Room temperature ferromagnetic *n*-type semiconductor in $(In_{1-x}Fe_x)_2O_{3-\sigma}$

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The thin film synthesis and characterization of room temperature ferromagnetic semiconductor $(In_{1-x}Fe_x)_2O_{3-\sigma}$ are reported. The high thermodynamic solubility, up to 20%, of Fe ions in the In_2O_3 is demonstrated by a combinatorial phase mapping study where the lattice constant decreases almost linearly as Fe doping concentration increases. Extensive structural, magnetic and magneto-transport including anomalous Hall effect studies on thin film samples consistently point to a source of magnetism within the host lattice rather than from an impurity phase. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1851618]

Room temperature ferromagnetic semiconductors have been of great interest due to their potential spintronics applications. Many candidates have been discovered through conventional and combinatorial approaches.[1–11] In most of the other magnetic semiconductors, doped magnetic ions exhibit very low solubility in host semiconductors, and the origins of ferromagnetism in some of the compounds have been attributed to magnetic impurities.[12] Therefore, materials systems based on host semiconductors with high solubility of magnetic ions are highly desirable to form thermodynamically stable magnetic semiconductors. In this letter, we describe the discovery and characterization of a ferromagnetic semiconductor system based on In_2O_3 host lattice in thin film format.

In_2O_3 is a wide band gap semiconductor with cubic bixbyite crystal structure. Its lattice constant is 10.12 Å in a bcc unit cell. In_2O_3 can be made to a highly conducting *n*-type semiconductor by introducing oxygen deficiencies (σ) or Sn doping. The high solubility of Fe in In_2O_3 host lattice was first identified by a combinatorial experiment using a continuous phase diagram mapping technique. A thin film $(In_{1-x}Fe_x)_2O_3$ with $0<x<0.4$ was fabricated on an $Al_2O_3(0001)$ substrate using a combinatorial ion beam sputtering system. The resulting continuous phase diagram was investigated using a scanning microbeam diffractometer with a focus spot of 50 μm.[13,14] Figure 1 shows Vegard's law plot derived from Lorentzian fitting of (222) peak. The lattice constant decreases linearly as x increases (the Fe^{3+} ion is smaller than the In^{3+} ion), indicating solubility up to 20% Fe concentration. Above 20% Fe concentration, the lattice constant remains constant and the impurity phase, likely to be Fe_3O_4 or $InFeO_3$,[15] starts to appear as evidenced by the XRD map. The high solubility of Fe in In_2O_3 lattice may be explained by the fact that the most probable valence states of both In and Fe ions are the same, i.e., In^{3+} and Fe^{3+}, while those of other semiconducting oxides, such as $Zn^{2+}O$, $Ti^{4+}O_2$, $Sn^{4+}O_2$, are different.

The $(In_{1-x}Fe_x)_2O_{3-\sigma}$ thin films of single compositions were grown on $Al_2O_3(0001)$ substrate by pulsed laser deposition (PLD) using corresponding stoichiometric targets. Valence variations of doped magnetic elements were induced by growing the samples in high vacuum (i.e., oxygen deficient), and/or co-doped with a small amount of Cu in the range of 2 at. %, in order to create mixed valence cations, i.e., Fe^{2+}, Fe^{3+}, necessary for ferromagnetism and charge transport.[16] The background pressure of PLD system is in 10^{-7} Torr. Different flow rates of high purity O_2 gas were introduced to vary the O_2 partial pressures. The pulsed Excimer laser of KrF($\lambda=248$ nm) with the beam energy density of 2.4–2.8 J/cm^2, repetition rate of 10 Hz, and pulse duration of 10 ns was used, yielding a typical deposition rate of 2.8 Å/s. The substrates were heated during thin film deposition, and a typical film thickness of a sample was 5000 Å measured by Dektak 3 profilometer.

