Temperature dependence of magnetoresistivity of cobalt-polytetrafluoroethylene granular composite films

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Heterogeneous granular films consisting of ferromagnetic cobalt particles embedded in a polytetrafluoroethylene polymer matrix were fabricated by the pulsed laser deposition technique carried out with a Nd-doped yttrium aluminum garnet laser at 355 nm. The samples exhibit a magnetoresistance (MR) change of 4% (at 8 kOe) at room temperature. An enhancement of MR to a value of 6% was observed at 20 K which is attributed to the increasing order of magnetic moments in the ferromagnetic state at low temperature. Significant loop opening of the MR profile at low temperature and the temperature dependence of MR reveal the interplay of superparamagnetic relaxation behavior and spin-dependent electron tunneling. © *2007 American Institute of Physics*.
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INTRODUCTION

Granular composite materials consisting of nanosized metal particles in a matrix of insulating material, first studied by Gittleman *et al.*,[1] show many interesting physical properties. They can be prepared in the form of a thin film and have been developed for sensing, optical and medical applications, as well as data recording and storage. In the case that the nanoparticles are ferromagnetic in the granular composite film, they also exhibit a tunneling magnetoresistance (TMR) effect which can be interpreted by the spin-dependent tunneling of electrons between magnetic particles through the insulator.[2] Therefore, granular systems with different magnetic nanoparticles embedded in various kinds of inorganic insulating matrix with different fabricating technique were studied in detail in the last decade.[3–6] On the other hand, magnetic nanoparticles composite systems utilizing polymer as the insulating matrix have also been investigated with the focus on their optical, electrical magnetic properties, and microstructures.[7–10] Their magnetoresistance and its temperature dependence have not gained much attention.

Following the success in fabrication of cobalt-polytetrafluoroethylene (cobalt-PTFE) granular composite by pulsed laser deposition (PLD) technique and the achieved significant magnetoresistance change of 5% at room temperature,[11] we have further studied the performance of a cobalt-PTFE system at low temperature. Measurement on the temperature dependence of the magnetoresistance and the loop opening of the MR profile reveal that the samples prepared consist of nanosized cobalt particles of which the MR can be interpreted by the spin-dependent tunneling of electrons[2,12,13] and the superparamagnetic relaxation behavior appeared in many nanostructured magnetic granular materials.

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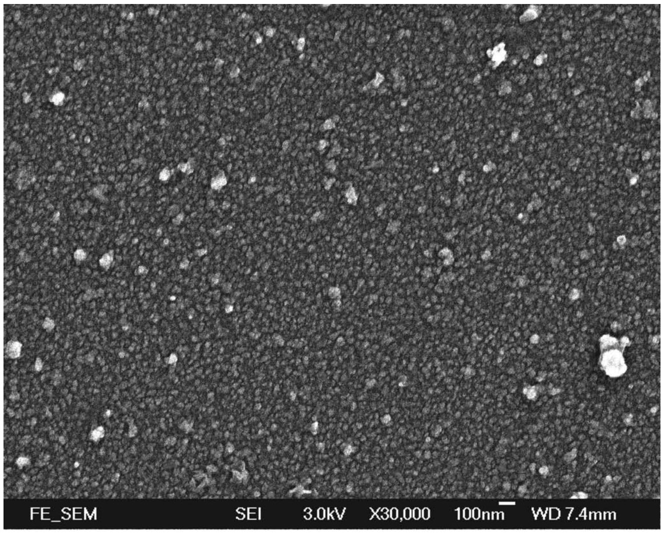
EXPERIMENTAL PROCEDURE

