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Magnetic properties and giant magnetoresistance in $Fe_{0.35}(In_2O_3)_{0.65}$ granular film

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Abstract

Fe/In_2O_3 granular films have been prepared by the radio frequency sputtering method. The magnetic and transport measurements of a representative sample, $Fe_{0.35}/(In_2O_3)_{0.65}$, showed that there exist different magnetic states in different temperature regions. At room temperature, the film shows superparamagnetic behaviour, and a 5.2% magnetoresistance (MR) ratio was obtained. The susceptibility measurements showed that the blocking temperature is 50 K. Below a certain freezing temperature T_f of about 10 K, the film transits from the ferromagnetic state to the particle-spin-cluster state. In this event, the MR ratio of the film increases dramatically with decreasing temperature. A maximum giant magnetoresistance (GMR) ratio up to 506% is obtained at the metal–semiconductor transition temperature of about 2.2 K. The mechanism of this GMR is related to the interaction with the impurities influencing the local magnetization which is quite different to the spin-dependent tunnelling effect at room temperature.

1. Introduction

The mechanism of giant magnetoresistance (GMR) in multilayers and metallic granular systems is believed to arise from the spin-dependent scattering of conductive electrons. Another kind of GMR was found in tunnelling junction systems [1, 2], consisting of two ferromagnetic electrodes separated by a nonmagnetic tunnelling barrier, and in dielectric granular magnets where the superparamagnetic metal particles are embedded in an immiscible insulating matrix. The mechanism of GMR in these two kinds of system is interpreted as the spin-dependent tunnelling effect.

Although GMR has been discovered in metallic multilayered films and also in metallic granular films, generally speaking, GMR is much better in multilayers than in granular films. The maximum magnetoresistance (MR) ratio in Fe/Cr multilayers is 220% at 1.5 K [3], and the maximum MR ratio in Co–Ag granular films is only 60% at 4.2 K [4]. This difference comes from the fact that the maximum value of resistance in multilayers appears when the magnetic moments between the neighbour magnetic layers align antiparallel while the maximum value of resistance in granular films appears when the magnetic moments in granules align in a highly random manner. In this paper, we present a special kind of granular film, which consists of Fe particles dispersed into an In_2O_3 matrix. The maximum MR ratio is up to 5.2% at room temperature and 506% at 2 K in this granular film.

2. Experimental details

Samples were prepared by an rf sputtering system. The composite target was a sintered In_2O_3 disc on which some small Fe discs were placed uniformly. Changing the total area of Fe discs on the target, the volume concentration of the film can be altered. The substrates were 0.2 mm thick glass slides. Both target and sample holder were cooled by water. After the chamber system was evacuated to a high vacuum of about 4×10^{-6} Torr, 99.999% pure Ar gas was introduced and controlled at 5×10^{-3} Torr during the sputtering process. The rf input power was about 200 W. The deposition rate was 0.15 nm s^{-1}.

The microstructure was examined by transmission electron microscope (TEM) and x-ray diffraction. The composition of the samples was determined by energy dispersive x-ray analysis (EDXA), and the volume concentration can be estimated from the composition results. The magnetic properties and MR of samples were measured at room temperature by a vibrating sample magnetometer (VSM) with the magnetic field up to 10 kOe, while they were also measured by a commercial superconducting quantum interference device (SQUID) magnetometer with the magnetic field up to 20 kOe in the temperature range from 1.5 to 300 K. The MR was measured by using the standard four-point technique. The film used in the MR measurements was about 3 mm wide and 15 mm long. The probe current was along the film length. The magnetic field was parallel to the current direction in the film plane.