The x-ray diffraction patterns for the individual thin films were obtained using Rigaku Mini Flex$^+$ Diffractometer. The respective XRD patterns for $(In_{1-x}Fe_x)_2O_{3-\sigma}$ with $x=15\%$ and Cu co-doping, and the sample with $x=10\%$ and no Cu doping, grown at 550 °C under 10^{-7} Torr, are shown in Fig. 2. The data exhibit only (222) and (444) orientation peaks of In_2O_3, indicating highly oriented growth along

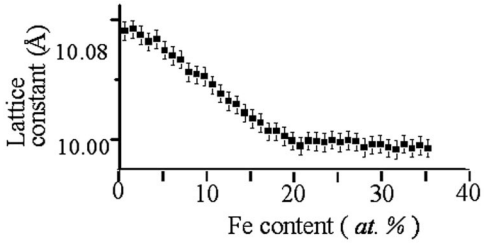

FIG. 1. Vegard's law (lattice constant as a function of Fe doping concentration) plot of thin film $(In_{1-x}Fe_x)_2O_3(x=0-0.4)$ phase diagram.

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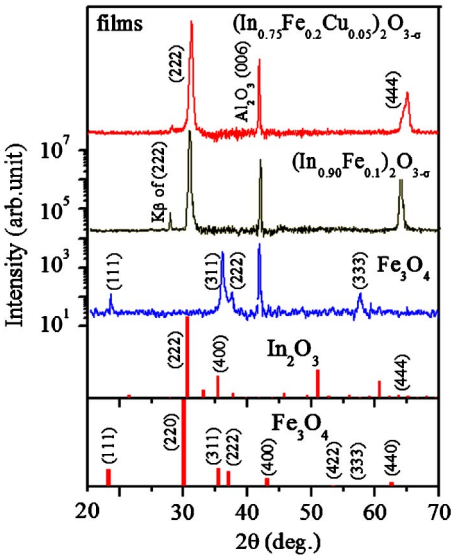

FIG. 2. (Color online) XRD of thin film samples of $(In_{1-x}Fe_x)_2O_{3-\sigma}$ and Fe_3O_4 in logarithmic scale. The intensity bars from standard diffraction patterns for bulk In_2O_3 and Fe_3O_4 are also included for comparison.

[111] direction. No impurity peak was detected in both thin film samples, indicating a single-phase growth. For comparison, the XRD pattern of a Fe_3O_4 thin film sample grown on the same substrate at 650 °C under 10^{-7} Torr is presented in Fig. 2, along with standard XRD patterns for bulk In_2O_3 and Fe_3O_4. Although not all peaks are visible due to the preferred growth orientation of thin film samples, it is clear that the XRD of the doped In_2O_3 thin film samples is completely different from that of Fe_3O_4.

The magnetic field dependence of sample magnetic moment was measured by superconducting quantum interference device magnetometer. Only those thin films with good conductivity grown under high vacuum were found to be ferromagnetic. The *M-H* curve taken at 5 K for the thin film sample of Fe 15% with Cu co-doping, grown at 550 °C in vacuum (5×10^{-7} Torr), is shown in Fig. 3. Ferromagnetic behavior is evident with measured coercive fields of about 450 Oe. The inset shows the room- temperature *M-H* curve of a different sample, with $x=0.2$, indicating room temperature ferromagnetism (T_c of 750 K was measured on bulk ceramic samples[17]). The saturation magnetization is

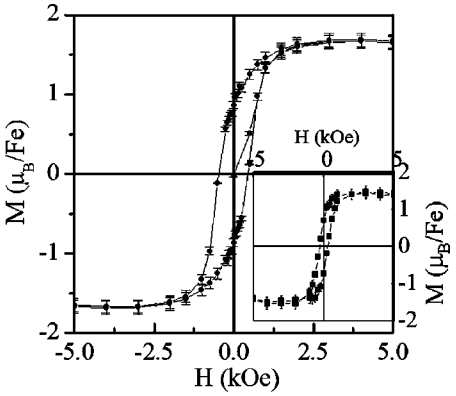

FIG. 3. *M-H* curves at 5 K for $(In_{1-x}Fe_x)_2O_{3-\sigma}$ thin film sample with 15% Fe and 2% Cu co-doping. The magnetic field is applied to parallel ($H_{\parallel}$) to the film surface. The inset shows room temperature *M-H* curve of $(In_{1-x}Fe_x)_2O_{3-\sigma}$ thin film sample with 20% Fe and 2% Cu co-doping.

