Ferromagnetic, Transparent and Conducting ITO-Fe-Cluster Composite Films

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Indium-tin oxide (ITO)-Fe-cluster composite films were fabricated by plasma-gas-condensation-type cluster beam deposition and RF helicon sputtering method, and the structural, optical, electrical and magnetic properties of the films were investigated. The optical transmittance of about 90% is obtained for the Fe cluster layer thickness of 10 nm although it is decreased with increasing the cluster layer thickness. The resistivity is further decreased by embedding metalic Fe clusters into ITO matrix and a resistivity value of about an order of $10^{-4}\,\Omega$ cm was obtained. Moreover, the ITO-Fe cluster composite films show ferromagnetism at room temperature even for a cluster layer thickness of 10 nm.

***Index Terms*—High electrical conductivity, indium-tin oxide (ITO) Fe-cluster composite films, room-temperature ferromagnetism, transparency.**

I. INTRODUCTION

DILUTED magnetic semiconductors have attracted considerable attention because of their potential for novel technological applications utilizing both the semiconductor and ferromagnetic characteristics, the so-called "spintronics" [1]–[3]. Most of the Curie temperatures of these diluted magnetic conductors are much lower ($T_c < 100$ K) than the room temperature, being not appropriate for technical application. Recently, co-doped anatase TiO_2 thin films were reported to be ferromagnetic even above 400 K [4], [5], while they have high resistivity ($>0.5\ \Omega$ cm).

For developing ultimately new multifunctional devices, moreover, it is desired to utilize simultaneously optical, electrical and magnetic properties of materials and their inter-correlation effect. In conventional materials, however, good optical transparency, high electrical conductivity and ferromagnetism above room temperature are usually incompatible. Since indium-tin oxide (ITO) thin films have low resistivty, high transmittance, and good etching properties, which have been widely used as optoelectronic devices such as touch panels, flat panel display and thin film solar cells, we try to prepare the ITO-Fe-cluster composite film by film sputtering deposition combining with magnetic cluster beam deposition, and study their optical, electrical and magnetic properties.

II. EXPERIMENT

Fe clusters were prepared by the plasma-gas-condensation (PGC)-type cluster beam deposition apparatus (Fig. 1), which is based on plasma-glow-discharge vaporization (sputtering) and inert gas condensation techniques [6]. The apparatus is composed of the three main parts: a sputtering chamber, a cluster growth region and a deposition chamber. The background pressure of all chambers was $<1.3 \times 10^{-5}$ Pa. During cluster deposition, a large amount of high purity Ar and He gases of $(1.87 - 4.1) \times 10^{-4}$ mol/s were introduced continuously into the sputtering chamber and evacuated by a mechanical booster pump (MBP) through a nozzle, making the sputtering chamber pressure approximately $(1 - 7) \times 10^2$ Pa. Fe atoms sputtered into the inert gas space are decelerated by collisions with inert gas atoms and collide with each other to form Fe clusters. We can control the mean cluster size d by changing the flow rate of Ar and He gases from 7 to 16 nm with a standard deviation less than 10% of d [7]. ITO films were generated by a hericon sputtering system in the deposition chamber. Fe clusters and ITO films were deposited on a substrate in a sandwich form ($\mathrm{ITO}_{100\ \mathrm{nm}}$/Fe-cluster-layer$_{10\text{–}30\ \mathrm{nm}}$/$\mathrm{ITO}_{100\ \mathrm{nm}}$) [Fig. 2(a)] or in a multilayer form $(\mathrm{ITO}_{40\ \mathrm{nm}}/\mathrm{Fe}-\mathrm{cluster}-\mathrm{layer}_{2.5\mathrm{nm}}) \times 4/\mathrm{ITO}_{40\mathrm{nm}})$ [Fig. 2(b)], where the subscript numbers indicate the effective thicknesses t_e. The substrate temperature was kept at $T_s = 473K$. The obtained ITO-Fe composite films were annealed at $T_a = 623$ and 743 K for 2 h in a vacuum of about 2.7×10^{-5} Pa. The effective thickness of Fe cluster layers t_e was measured using a quartz crystal thickness monitor and the thickness of ITO films was obtained by the calibrated relation between the input power, deposition time and