The cobalt-PTFE granular composite thin film was deposited on glass substrates by PLD. Third harmonic ($\lambda = 355$ nm) of the Nd:YAG (YAG denotes yttrium aluminum garnet) laser (Spectra-Physics GCR 16) with a repetition rate of 10 Hz was used in the sample fabrication. The laser beam was focused to obtain a fluence of about 2 J/cm^2, which was high enough to achieve efficient ablation of metal in the ultraviolet wavelength region. Other deposition conditions are the same as described earlier.[11] A pair of gold electrodes was sputtered on the glass substrate before the PLD, such that the resistance of the deposited sample can be performed using the two terminal method with an electrometer (Keithley 6517A) with internal source provided. In order to investigate the polymer matrix structures, samples were etched by hydrochloric acid (~0.1 M) to remove the deposited cobalt particles. Infrared absorption spectra of the deposited PTFE films were measured with a Fourier transform infrared (FTIR) spectrometer (Nicolet Magna-IR 760). The surface morphology of the prepared samples was inspected by a field-emission scanning electron microscope (SEM) (JEOL JSM-6335F) at a voltage of 3 kV. The temperature dependence of magnetoresistance was measured at temperatures from 20 to 300 K in a helium filled close cycle cryostat placed in an electromagnet (LDJ 9500).

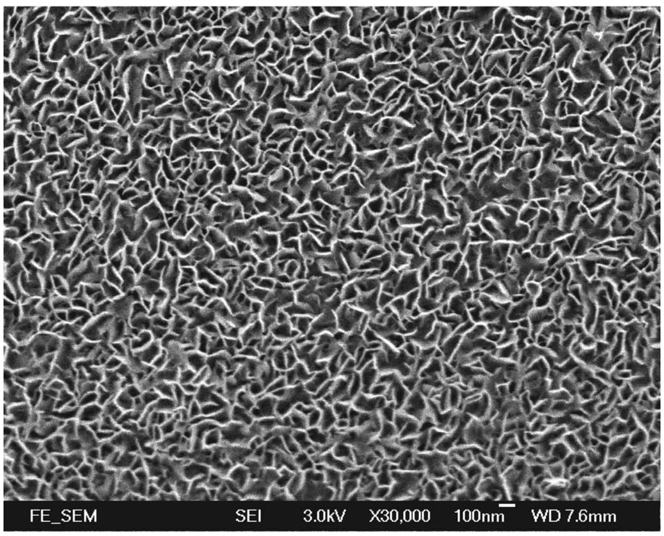
RESULTS AND DISCUSSION

From the FTIR spectra of the prepared samples (which are not shown here), they all show the typical features of the absorption bands of the polymer polytetrafluoroethylene. This confirms that PTFE-containing composite film was successfully deposited.

The SEM image of the cobalt-PTFE composite film is shown in Fig. 1(a). It shows a granular morphology consisting of two kinds of particles. One kind is the spherelike particles of sizes smaller than 50 nm which are the cobalt particles. The others are particles of sizes larger than 200 nm



(a)



(b)

FIG. 1. SEM micrographs of the cobalt-PTFE film produced by PLD (a) before etching and (b) after etching with HCl (~0.1 M).

with irregular shape, appearing brighter, which is owing to the charge accumulation. These are PTFE particulates that were commonly found in the deposition of polymeric materials by PLD.[14] It is well known that PTFE has excellent chemical stability; in order to differentiate the cobalt and PTFE phase, diluted hydrochloric acid was used to remove the Co particles leaving the PTFE matrix on the substrate. As shown in Fig. 1(b), the SEM picture reveals the PTFE matrix in the form of a well connected porous network. The sizes of the voids range from one to several hundred nanometers. Considering the polymer structural relaxation after etching, it can be inferred that the polymer deposited by PLD formed a more or less continuous but porous network, several nanosized cobalt particles and/or some large PTFE particulates are embedded in the voids of the PTFE network. Cobalt particles are thus separated by the PTFE barriers. From the SEM image, the estimated thickness of the barriers should be less than 10 nm.

Temperature dependence of resistance of the composite

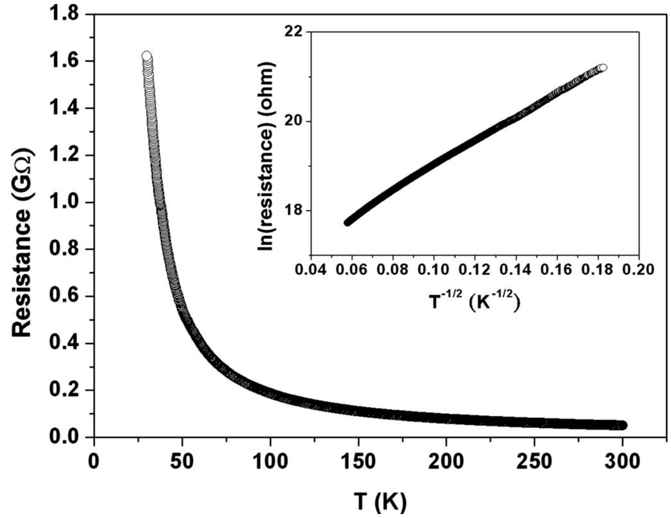


FIG. 2. Temperature dependence of the resistance of cobalt-PTFE composite film. The inset is a plot of $\ln R$ against $T^{-1/2}$.

