Magnetoresistivity of cobalt-polytetrafluoroethylene granular composites

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Giant magnetoresistance (GMR) was observed in a heterogeneous granular film with polymer matrix. Cobalt and polytetrafluoroethylene (PTFE) were deposited on glass substrates by using the pulsed laser deposition technique. IR absorption spectra of the deposited PTFE showed similar characteristics with the bulk PTFE. The granular samples exhibit a resistance change of about 5% (at 10 kOe) at room temperature. The temperature dependence of resistance of the samples shows that charge transportation is mainly due to tunneling between the metal particles. The GMR can thus be interpreted by the spin-dependent electrons tunneling through the ferromagnetic metal granules (cobalt) in the insulating matrix (PTFE). © *2006 American Institute of Physics*.
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Metal-insulator granular materials, consisting of ferromagnetic particles embedded in an insulating matrix, were studied for the $Ni-SiO_2$ granular films by Gittleman *et al.*[1] The tunneling magnetoresistance (TMR) effect of the granular films observed is caused by spin-dependent tunneling of electrons between magnetic particles through the insulator.[2] Subsequently, different granular films with ferromagnetic particles (Fe, Co, and CoFe) embedded in insulators (Al_2O_3, SiO_2, and MgF_2) have been studied in detail,[3–6] with different fabricating techniques including cosputtering and pulsed laser deposition (PLD) methods. TMR values up to about 10% at room temperature have been reported.[2] In fact, most of these studies are mainly focused on utilizing inorganic materials as the insulating matrix. However, based on the spin-dependent tunneling mechanism, there should not be any physical reason to exclude using the organic materials, such as the polymers to serve as the insulating phase from obtaining the TMR effect. Nevertheless, as far as we know, few works have been done on studying the magnetoresistance of granular composites using polymers as the insulating matrix.

In the present study, we report a type of granular composite film that has been prepared by using the PLD technique. The composite consists of the polymer polytetrafluoroethylene (PTFE) as the insulating matrix and the ferromagnetic cobalt particles as the granular phase. Using polymer as the matrix has many advantages, such as its light weight and flexibility, which are important for sensor applications. It is well known that PTFE have excellent chemical stability among the polymers and its working temperature can be close to 250 °C. It is no doubt that this type of granular composite film utilizing PTFE as the matrix can maintain its performance even in harsh environment. A significant MR% of 5% has been observed at room temperature with an applied magnetic field of 10 kOe. Measurement on the temperature dependence of resistance of the film and the MR being observed can be interpreted by the spin-dependent tunneling of electrons,[2,7,8] which implies that the MR exhibits in the cobalt-PTFE granular composite film are TMR type.

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The cobalt-PTFE granular composite thin film was prepared on glass substrates by using PLD technique. A Nd doped yttrium aluminum garnet laser ($\lambda = 1064$ nm, Spectra-Physics GCR 16) with a repetition rate of 10 Hz was used in the sample fabrication. The laser fluence of about 30 J/cm^2 was used. The deposition process was carried out at room temperature in vacuum at a pressure of about 10 mTorr. The deposition time was kept at 15 min for all samples. The semicircular cobalt and PTFE plates formed a split target which was used in the PLD. The split target was mounted on a holder which was swung through a computer controlled stepping motor. The composition of the film was changed by varying the swing ratio between the metal and polymer targets. Au electrodes for resistance measurements were sputtered on the glass substrate before the composite film deposition. The surface and cross-section morphologies of the prepared samples were inspected by a field-emission scanning electron microscope (SEM) (JEOL JSM-6335F) at a voltage of 3 kV. Fourier transform infrared (FTIR) absorption spectra of the laser-deposited PTFE films were measured with a spectrometer (Nicolet Magna-IR 760). All resistance measurements were performed using the two terminal method with an electrometer (Keithley 6517A). Temperature dependence measurement was performed at temperatures ranging from 80 to 300 K. Magnetic field for the magnetoresistance measurements was produced by an electromagnet (LDJ 9500).