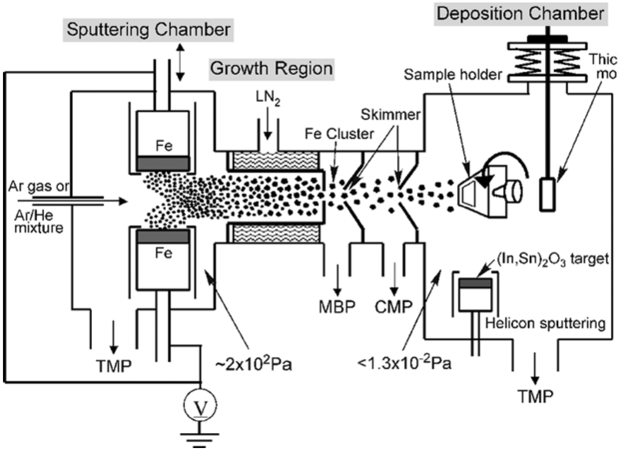

Fig. 1. Schematic drawing of PGC-type cluster deposition apparatus and RF hericon sputtering method. TMP, MBP, and CMP represent turbo-molecular pump, mechanical booster pump, and compound molecular pump, respectively.

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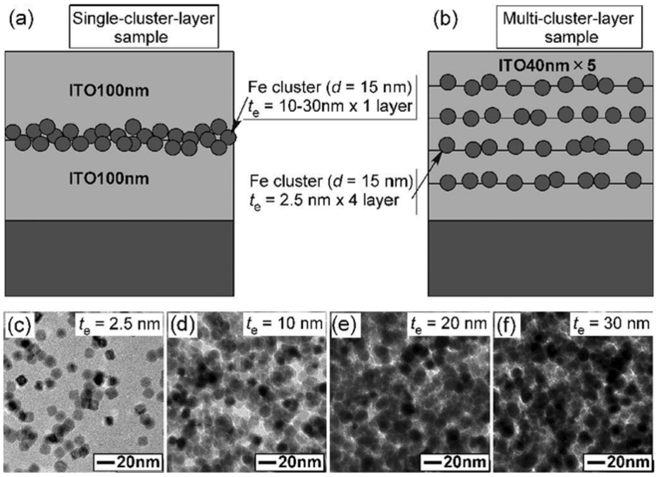

Fig. 2. (a) and (b) Schematic drawing of the ITO-Fe-cluster composite films with a sandwich form and a multilayer form. (c)–(f) TEM image of single Fe cluster layer with different effective thicknesses.

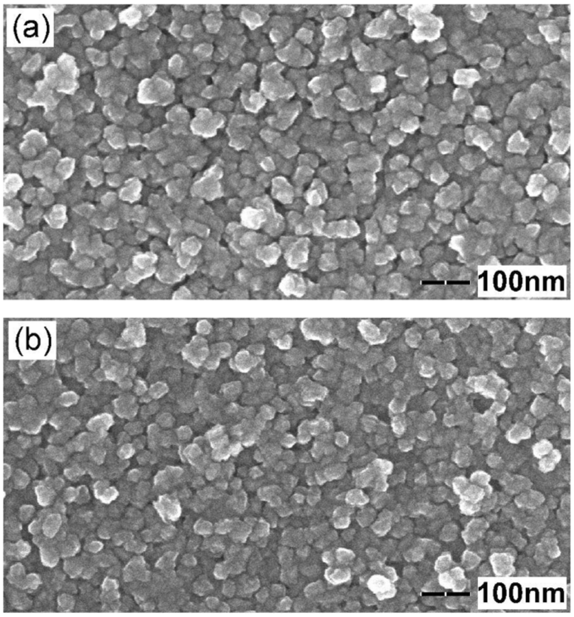

Fig. 3. Plan-view SEM image of the ITO-Fe-cluster composite films with (a) the sandwich form (ITO-Fe10 nm) and (b) the multilayer form $(\mathrm{ITO}-\mathrm{Fe}2.5\ \mathrm{nm}\ \times\ 4)$.

thickness. The structure and morphology were measured by X-ray diffraction, transmission electron microscope (TEM) and scanning electron microscope (SEM), optical transmittance by a spectrophotometer, and electrical resistivity by a conventional dc four-probe method. Magnetic measurement was performed using a super-conducting quantum interference device magnetometer.

