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MAGNETORESISTIVITY OF COBALT-PTFE GRANULAR COMPOSITE FILM PRODUCED BY PULSED LASER DEPOSITION TECHNIQUE

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Abstract. Giant Magnetoresistance (GMR) was observed in Cobalt-PTFE heterogeneous granular films. The samples were deposited on glass substrates by using the Pulsed Laser Deposition (PLD) technique. IR absorption spectra of the deposited PTFE showed similar characteristics with the bulk PTFE. The samples prepared exhibit a percentage change in resistance (MR%) of about 5% at room temperature with an applied magnetic field (H) of 10 kOe. A significant change of the MR profile was observed when the magnetic field was applied in-plane and out-of-plane to the film. The temperature dependence of resistance of the samples shows that charge transportation is mainly due to tunneling between the metal particles in the sample. The magnetization curve reveals the superparamagnetic nature of the sample. The GMR effect can thus be interpreted by the spin-dependent electrons tunneling through the ferromagnetic metal granules (cobalt) in the insulating matrix (PTFE). An enhancement of MR% was observed at low temperature.

1. INTRODUCTION

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, CoFe) embedded in insulators (Al_2O_3, SiO_2, MgF_2) have been studied in details [3-6], with different fabricating techniques including co-sputtering and Pulsed Laser Deposition (PLD) methods. 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 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. 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 10kOe. Measurement on the temperature dependence of resistance of the film and the MR being observed can be interpreted by the spin-dependent

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tunneling of electrons [2, 7,8], which infers that the MR exhibits in the Cobalt-PTFE granular composite film are TMR type.

2. EXPERIMENTAL

The Cobalt-PTFE granular composite thin film was prepared on glass substrates by using Pulsed Laser Deposition (PLD) technique. A Nd:YAG laser (λ=1064 nm, Spectra-Physics GCR 16) with a repetition rate of 10 Hz was used in the sample fabrication. The laser fluence was kept at ~30 J/cm^2. The deposition process was carried out at room temperature in vacuum at a pressure of about 1.3 Pa. The deposition time was kept at 15 minutes for all samples. The semi-circular Cobalt and PTFE plates formed a split target 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 morphology of the prepared samples was 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). Magnetization curves were measured with a vibrating sample magnetometer (VSM) equipped with a cryostat for low temperature measurement. Temperature dependence measurement was performed at temperatures ranged from 80K to 300K. Magnetic field for the magnetoresistance measurements was produced by an electromagnet (LDJ 9500).

3. RESULTS AND DISCUSSION

Figs. 1a and 1b show the Fourier Transform Infra-Red (FTIR) spectra of PTFE target and the PTFE film produced by PLD. The absorption band at 1300-1100 cm^{-1} are 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]. The high degree of similarity of both spectra confirmed that the composition of the PTFE film produced was almost the same as the target material.

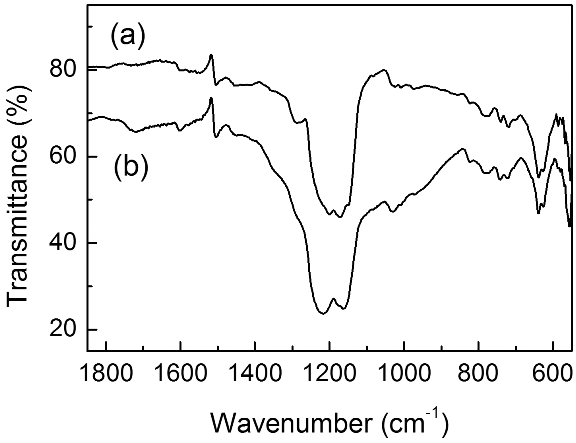

Fig. 1. FTIR spectra of (a) bulk PTFE and (b) PTFE film produced by PLD.

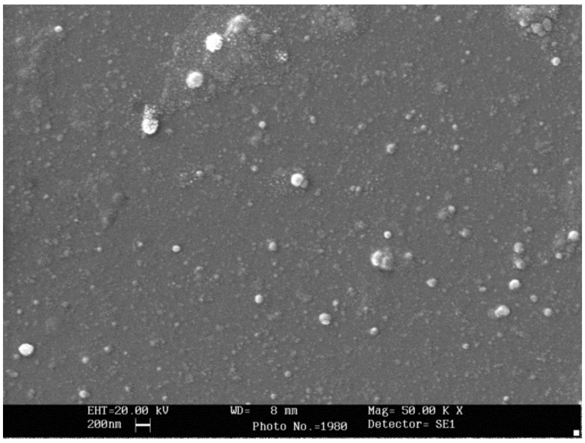

Fig. 2. SEM micrograph of the Cobalt-PTFE composite film produced by PLD.

The Scanning Electron Microscope (SEM) image of the Cobalt-PTFE composite film 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 others are particles of sizes larger than 0.5 mm with irregular shape. These are PTFE particulates that were commonly generated during the deposition of polymeric materials by PLD [9]. The thickness of the deposited films is ranged from 200 to 400nm which was measured from the cross section image of SEM micrographs.