film at zero applied magnetic field was studied. As shown in Fig. 2, temperature T of the sample increases, its resistance R decreases nonlinearly. A logarithm of R plot is found linearly proportional to $T^{-1/2}$. This result shows a characteristic of the granular composite which is attributed to the tunneling conduction mechanism exhibited in most granular metal-insulator systems.[15,16] In connection with the observed structure shown in the SEM image of the etched samples, it is clear that the conduction electrons are thermally assisted to tunnel through the polymer barriers in this composite system. Figures 3(a) and 3(b) show the effect of an applied magnetic field on the resistance of the sample, at out-of-plane and in-plane measurement, respectively. The magnetoresistance shown is the relative change of resistance and is defined as $\mathrm{MR}=[R(H)-R(H_0)]/R(H_0)$, with H and H_0 being the applied magnetic field and the magnetic field of maximum resistance, respectively. The cobalt-PTFE composite film exhibits about 4% change in MR at an applied field of 8 kOe at room temperature. It should be noted that the MR has not

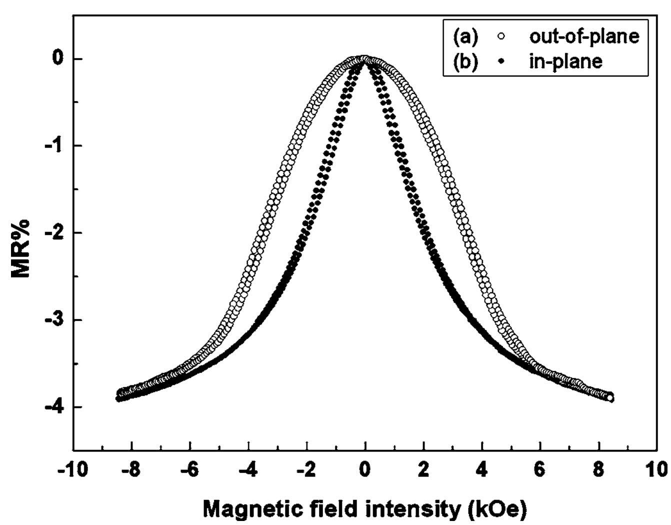


FIG. 3. Magnetic field dependence of the magnetoresistance of the cobalt-PTFE composite film with (a) out-of-plane measurement and (b) in-plane measurement.

reached saturation at 8 kOe, which implies that a larger value of MR could be achieved at a higher magnetic field. The sample reveals a negative MR effect, which denotes the resistance of the sample was decreased with an increase in magnetic field. The difference in out-of-plane and in-plane measurement of the MR profiles as revealed in curves (a) and (b), respectively, is mainly due to the demagnetization field generated inside the sample. The magnitude of the demagnetization field is related to the geometry of the sample and the direction of the applied magnetic field. The applied field parallel to the film surface, which corresponds to the in-plane measurement, produces a weak demagnetization field. On the other hand, the demagnetization field is stronger when the magnetic field is applied perpendicularly to the film surface, which corresponds to the out-of-plane measurement. Thus a larger external magnetic field is needed in order to produce the same magnitude of internal field compared with the in-plane configuration. Therefore, the in-plane MR profile shows a more sharp change at low field. As the field increases the magnetization of cobalt particles approach saturation, the demagnetization field becomes of the same magnitude at both configuration of measurement, thus the MR profiles merge together at high field, as clearly seen in Fig. 3.

In addition, as the applied magnetic field was scanned through a cycle in the MR measurement, both MR profiles of the sample are most likely symmetrical on both directions of the applied magnetic field but with a slightly hysterical effect. This implies that a remanent magnetization is left in the magnetized cobalt particles in the composite film.