Figures 1(a) and 1(b) show the FTIR spectra of PTFE target and the PTFE film produced by PLD at a laser fluence of about 30 J/cm^2. The absorption band at 1300–1100 cm^{-1} is associated with the stretching mode of CF_2 bond, which is a typical characteristic absorption band for the fluoropolymer. The band with smaller intensity around 650–400 cm^{-1} is attributed to the rocking and wagging modes of CF_2 bond.[9] As both spectra obtained from the target and the film show very similar features, it can be confirmed that the composition of the PTFE film produced was almost the same as the target material.

The SEM image of the cobalt-PTFE composite film deposited at ~30 J/cm^2 was shown in Fig. 2. It shows a granular morphology consisting of two kinds of particles embedded in the PTFE matrix. One kind is the spherical-like cobalt particles of sizes around and smaller than 100 nm. The oth-

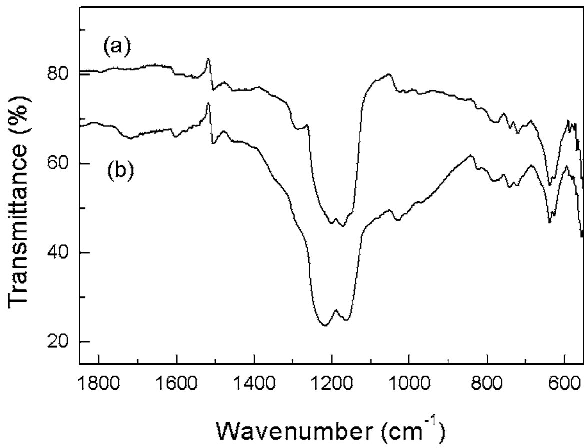

FIG. 1. FTIR spectra of (a) bulk PTFE and (b) PTFE film produced by PLD.

ers are particles of sizes larger than 0.5 μm with irregular shape. These are PTFE particulates that were commonly generated during the deposition of polymeric materials by PLD.[9] Single crystalline films of PTFE deposited by PLD with large spherulites and without such particulates were also reported.[10–12] The thickness of the deposited films ranged from 200 to 400 nm which was measured from the cross-section image of SEM micrographs.

Figure 3 shows the temperature dependence of the resistance of cobalt-PTFE composite film at zero applied magnetic field. As the temperature increases, the resistance of the sample decreases nonlinearly. It suggests a semiconductor-like or tunneling conduction mechanism. The tunneling conductivity for granular metals embedded in insulator has been studied by Abeles and co-workers[13,14] They suggested that a temperature dependence of resistance R can be expressed in a functional form of $\ln R = 2(C/k_B T)^{1/2} + \text{constant}$, where k_B is the Boltzmann constant, and C is the activation energy which is proportional to the tunneling-barrier thickness, potential height of the barrier, and the charging energy of the metallic granule. Therefore, a plot of $\ln R$ against $T^{-1/2}$ would give a straight line. As shown in the inset of Fig. 3, such plot of the composite sample reveals a linear relationship. This characteristic suggests the tunneling effect of electrons between cobalt granules through the PTFE barriers. It must be noted that the plot still shows a small degree of nonlinearity, it indicates the charging effect of the broad size distribution of the cobalt granules (Coulomb blockade).[13,14] However, it could also be other electron transport mechanisms involved as well as the tunneling effect. Electron scattering by impurities and metallic conducting paths formed by incomplete isolation of individual cobalt granules could contribute to this result.

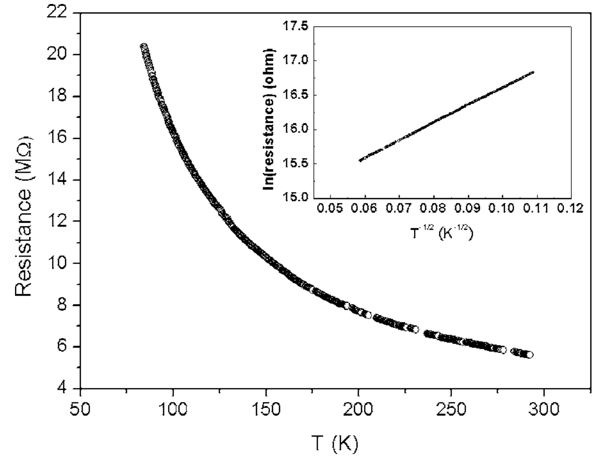

FIG. 3. Temperature dependence of the resistance of cobalt-PTFE composite film. The inset is a plot of $\ln R$ against $T^{-1/2}$.