3. Results and discussion

A series of samples with different compositions has been prepared [5]. The most interesting sample with the composition of $Fe_{0.35}/(In_2O_3)_{0.65}$ was obtained. We only give the experimental results of this sample in this paper. The bright-field TEM measurements showed that the prepared $Fe_{0.35}/(In_2O_3)_{0.65}$ film had a granular structure with uniform particle size about 5 nm [5]. The x-ray diffraction pattern showed that the sample is in an amorphous state. The magnetization M versus applied magnetic field H at room temperature for this sample is shown by the dotted curve in figure 1. This is a typical magnetization curve for the superparamagnetic samples. Under the assumption of weak interparticle interactions, the magnetization $M(H)$ of a superparamagnetic system is described by the Langevin equation [6],

$$M(H) = M_S\left(\coth\frac{\mu H}{k_B T} - \frac{k_B T}{\mu H}\right) \tag{1}$$

where M_S is the saturation magnetization of the film, $\mu = mM_{\mathrm{Fe}}$, M_{Fe} is the saturation magnetization of Fe particles, m is the average mass of each Fe particle and k_B is the Boltzmann constant. A best fitting of equation (1) to experimental data obtained at room temperature gives the fitting parameters as the following: $M_S = 60$ emu g^{-1} and $\mu = 8 \times 10^3 \mu_B$ (μ_B is the Bohr magneton). According to the fitting value of M_S and the volume ratio of Fe in the films, $M_{\mathrm{Fe}} = 162$ emu g^{-1} can be obtained, which is much smaller than that of bulk Fe, 221.7 emu g^{-1}. A similar result was obtained by Wang and Xiao [7] in an Fe–Ag granular system, and it was explained that the spin waves in small particles are softened substantially

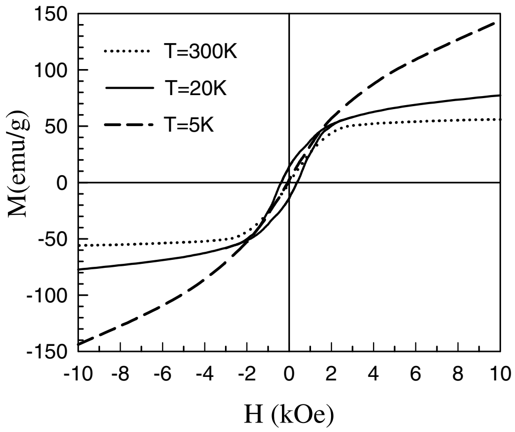

Figure 1. Magnetization M of the $Fe_{0.35}/(In_2O_3)_{0.65}$ film versus magnetic field H at different temperatures.

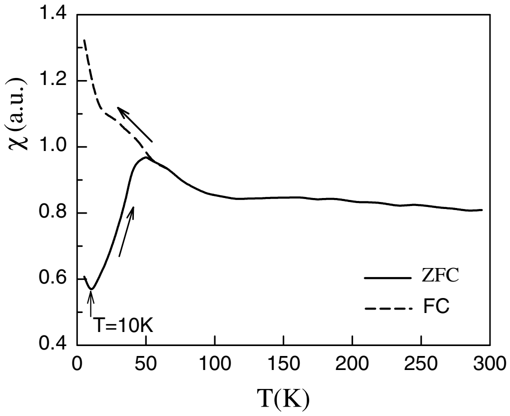

Figure 2. Magnetic susceptibilities χ as a function of temperature T for $Fe_{0.35}/(In_2O_3)_{0.65}$ film in the ZFC and FC modes.

due to the magnetic surface effect and the finite-size effect [6]. Furthermore, some Fe atoms at the interface of Fe particles will lose their magnetic moments because their Fe neighbours are too few, i.e., there is a magnetic dead layer on the Fe particle surface, similar to that found in multilayered films [8]. According to the fitting values of M_{Fe} and μ, the average diameter of particles, $d = 4.8$ nm, can be estimated, which fits well with that observed by TEM.

Susceptibilities of the film were measured at temperature ranging from 5 to 295 K. Figure 2 shows the temperature dependence of the low-field susceptibility $\chi(T)$ of the $Fe_{0.35}/(In_2O_3)_{0.65}$ film in zero-field-cooled (ZFC) and field-cooled (FC) modes. The magnetic field used in the measurements was 50 Oe. As shown in figure 2, the FC and ZFC curves coincide with each other above 50 K, but they are quite different and irreversible below 50 K. This indicates that 50 K is the blocking temperature marking a transition from the superparamagnetic to the ferromagnetic state. The solid curve shown in figure 1 gives the hysteresis curve of the sample measured at 20 K. One can see that hysteresis is exhibited at 20 K indicating a ferromagnetic state.