III. Results and Discussion

In this work, the size-monodispersed Fe clusters with $d =$ 15 nm were used. Fig. 2(c)–(d) show the TEM images of single Fe cluster layer with different effective thicknesses. In those images, individual Fe clusters are distinguishable though they touch and overlap each other. Fig. 3 shows the plan-view SEM images of the samples with the sandwich form and the multilayer form. The ITO-Fe-cluster composite films thus obtained have a clear polycrystalline structure in which the grain size ranges from 30 to 50 nm. The X-ray diffraction measurement (Fig. 4) indicates that the ITO-Fe-cluster composite films are the bixbyite phase.

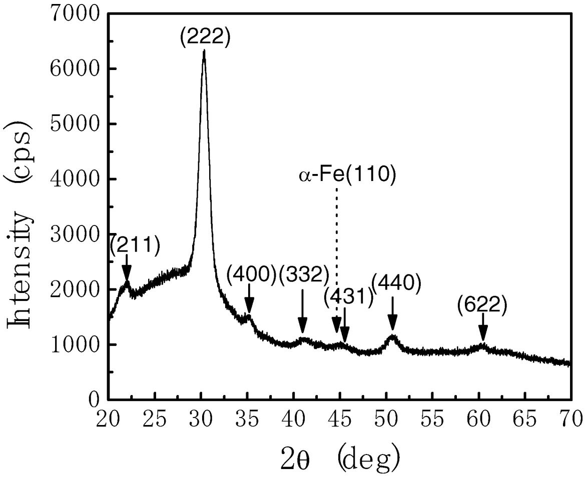

Fig. 4. X-ray diffraction pattern of the ITO-Fe-cluster composite films with the sandwich form (ITO-Fe10 nm).

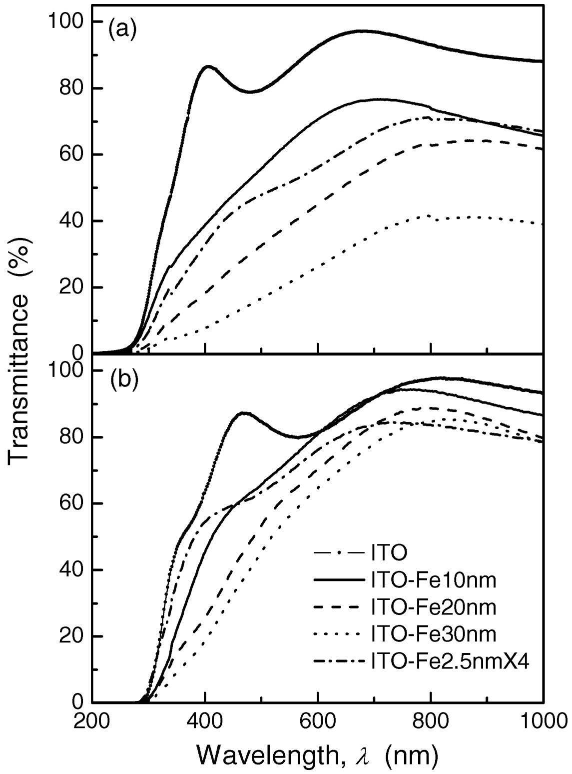

Fig. 5. Optical transmission spectra of the ITO film and the ITO-Fe-cluster composite films after heat treatment at (a) $Ta = 623$ and (b) 743 K.

