1. Introduction

 Diluted magnetic semiconductors (DMSs) have attracted much attention for their potential applications in spintronic devices [1–3], Fe-doped In$_2$O$_3$ 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$_2$O$_3$ host lattice (~20%) [4,5], therefore many research groups, including ourselves, have paid more attention to the Fe-doped In$_2$O$_3$ 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$_2$O) 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$_2$O$_3$ 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$_2$O$_3$ 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$_2$O$_3$ 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$_2$O$_3$ [13], the fundamental mechanism regarding the contributions of Cu codopant toward the magnetic ordering of In$_2$O$_3$-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$_2$O$_3$ 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$_2$O$_3$ 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$_2$O$_3$ films leading to the inhomogeneous ferromagnetism. The role of adding Cu on the formation of Fe clusters in Fe-doped In$_2$O$_3$ DMSs is also discussed.

2. Experiments

The (In$_{0.95}$Fe$_{0.05}$)$_2$O$_3$ and (In$_{0.92}$Fe$_{0.05}$Cu$_{0.03}$)$_2$O$_3$ films were grown on c-cut sapphire substrates by a PLD technique from their corresponding targets with thickness varying from 100 to 400 nm
To gain a further insight into the magnetic origin in the Fe and Fe,Cu-codoped In$_2$O$_3$ 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$_{0.90}$Fe$_{0.05}$Cu$_{0.03}$)$_2$O$_3$ 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$_{0.90}$Fe$_{0.05}$Cu$_{0.03}$)$_2$O$_3$ films with blocking temperatures $\approx$32 K. The larger coercivities ($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}$)$_2$O$_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$_{0.05}$)$_2$O$_3$ films $^{[16,17]}$.

All the magnetic results presented above demonstrate the presence of hidden ferromagnetic nano-clusters in the Fe,Cu-codoped In$_2$O$_3$ 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$_2$O$_3$ 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$_{0.95}$Fe$_{0.05}$Cu$_{0.03}$)$_2$O$_3$ film compared to data from Fe metal and Fe-doped In$_2$O$_3$ sample whose extended fine structure (EXAFS) shows the Fe to be entirely substitutional. The spectra have been normalized to the incident intensity $I_0$ 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$_{0.95}$Fe$_{0.05}$Cu$_{0.03}$)$_2$O$_3$ 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$_{0.95}$Fe$_{0.05}$Cu$_{0.03}$)$_2$O$_3$ 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
its analysis should be a more reliable measure of the relative amounts of Fe metal and substitutional Fe. Our XAFS results for (In0.92Fe0.05Cu0.03)2O3 film are different from those observed for (In1−xFe)x2O3 films with 2% Cu [20], where Fe is in substitutional site with a mixture valence of Fe3+ and Fe2+.

XAFS was also measured for the Cu edge. Fig. 4(c) shows the XANES spectrum compared to some Cu standards. The data does not match well any of the standards, but the position of the edge rules out a significant amount of Cu2+. The Fourier transform of the EXAFS in Fig. 4(d) is complex and likely a mixture of phases. Simple models of mixtures of Cu metal, Cu2O, and Cu substituting for In in In2O3 did not provide a good fit to either the XANES or EXAFS.

However, analysis of the backscattering amplitude of the main peak near R = 2 Å finds it consistent with either Cu or Fe neighbors, although the peak is shifted somewhat lower compared to fcc Cu metal. Therefore, we can conclude that the Cu is a mixture of Cu0 and Cu+ with a metal component likely different from bulk fcc Cu.

The magnetic circular dichroism (MCD) data for the Fe,Cu-codoped In2O3 film of thickness 180 nm was very different from those of the Fe-doped In2O3 film where the Fe was known to be located at In sites [9]. The data could be fitted as shown in Fig. 5 by assuming that there is a fraction of the samples that is in ferromagnetic clusters of metallic iron and that the In2O3 matrix is also magnetic. The contribution of clusters of ferromagnetic

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**Fig. 3.** The FC (open symbols) and ZFC (solid symbols) magnetization curves recorded at 100 Oe for the (In0.92Fe0.05Cu0.03)2O3 films with different thickness: (a) 100 nm, (b) 180 nm, (c) 260 nm, and (d) 350 nm. The insets show the hysteresis loops of the corresponding films at 5 and 300 K on the expanded scale.

**Fig. 4.** Comparison of the XAFS from an (In0.92Fe0.05Cu0.03)2O3 film (thickness 180 nm) compared to data from bcc Fe metal and a Fe-In2O3 film (thickness 142 nm) with substitutional Fe. (a) Normalized near edge data. (b) K² weighted Fourier transform of the EXAFS. The Fe metal data has been scaled by 0.25 as described in the text. (c) Normalized XANES spectra for the Cu edge in the (In0.92Fe0.05Cu0.03)2O3 film compared to Cu metal, Cu2O, and CuO. (d) Fourier transform of the K² weighted EXAFS data from the Cu edge compared to similar transforms for Cu metal and Cu2O. The transform range is 2–12 Å⁻¹.
metallic Fe is calculated using the Maxwell–Garnett theory [21,22] and the results fitted to this data for energies $1.8 < E < 2.5$ eV below the band edge of In$_2$O$_3$ matrix. The results fit the theory with the plasma frequency of bulk iron [23] with a reduced relaxation time and with $\omega_{\text{pl}} = 0.42 \pm 0.05$ which corresponds to metallic particles elongated along $\gamma$-direction. The fraction of the sample that is occupied by materials with a dielectric function characteristic of ferromagnetic metallic Fe is found to be $0.5 \pm 0.1\%$. Closer to the band edge there is a clear negative signal corresponding to polarized defect states. We note this has the opposite sign to that seen before [9]; this difference occurs because of the difference in population of the defect states.