One can also see from figure 2 that there is a minimum value in the ZFC curve and an upturn knee in the FC curve at about 10 K suggesting another magnetic transition. In order to ascertain the property of this magnetic transition, we measured the magnetization curve at 5 K and the result is shown by the dashed curve in figure 1. There are two evident characteristics for this sample. Firstly, there is no hysteresis in the magnetization curve. Secondly, the magnetization process is a signature of magnetic moment rotation and it is difficult to reach saturation until $H = 10$ kOe. This phenomenon can be explained in the following way. During the process of preparation, there are inevitably some Fe atoms dispersed in the In_2O_3 matrix as interspacing atoms. The spacings between these Fe atoms are too large for them to couple with each other by the exchange interaction at higher temperature. When the temperature decreases to a critical value T_f (freezing temperature), the exchange interaction between isolated Fe atoms becomes strong enough to couple them into the composite clusters. In this case, the Fe particles can be coupled into local particle groups (called particle-spin clusters) by means of exchange coupling between the interspacing Fe atoms and the interface Fe atoms in the Fe particles. Thus, each particle-spin cluster has a total magnetic moment. Because of the random arrangements of Fe atoms and Fe particles in the In_2O_3 matrix, the direction of magnetic moments of particle-spin clusters is in disorder, resulting in a magnetic state similar to the cluster glass in diluted transitional metal alloys. For such a particle-spin-cluster system, the magnetization process has to overcome the anisotropy and rotate the moment of each particle-spin cluster to the direction of the applied magnetic field. The magnetization process of this system is similar to that of the speromagnetic state in amorphous rare-earth–transition-metal alloys. The freezing temperature T_f should be about 10 K, which is obtained from the minimum value in the ZFC curve in figure 2. Below T_f, the magnetization of film is related to three contributions: one comes from the core of Fe particles, the second comes from the ‘revived’ Fe atoms at the interfaces of Fe particles due to the exchange coupling with Fe atoms dispersed in the In_2O_3 matrix and the last one is from the interspacing Fe atoms in the In_2O_3 matrix. The last two contributions induce the magnetization of the film to increase. Therefore, a rotating magnetization curve with an enhanced magnetization was obtained at 5 K as shown by the dashed curve in figure 1.

Dots shown in figure 3 are the MR ratio, $\Delta\rho/\rho_H = [\rho_H - \rho_0]/\rho_H$, versus magnetic field H at room temperature, where ρ_0 and ρ_H are the resistivities of the sample in zero field and in field H. When the magnetic field is along the current direction (longitudinal case) or perpendicular to the current in the film plane (transverse case), the same results were obtained. A maximum value of 5.2% was obtained at $H = 10$ kOe. Many experiments have shown that in the case of metallic or insulating granular systems, the MR ratio is proportional to the square of magnetization, $(M/M_S)^2$ [7].

$$\Delta\rho/\rho_H = C(M/M_S)^2 \tag{2}$$

where C is the proportional constant and M_S is the saturation magnetization of the sample. Using equations (1) and (2), a perfect theoretical fitting result $\Delta\rho/\rho_H$ versus H to the experiments can be obtained as shown by the solid curve in figure 3, where $C = -0.05$. This result confirms that the MR in the present film really arises from that of granular type and closely relates to the magnetization process of the film, i.e., GMR at room temperature is related to the spin-dependent tunnelling effect.

The dependences of ρ on T for the $Fe_{0.35}(In_2O_3)_{0.65}$ granular film were measured at temperature ranging from 1.5 to 300 K without field and with a field of $H = 2$ T, respectively. Figure 4 gives the results in the most interesting temperature region. The inset of figure 4 is the GMR ratio of the film versus temperature T, where $\Delta\rho/\rho = [\rho_0 - \rho_S]/\rho_S$, with ρ_0 and ρ_S being the resistivities of the film in zero field and in field $H = 20$ kOe, respectively. Curves in the