The origin of the MR in the cobalt-PTFE granular composite film can be interpreted by the "spin-dependent tunneling" mechanism.[2,12,13] In the granular system, the cobalt nanoparticles with their anisotropic easy-axes orient randomly, so in the absence of an applied magnetic field the magnetic moments of the nanoparticles in the composite film have no preferred orientation. When an external magnetic field is applied, the magnetic moments of the cobalt particles will tend to align in parallel with the field direction. Consequently, the resistance of the film decreases as a function of the applied magnetic field, because the probability of electron tunneling process increases when the magnetization of the cobalt particles are in a parallel state.

Another feature of the spin-dependent tunneling current is its temperature dependence. Lowering the temperature of the sample will reduce the tunneling current, however, it will also reduce the thermal fluctuation of the magnetic moment of the cobalt nanoparticles. Thus, an increase in the number of cobalt particles aligned to the applied magnetic field tends to increase the change in current, albeit a smaller magnitude of this tunneling current in the sample at lower temperature. The curves (a) and (b) in Fig. 4 give the MR profile measured at 20 and 300 K, respectively, which are both in-plane measurements. A significant enhancement of MR value to 6% was achieved at 20 K at 8 kOe. The MR profile at 20 K is symmetric and still does not reach saturation at 8 kOe, which exhibits a significant hysteresis compared with the room temperature profile. The two peaks of the profile within a complete magnetic cycle are located at ±0.8 kOe which correspond to the coercive field of the cobalt particles at

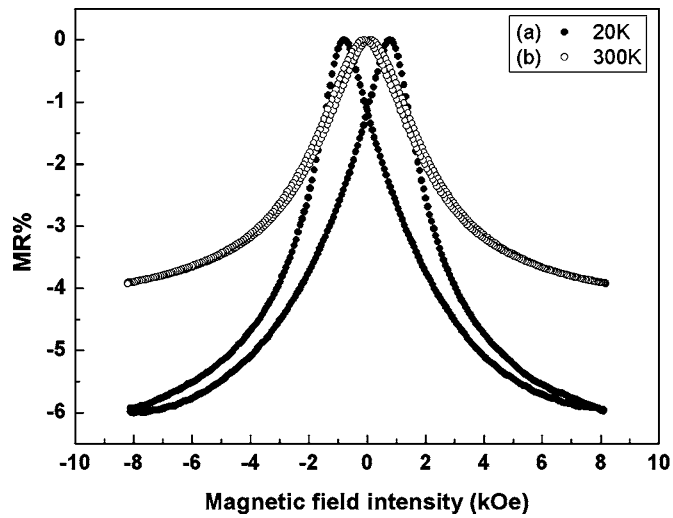


FIG. 4. Magnetic field dependence of the magnetoresistance of the cobalt-PTFE composite film measured at (a) 20 and (b) 300 K, both are with in-plane measurements.

20 K. This is the hysteresis feature which shows that the cobalt nanoparticles already regain their ferromagnetic state.[17] For a system consisting of nanosized ferromagnetic particles, there exists a blocking temperature above which the nanoparticles behave paramagnetically. The blocking temperature depends on both the particle size and the applied magnetic field.[18] The energy barrier $E(H)$ is related to the applied magnetic field H as $E(H)=E_0(1-H/H')^{\alpha}$, where E_0 is the energy barrier at zero field and H' is the field required to switch the magnetization of the particles. In general, the superparamagnetic regime would shift to lower temperatures with a stronger applied magnetic field and a reduction in particle size.[19–21] A nonzero magnetic field is needed in order to oppose the coercive field of the cobalt particles in the sample and bring the sample to the highest resistance at zero internal magnetic field. This result also inferred that the sizes of the cobalt particles in the sample are small enough to be superparamagnetic at room temperature.

A plot of the separation of the peaks, i.e., twice that of the coercive field from 20 to 300 K, is given in Fig. 5. It shows that the peak separation is about 200 Oe at 300 K, which refers to a coercive field of about 100 Oe in the composite film. The peak separation does not change much from 300 to around 120 K. Below this temperature, the peak separation starts to increase. With a decrease in temperature of the sample, the separation increases to a value of 1.65 kOe at 20 K. This result indicates that the nanosized cobalt particles of the sample exhibit a superparamagnetic nature. The blocking temperature occurs at around 120 K.