Figure 4 shows the effect of applied magnetic field on the resistance of the sample. The MR shown is the relative change of resistance and is defined as $\text{MR} = [R(H) - R(H_0)]/R(H_0)$, where H and H_0 being the applied magnetic field and zero magnetic field, respectively. These results were measured with H perpendicular to the film surface at room temperature. As shown in Fig. 4, the cobalt-PTFE composite film exhibits a 5% change of MR at an applied field of 10 kOe at room temperature. It should be noted that the MR has not reached saturation at 10 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 that the resistance of the sample was decreased with an increase in magnetic field. A negative MR effect has also been observed in most of the oxide based granular films.[15] In addition, the MR profile is symmetrical on both directions of the applied magnetic field which implies an insignificant coercive field of the ferromagnetic particles in the composite film.

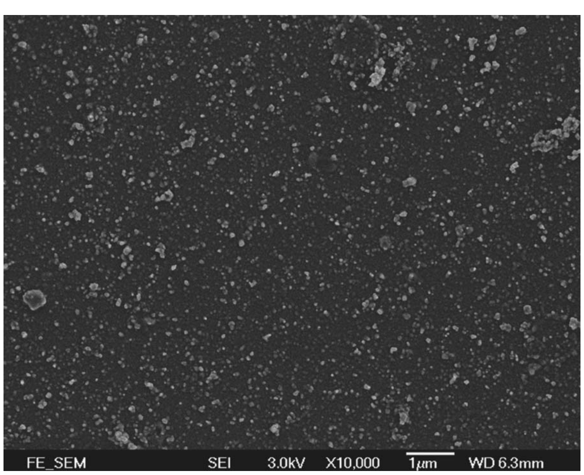

FIG. 2. SEM micrograph of the cobalt-PTFE film produced by PLD.

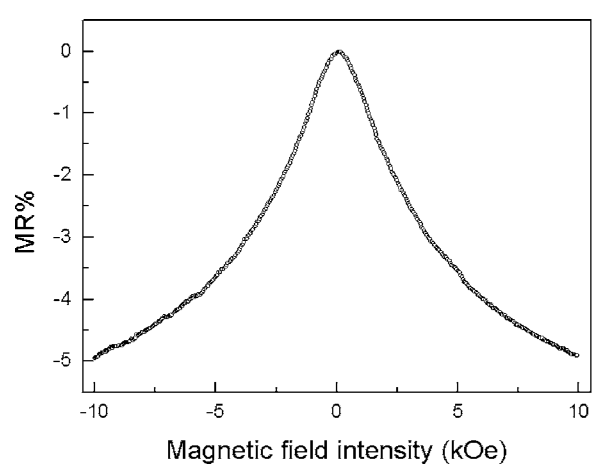

FIG. 4. Magnetic field intensity dependence of the magnetoresistance of the cobalt-PTFE composite film.

The origin of the MR exhibited in the cobalt-PTFE granular composite film can be interpreted by the "spin-dependent tunneling" mechanism.[2,7,8] At room temperature, the thermal energy is large enough to randomize the magnetic moment of the cobalt particles due to the superparamagnetic state, such that the magnetic moments of the cobalt particles are randomly oriented in the cobalt-PTFE granular composite film. When an external magnetic field is applied, the magnetic moments of the cobalt particles will tend to align in parallel to 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 is in parallel state.

The cobalt-PTFE granular composite film has been prepared by the PLD technique. The surface morphology and the electrical transport properties over a wide range of temperature of the film have been studied. A large MR% value of 5% at room temperature in an applied magnetic field of 10 kOe has been observed. From the experimental results, the MR of the samples observed can be interpreted by the spin-dependent tunneling which indicates that the samples reveal the TMR effect. This study opens the area of using polymeric material, PTFE in our case, as the insulating matrix for fabricating magnetic granular composite of GMR effect by PLD method.

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