Fig. 5 shows transmission spectra of the ITO and ITO-Fe-cluster composite films after heat treatment at (a) $T_a = 623$ and (b) 743 K. For both heat treatment conditions, the optical transmittance is decresed with increasing the Fe cluster layer thickness. As shown in Fig. 5(b), however, it can be seen that after heat treatment was carried out at $T_a = 473$ K, the transmittance

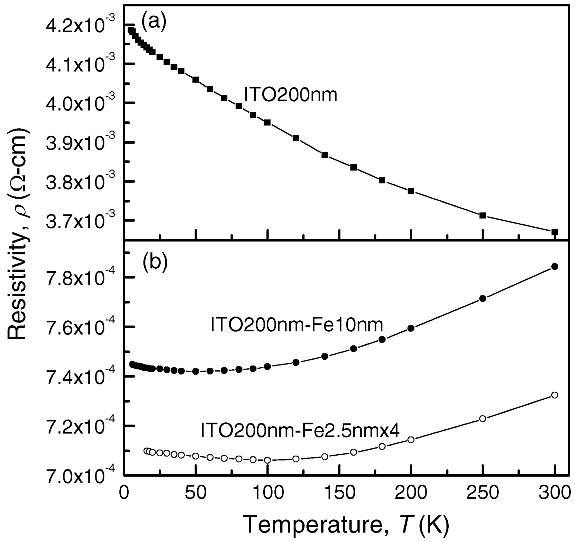

Fig. 6. Electrical resistivity ρ as a function of temperature $T$for (a) the ITO film and (b) the ITO-Fe-cluster composite films with the sandwich form (ITO-Fe10 nm) and the multilayer form $(\mathrm{ITO} - \mathrm{Fe}2.5\ \mathrm{nm}\ \times\ 4)$.

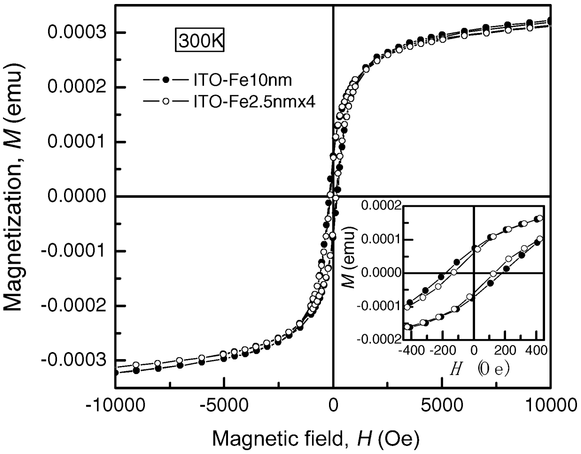

Fig. 7. In-plane hysteresis loops of the ITO-Fe-cluster composite films with the sandwich form (ITO-Fe10 nm) and the multilayer form $(\mathrm{ITO} - \mathrm{Fe}2.5\ \mathrm{nm}\ \times\ 4)$. The inset shows the data for low field regions.

is not so much degraded and reaches above 90% for the sample with a 10 nm Fe cluster layer for $\lambda > 600$ nm. This feature is attributable to the fact that Fe clusters are much smaller than the wavelength of visible light.

Fig. 6 shows the electrical resistivity, ρ, as a function of temperature for the ITO and ITO-Fe-cluster composite films. For the ITO film [Fig. 6(a)], the temperature coefficient of resistivity is negative below room temperature. For the ITO-Fe-cluster composite films [Fig. 6(b)], the resistivity exhibits a minimum between 5 K and room temperature. Clearly, by embedding Fe clusters into ITO matrix, the resistivity is decreased by an order of magneitude in comparison with that of the ITO film and its value is of an order of $10^{-4}\Omega$cm, which is three orders of magnitude smaller than that of the Co-doped TiO_2 thin films [4], [5].

Fig. 7 shows the magnetization curves at room temperature for the samples with the sandwich form (ITO-Fe10 nm) and the multilayer form $(\mathrm{ITO} - \mathrm{Fe}2.5\ \mathrm{nm}\ \times\ 4)$. The hysteresis is observed, revealing that the present ITO-Fe-cluster composite films are ferromagnetic at room temperature. Moreover, both the samples with the sandwich form and the multilayer form make no clear difference in their magnetic properties. In the inset of Fig. 7, we plotted the low-field region of the loops showing coercivity values of about $H_c = 181$ and 132 Oe, respectively.

IV. CONCLUSION

We have studied the optical, electrical and magnetic properties of the ITO-Fe-cluster composite films prepared by combining the film sputtering deposition with the PGC-type cluster beam deposition. The present experimental results show that it is possible to produce a film material with high optical transmittance, low resistivity and ferromagnetism at room temperature by embedding Fe clusters into ITO matrix.

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