Figure 6 shows the temperature dependence of MR values of two different cobalt-PTFE composite films fabricated by using different laser pulse ratio, measured at 8 kOe. Samples A and B were fabricated with the cobalt:PTFE laser pulse ratio of 30:2 and 34:2, respectively. Although the MR values at room temperature of the two samples are different, they show similar temperature dependence. The MR values measured at 8 kOe of both samples increase steadily from 300 to about 60 K, followed by a steeper increase of MR

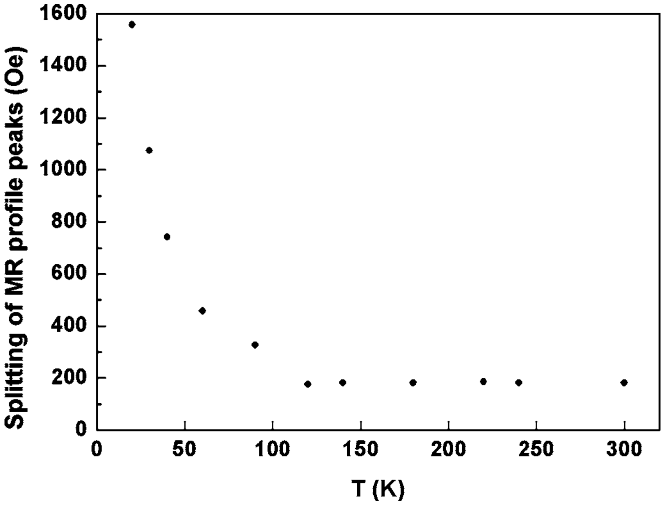


FIG. 5. Temperature dependence of the separations of the MR peaks at a temperature range from 20 to 300 K.

with a further decrease in temperature. It shows that the blocking temperature of the composite film at 8 kOe is about 60 K. Compared with the blocking temperature in Fig. 5, it is 120 K but it was measured at a relatively low field of around 200 Oe. This further verifies that the polymer composites prepared by PLD exhibit most of the interesting features of a granular magnetic system which also possesses the interesting TMR effect.

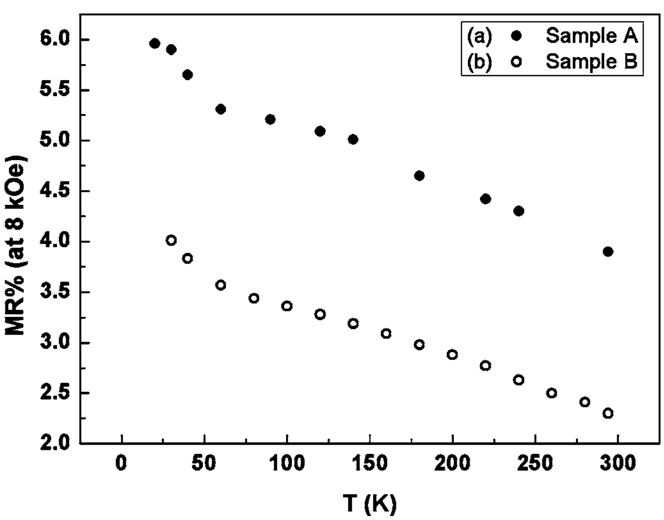


FIG. 6. (Color online) Temperature dependence of MR of two cobalt-PTFE composite films fabricated by a cobalt:PTFE laser pulse ratio of 30:2 and 34:2 respectively, measured at the applied magnetic field of 8 kOe.

CONCLUSIONS

The cobalt-PTFE granular composite film has been prepared by the PLD technique using a Nd:YAG laser of 355 nm. The surface morphology, polymer structure, and the electrical transport properties over a wide range of temperature of the film have been studied. A large MR value of 4% at room temperature in an applied magnetic field of 8 kOe has been observed. Enhancement of the MR value to 6% was obtained for the measurement at 20 K. The temperature dependence of MR can be interpreted by the spin-dependent tunneling of electrons and the superparamagnetic relaxation behavior of the cobalt nanoparticles embedded in the PTFE matrix.

ACKNOWLEDGMENTS

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