Fig. 3a shows the temperature dependence of the resistance of Cobalt-PTFE composite film at zero applied magnetic field. The resistance of the

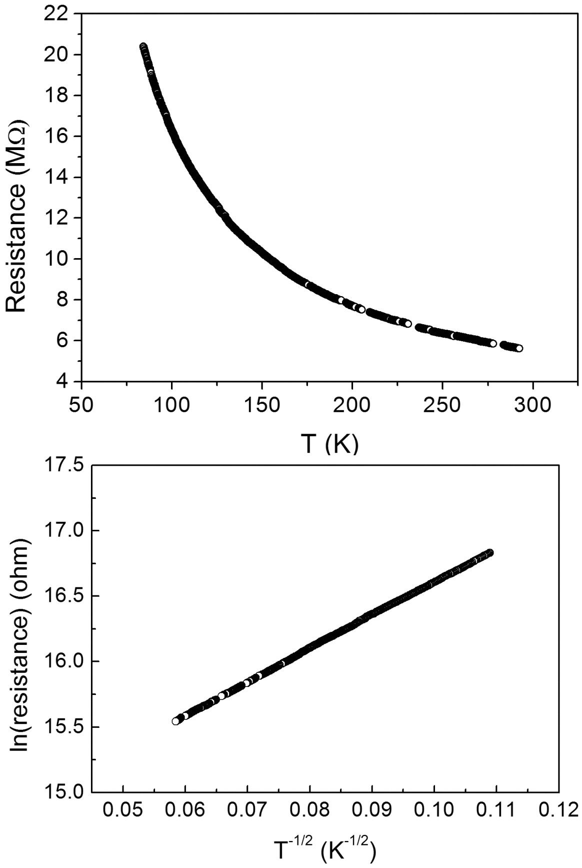

Fig. 3. (a) Temperature dependence of the resistance of Cobalt-PTFE composite film. (b) A plot of ln$R$ against $T^{-1/2}$.

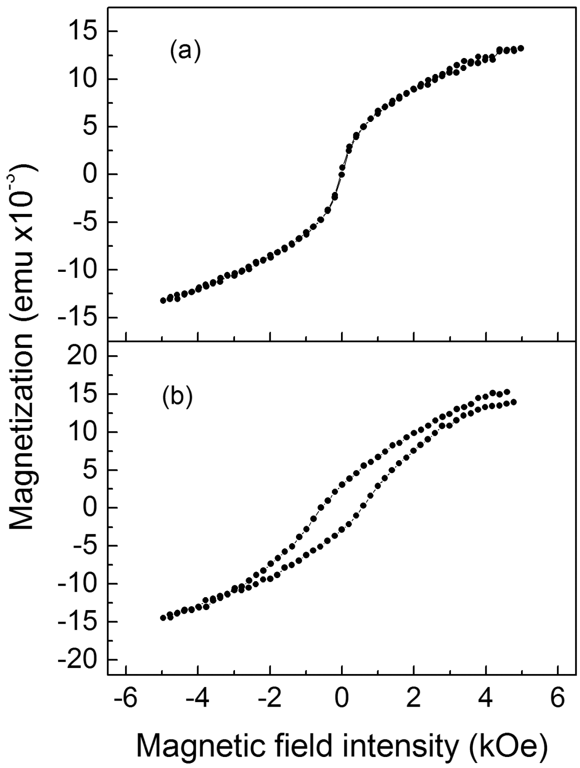

Fig. 4. Magnetization curves of Cobalt-PTFE composite film measured at (a) room temperature and (b) 10K.

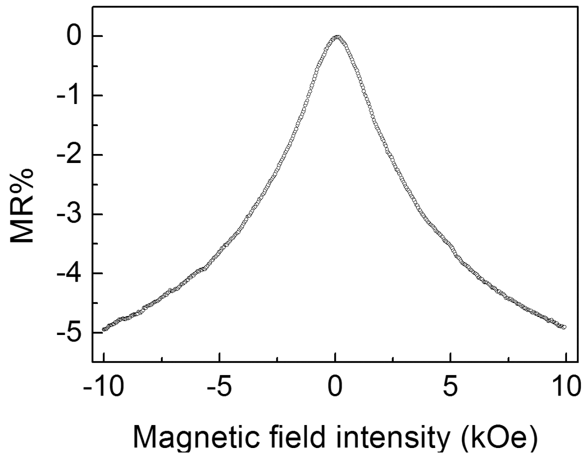

Fig. 5. Magnetic field intensity dependence of the magnetoresistance of the Cobalt-PTFE composite film.

sample decreases nonlinearly when the temperature increase. It suggests a semiconductor-like or tunneling conduction mechanism. The tunneling conductivity for granular metals embedded in insulator has been studied by Helman *et al*. [10,11]. They suggested a temperature dependence of resistance R can be expressed in a functional form of $\ln R = 2(C/k_B T)^{1/2}$ + constant , where k_B is Boltzmann constant, C is the activation energy which is a function of the tunneling-barrier thickness, potential height of the barrier and the charging energy of the metallic granule. As shown in Fig. 3b, the plot of ln$R$ against $T^{-1/2}$ 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 show a small degree of nonlinearity, it indicates the charging effect of the broad size distribution of the cobalt granules (Coulomb blockade) [10,11]. Electron scattering by impurities, and metallic conducting paths formed by incomplete isolation of individual cobalt granules could contribute to this result.