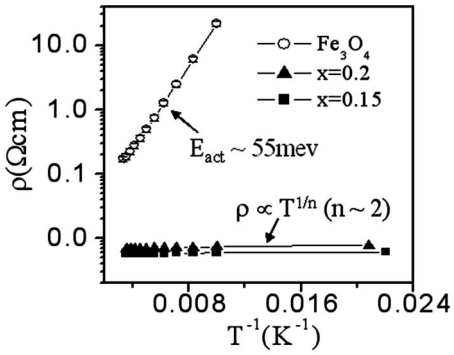

FIG. 4. The resistivity of $(In_{1-x}Fe_x)_2O_{3-\sigma}$ with Cu co-doping and Fe_3O_4 thin films as function of T^{-1}. $(In_{1-x}Fe_x)_2O_{3-\sigma}$ with Fe 20% was grown at 650 °C while Fe 15%, at 550 °C.

$\sim 1.45\mu B/Fe$ atom, assuming all the Fe atoms contribute to the magnetization. The coercive fields are much larger than those of bulk samples[17] indicating a larger magnetocrystalline anisotropy, probably due to stress-induced inverse magnetostriction caused by lattice and thermal expansion mismatches with the substrate. Higher temperature measurements of thin films were not made since oxygen content in a thin film will change significantly due to slow heating process.

The possible magnetic impurity phases in the system are Fe_3O_4 and $CuFe_2O_4$. $CuFe_2O_4$ samples annealed in oxygen gain maximum magnetization (Fe 3+ is responsible for the magnetism in the system) while $(In_{1-x}Fe_x)_2O_{3-\sigma}$ thin films with Cu co-doping annealed in a slightly high O_2 partial pressure show no sign of ferromagnetism. This observation rules out contribution by $CuFe_2O_4$ impurity phase, because, if $CuFe_2O_4$ impurity phase had been responsible for the observed magnetism in the $(In_{1-x}Fe_x)_2O_{3-\sigma}$ samples with Cu co-doping, the ferromagnetism must be present in the samples annealed in oxygen. Since the saturated magnetic moment of Fe_3O_4 is reported to be about 1.3 μ_B/Fe,[18] if the observed magnetic moment of about 1.45 μ_B/Fe had been attributed to Fe_3O_4, one would have to assume that almost 100% of doped Fe ions ended up forming Fe_3O_4. This is impossible because significant XRD peaks of Fe_3O_4 would appear if such a large amount of Fe_3O_4 were present. Also, if most of the doped Fe ions had formed Fe_3O_4, the significant lattice constant change, indicative of incorporation of Fe ions into In_2O_3, would not have been observed in Fig. 1. Further investigation using extended x-ray absorption fine structure (EXAFS) spectrum has confirmed that indeed, the magnetism is originated from mixed valence of Fe^{2+}/Fe^{3+} situated in In_2O_3 lattice (due to space limitation, this data will be

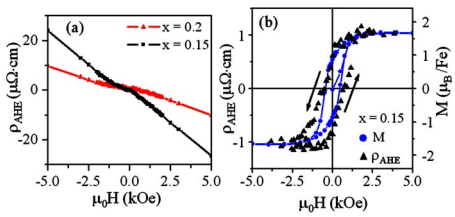

FIG. 5. (a) Hall resistivity vs μ_0H of the $(In_{1-x}Fe_x)_2O_{3-\sigma}$ thin films with Cu co-doping ($x=0.2$ and 0.15, respectively). (b) is the AHE term after subtracting the ordinary Hall effect term for the thin film sample with Fe 15%; the data were collected at 286 K. Also shown is the *M-H* curve of the same sample measured at 5 K.

TABLE I. Various physical parameters from Hall measureaments at 286 K: μ_H: Hall mobility; n: carrier density; M_s: saturated magnetic moment (at 5 K).