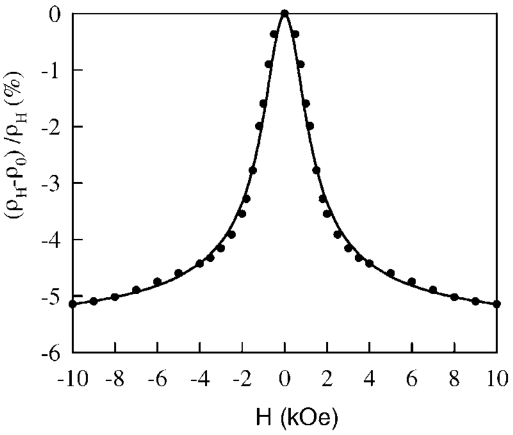

Figure 3. GMR ratio of $Fe_{0.35}/(In_2O_3)_{0.65}$ versus magnetic field H at room temperature. Dots are the experimental results and the solid curve is the fitting result.

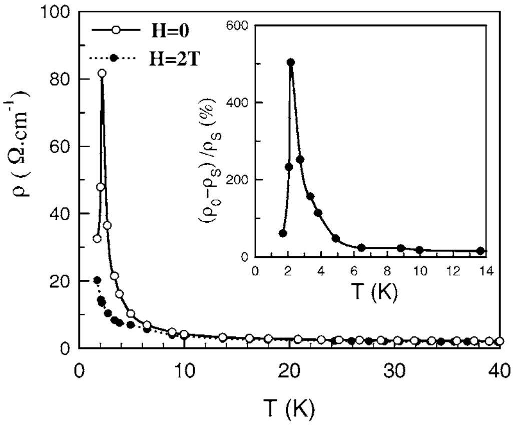

Figure 4. Resistivity ρ of film versus temperature T. The inset is the GMR ratio versus temperature curve. Curves in the figure are guides for the eye.

figure are guides to the eye. One can see from figure 4 that a transition temperature, $T_P = 2.2$ K, from metal to semiconductor exists when $H = 0$, but this transition disappears when a magnetic field of 20 kOe is applied. The peak resistance at T_p is as large as 6 MΩ. Magnetic field suppresses the resistivity of the film dramatically around the transition temperature. A maximum GMR ratio up to 506% is obtained at T_P. This behaviour is very similar to the colossal magnetoresistance (CMR) obtained in the doped rare-earth manganites [9]. However, in CMR materials the magnetic field usually shifts the transition temperature (around the magnetic transition point T_C) to higher temperature. This phenomenon has never been observed in any other granular systems to date. This GMR cannot be induced by the spin-dependent scattering or spin-dependent tunnelling effect as happened at room temperature. We suppose that the resistivity peak and significant change of resistivity in the field is related to a certain magnetic mechanism, perhaps related to the transition from ferromagnetic to particle-spin-cluster state. The transition temperature T_P is below the freezing temperature T_f, which is similar to what happened in CMR materials in which a metal–insulator transition appears below

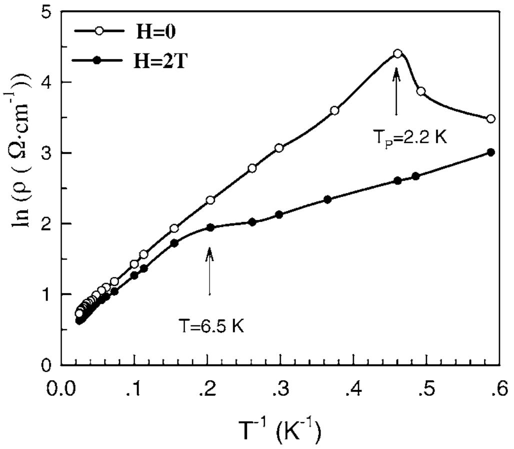

Figure 5. The logarithmic resistivity ln ρ of the film versus reciprocal temperature T^{-1}. Curves in the figure are guides for the eye.

the magnetic transition temperature. Nagaev [10] indicated that the Jahn–Teller effect cannot be an origin of CMR in the doped rare-earth mangnites. His theoretical analysis showed that the CMR is related to the interaction with the impurities influencing the local magnetization. He indicated that the resistivity peak is related to a joint action of the magnetization and of the impurity. Our results seem to agree with Nagaev's proposal. The dispersive Fe atoms in the In_2O_3 matrix act as the impurities. Below T_f, the charge carriers entering the clusters will be polarized and become the self-trapping state. The hopping mobility of charge carriers between clusters is lower than that within one cluster because the carriers must change their spin direction when they hop from one cluster into another. A magnetic field aligns the moments of local clusters along the field direction and increases the inter-cluster hopping mobility of carriers. This causes the resistivity of the sample to decrease. Therefore, this is another type of GMR observed in granular films.