Figs. 4a and 4b show the magnetization curves of the composite film at 300K and at 10K. At high temperature, the magnetization curve is a hyster-

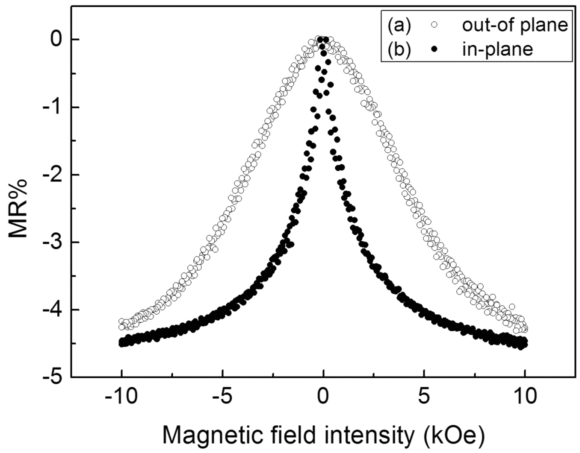

Fig. 6. MR curves of Cobalt-PTFE composite film with (a) out-of-plane (b) in-plane measurement.

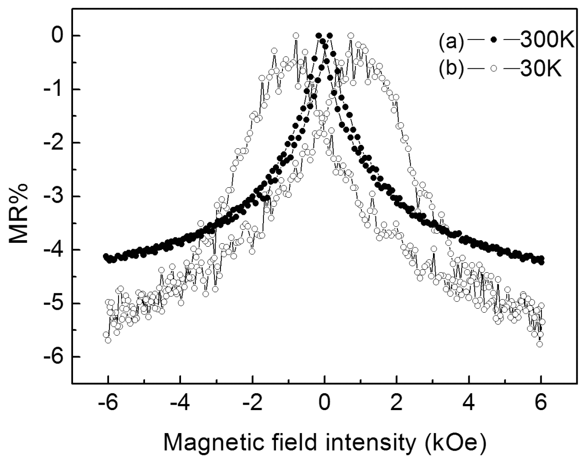

Fig. 7. MR curves of Cobalt-PTFE composite film measured at (a) room temperature (b) 30K.

esis of zero coercive field where hysteresis occurs at low temperature. This characteristic reveals that the composite film prepared exhibits superparamagnetic nature, which consists of nano-sized cobalt particles.

Fig. 5 shows the effect of applied magnetic field on the resistance of the sample. The magnetoresistance (MR) shown is the relative change of resistance and is defined as 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. 5, 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 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. A negative MR effect has also been observed in most of the oxide based granular films [12]. In addition, the MR profile is symmetrical on both direction of the applied magnetic field which implies an insignificant coercive field of the ferromagnetic particles in the 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 randomise 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 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 parallel state.

Figs. 6a and 6b show the MR% profile of the sample, with out-of-plane and in-plane measurement respectively. The differences of the graphs show that anisotropic properties exhibit in the composite film. This result can be interpreted by the demagnetization field exhibits inside the sample, which the magnitude of the demagnetization field is related to the dimension of the sample and the direction of the applied magnetic field. The demagnetization field becomes stronger when the applied magnetic field is perpendicular to the film surface. Therefore, a larger magnetic field is needed in order to align the magnetization of individual cobalt particles along with the magnetic field direction for the out-of-plane measurement, when comparing with the case for in-plane measurement. Therefore, the resistance change is slower at the low magnetic field region for the out-of-plane measurement as shown in Fig. 6a.

Figs. 7a and 7b show the MR% profile measured at room temperature and 30K respectively, both with the in-plane measurement. A significant enhancement of MR% was achieved at 30K, to a value larger than 5% at 6 kOe, when comparing with about 4% at room temperature. The profile is symmetric and still does not reach saturation even at 30K. Shifting of the MR% profile becomes highly significant at 30K, when the direction of the magnetic field is applied oppositely. This result can be interpreted by the superparamagnetism of the cobalt particles embedded in the PTFE matrix. At room temperature, the thermal energy is large enough to randomize the magnetic moments of the nano-sized particle, so the particle has nearly no coercive field. However, when the transition temperature is reached, the particle starts to become ferromagnetic state, which the coercive field becomes significant. This transition temperature is depended on the material and the particles size of the sample [13]. Therefore, a non-zero magnetic field is needed in order to oppose the coercive field of the cobalt particles in the sample and bring the sample to its original state with the highest resistance, resulting in the shifting of the MR% profile. This result also inferred that the particle size of our sample is small enough to reach the superparamagnetic state.

4. CONCLUSION

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. The MR of the samples observed can be interpreted by the spin dependent tunneling which indicates the samples reveals 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. Hysteresis in the magnetization curve and the significant shifting of the MR profile observed at low temperature inferred our samples exhibit the superparamagnetic state. Enhancement of the MR% value was observed at low temperature. Further investigations are needed to interpret this result.

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