$(In_{1-x}Fe_x)_2O_{3-\sigma}$ with 2% Cu	R_0 10^{-2} cm^3/C	μ_H cm^2 V^{-1} S^{-1}	n 10^{20} cm^{-3}	R_{AHE} cm^3/C	α cm^2 V^{-1} S^{-1}	ρ 10^{-3} Ω cm	M_s μ_B/Fe
1 $x=0.2$ 650 °C, 7×10^{-7} Torr	−5.84	8.55	1.07	0.06	9.3	6.84	1.53
2 $x=0.15$ 550 °C, 7×10^{-7} Torr	−19.1	32.2	0.33	0.28	48	5.79	1.47

published elsewhere[19]), not the impurity phase of Fe_3O_4 or $CuFe_2O_4$.

The electrical and magneto-transport properties were measured at various temperatures in a cryostat equipped with a 12 T superconducting magnet. Normal resistivitities (ρ) of different thin film samples as a function of T^{-1} are shown in Fig. 4. $\rho(T)$ of a pure Fe_3O_4 thin film, deposited at 650 °C in a similar vacuum condition as $(In_{1-x}Fe_x)_2O_{3-\sigma}$ thin film samples, is drastically different from those of $(In_{1-x}Fe_x)_2O_{3-\sigma}$ thin film samples, which better fit $T^{1/n}$ behavior in low temperature region with n close to 2. The activation energy E_{act} obtained for Fe_3O_4 is 55 meV, similar to the values reported for a single crystal sample and from other thin film studies.[20] However, the resistivity of ~170 mΩ cm at room temperature and saturation magnetic moment of 0.14 μ_B/Fe at 5 K are not optimized to the ideal values of bulk Fe_3O_4, which are ~10 mΩ cm at room temperature and 1.3 μ_B/Fe, respectively.[18,20] In fact, to our knowledge, no Fe_3O_4 thin film work has demonstrated magnetization value that is close to 1.3 μ_B/Fe. For this reason, it is unlikely that the observed saturation magnetic moment (1.45μ_B/Fe) and transport properties of $(In_{1-x}Fe_x)_2O_{3-\sigma}$ thin film samples originated from Fe_3O_4.

Hall resistivity ρ_{xy} in magnetic materials can be expressed as $\rho_{xy}=R_0B+\mu_0R_{AHE}M$. The first term is an ordinary Hall effect and the second is the anomalous Hall effect (AHE), where B is the internal magnetic induction, M the magnetization and R_{AHE} the anomalous Hall coefficient. $R_{AHE}(T)=\alpha\rho_{xx}(0,T)$, where $\rho_{xx}(0,T)$ is the normal resistivity at zero field and α is a T-independent parameter with dimension of mobility.[21] Hall resistivity $\rho_{xy}(\rho_H)$ μ_0H curve for two $(In_{1-x}Fe_x)_2O_{3-\sigma}$ thin films are plotted in Fig. 5(a); ρ_{xy} is linear up to high field as expected, with a vertical shift at low field indicating an AHE. If the ordinary Hall resistivity term is subtracted, as shown in Fig. 5(b) (formed by triangle symbol), the AHE term near zero field can be seen more clearly with a similar hysteretic loop as measured M-H curve, also shown in Fig. 5(b) (dotted curve). Note some small discrepancy in details of field dependence can be attributed to the effect of small negative magnetoresistance and sample alignment issue for each measurement. The M-H curve used here was measured at 5 K. As the T_c of the sample is about 750 K,[17] and the M-H curve is fully saturated, we do not expect significant difference between low temperature and room temperature magnetization due to ferromagnetism. Both thin film samples were measured to be n-type semiconductors and their corresponding physical parameters are listed in Table I. The observed AHE suggests that transport carrier interacts strongly with the local magnetism.

Discovery of thermodynamically stable ferromagnetic n-type semiconductor $(In_{1-x}Fe_x)_2O_{3-\sigma}$ system is an important advance for future coherent spin transport device applications. Because In_2O_3-based compounds have been widely used as transparent conductors, they are attractive for the semiconductor industry, where a wealth of knowledge is available regarding their interface with conventional semiconductors.

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