The volume fraction of $0.5 \pm 0.1\%$ may be used to estimate the fraction of Fe ions that are in ferromagnetic metallic clusters. The number of Fe ions in the clusters is found using the number density of Fe ions in metallic Fe to be $0.005 \times 8.5 \times 10^{22} = 4.25 \times 10^{20} \text{cm}^{-3}$. This should be compared with the total number of Fe ions in the film given by $4.58\%$ of the number density of In ions in In$_2$O$_3$ which is $0.046 \times 3.10 \times 10^{22} = 1.43 \times 10^{21} \text{cm}^{-3}$. Hence we may deduce from MCD measurements that a fraction $0.3 \pm 0.1$ of the Fe ions are in clusters characteristic of ferromagnetic metallic iron.

Assuming that all Fe sites in the metallic cluster contribute a moment of $2.2 \mu_B$ this translates to a total moment of $0.66 \pm 0.1 \mu_B$ per Fe atom which is similar to the experimental value of $\sim 0.65 \mu_B$ as shown in Fig. 2. There should be some contribution from the In$_2$O$_3$ matrix as an MCD band edge signal was seen although the near edge implied that the Fe in the lattice was in the Fe$^{2+}$ state which is known to be nonmagnetic [4,5,20]. The surprising result is that the magnetism of the Fe in nanoparticles may be more than enough to account for the total observed moment may be due to an enhanced dielectric response from small particles of Fe.

Both the K-edge data and MCD data provide evidence that the metallic Fe clusters are formed in the Fe,Cu-codoped In$_2$O$_3$ films, which is consistent with the ZFC/FC measurements. Different fractions are obtained from the near edge absorption (45 $\pm 5\%$), the EXAFS (25$\%$) and the MCD (30 $\pm 10\%$). This occurs because the three estimates measure different quantities, the near edge measures the ionization state and EXAFS is a structural measurement whereas the MCD is a magnetic measurement. All three measurements agree that a substantial fraction of the Fe is in the metallic state.

The occurrence of metallic Fe in the Fe,Cu-codoped In$_2$O$_3$ films and not in the Fe-doped In$_2$O$_3$ films is a striking conclusion and implies that we must have less oxygen in the Fe,Cu-codoped In$_2$O$_3$ films even though they were grown under identical conditions. We suggest it may be the ratio of Fe to Cu that is important. The (In$_{0.5}$Fe$_{0.4}$Cu$_{0.1}$)$_2$O$_3$ target is made from In$_2$O$_3$, Fe$_2$O$_3$ and CuO, so the CuO is contributing half an oxygen ion less per metal ion than the other two components. This means that the resulting film will have less oxygen. Since Cu can also exist as Cu$^{2+}$ and Cu$^{4+}$ (shown in Fig. 4(c) and (d)), it appears to lose a little more of its oxygen during the preparation of the target. At this case, when the oxygen deficiency target is ablated by pulse laser at the base pressure of $5 \times 10^{-3}$ mTorr, the part of Fe$^{4+}$ of Fe$_2$O$_3$ may easily be reduced to Fe$^0$, resulting in the formation of Fe clusters.

4. Conclusion

In summary, we have grown Fe, and Fe,Cu-codoped In$_2$O$_3$ films with different thicknesses on sapphire substrates by pulsed laser deposition and observed ferromagnetism at room temperature. The ferromagnetism in Fe-doped In$_2$O$_3$ films was almost homogeneous. The Fe,Cu-codoped In$_2$O$_3$ films showed an obvious thickness dependent magnetization, and the ferromagnetism was inhomogeneous. The X-ray absorption fine structure and magnetic circular dichroism characterizations confirm that the Fe oxides can be reduced and metallic Fe clusters are present in the Fe,Cu-codoped In$_2$O$_3$ films but not in the Fe doped films. This may also be the main origin for the observed inhomogeneous ferromagnetism in Fe,Cu-codoped In$_2$O$_3$ films. The confirmation of transition metal Fe clusters shows that, in this case, the presence of Cu increases phase segregation and hence acts against the production of a uniform magnetic oxide based DMS. However it may enable us to get a useful granular magnetoresistance in these films, which will be investigated further in the future.

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References


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**Fig. 5.** $\Delta m_{\text{ex}}$ from experimental MCD curve, $e$, the theoretical contribution from metallic nanoparticle, $m$, and difference, $d$, arising from In$_2$O$_3$ matrix. The inset shows a comparison of the measured and theoretical values of the dielectric function over the fitting range.