In order to realize further the conductive mechanism of the film, the ρ versus T curves are plotted on a new coordinate as shown in figure 5, where the ordinate is $\ln(\rho)$ and the abscissa is T^{-1}. Curves in the figure are guides for the eye. The straight line above T_P shows that the conductive mechanism in the semiconductor state in zero field belongs to the thermal active type, i.e., the resistivity of the film follows the Arrhenius law,

$$\rho = \rho_0 \exp[E_\sigma/(k_B T)] \tag{3}$$

where E_σ is the thermal activation energy and k_B is the Boltzmann constant. When $T > T_P$ and $H = 0$, $E_\sigma = E_\sigma^0 = 0.689$ meV. After a magnetic field of 20 kOe is applied, E_σ decreases to $E_\sigma^H = 0.2485$ meV below 6.5 K, and is almost the same as E_σ^0 above 6.5 K. Below 6.5 K, the magnetic field causes the activation energy to decrease remarkably. One can see from the inset of figure 5 that 6.5 K is about the point below which the MR ratio increases sharply. This indicates that the GMR mechanism above 6.5 K is as the same as that observed at room temperature, but it changes to the impurity mechanism below 6.5 K. The decrease in hopping activation energy of carriers in a magnetic field is the reason for GMR at low temperature in this granular film. This coincides with the above analysis.

4. Conclusions

$Fe_{0.35}/(In_2O_3)_{0.65}$ granular film has been prepared by the rf sputtering method. The magnetic and transport measurements have shown that this is a complex magnetic system. At room temperature, the film shows a superparamagnetic behaviour, and a 5.2% MR ratio is obtained. The fitting result shows that the MR ratio is proportional to the square of magnetization of the film, indicating a granular type of GMR, i.e., a spin-dependent tunnelling effect. The blocking temperature of 50 K was determined by the susceptibility measurements. Below a freezing temperature $T_f \cong 10$ K, the film transits from the ferromagnetic state to the particle-spin-cluster state. In this case, the MR ratio of the film increases dramatically with decreasing temperature. A maximum GMR ratio up to 506% is obtained at a metal–semiconductor transition temperature of about 2.2 K. The mechanism of this GMR is completely different from that obtained at room temperature, and is related to the interaction with the impurities influencing the local magnetization. The spin impurities of interspacing Fe atoms play an important role in the GMR at very low temperature.

Acknowledgments

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References

[1] Cassel D, Pcikartz G, Siegel M, Goldobin E, Konlstedt H H, Brinkman A, Golubov A A, Kuopriyanov M Y and Rogalla H 2001 *Physica* C **350** 276

[2] Ge S H, Xi L, Zhang Z Z, Liu Y P and Li C X 2001 *J. Magn. Magn. Mater.* **226** 1533

[3] Shigesato Y, Takaki S and Haranou T 1991 *Appl. Surf. Sci.* **48** 269

[4] Chapra K L, Major S and Pandya D K 1983 *Thin Solid Films* **102** 1

[5] Zhang L S, Zhang L, Zhang R Z, Liu Y H, Zhang W X and Huang B X 1998 *Acta Metall. Sin.* **34** 1095 (in Chinese)

[6] Xiao G and Chien C L 1987 *J. Appl. Phys.* **61** 3308

[7] Wang J Q and Xiao G 1994 *Phys. Rev.* B **49** 3982

[8] Ernst A, Lueders M, Temmerman W M, Szotek Z and van der Laan G 2000 *J. Phys.: Condens. Matter* **12** 5599

[9] Jin S, Tiefel T H, McCormack M, Fastnacht R A, Ramesh R and Chen L H 1994 *Science* **264** 413

[10] Nagaev E L 1998 *Phys. Lett.* A **239** 321