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Large room-temperature spin-dependent tunneling magnetoresistance in a Fe 3 O 4 -polymer composite system
Enhanced tunneling magnetoresistance of Fe$_3$O$_4$ in a Fe$_3$O$_4$-hexabromobenzene (C$_6$Br$_6$) composite system

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Magnetotransport of Fe$_3$O$_4$-hexabromobenzene (C$_6$Br$_6$) composite has been studied. Powders of C$_6$Br$_6$ and Fe$_3$O$_4$ nanoparticles were mixed together. They were annealed in hydrogen flow. There was a phase transformation from Fe$_3$O$_3$ to Fe$_3$O$_4$ after annealing. Giant negative magnetoresistance (MR) was observed at room temperature and the MR ratio is about 13.4% in an applied field of 5 T. The temperature dependence of the resistivity exhibits characteristics of intergranular tunneling in the samples. The enhancement of the MR ratio is attributed to the fact that the C$_6$Br$_6$ can act as barrier material and, more importantly, can prevent the oxidation of the surface of Fe$_3$O$_4$, which is believed to alter the half-metallic state at the surface. © 2009 American Institute of Physics. [DOI: 10.1063/1.3072779]

I. INTRODUCTION

There has been increased interest in the half-metallic magnetite (Fe$_3$O$_4$) due to its highly spin polarized nature (supposedly ~100%). In principle, a high spin polarization should result in large tunneling magnetoresistance (TMR) since the latter is proportional to the spin polarization of the tunneling electrons. Many studies have focused on the magnetoresistance (MR) ratio in Fe$_3$O$_4$ of different forms including epitaxial and polycrystalline films, powders, and tunnel junctions. However, in most cases the MR ratio is much smaller than expected, especially at room temperature. In fact, it is well known that in polycrystalline specimens and powder compacts of Fe$_3$O$_4$, the surfaces or interfaces at the grain boundaries have rather different magnetic properties and reduced spin polarization compared to those of the bulk. This is a consequence of off-stoichiometry, surface reconstruction, oxidation, defects, and bonding effects located at or close to the surfaces and interfaces. Recently, some investigations have focused on improving MR performance of Fe$_3$O$_4$. Zeng et al. reported 35% MR at 60 K for ordered three-dimensional arrays of Fe$_3$O$_4$ nanoparticles with annealing in high vacuum. Rychenko et al. showed enhancement in MR of bulk granular magnetite by annealing in paraflax wax. Lu et al. found relatively large low field MR in ultrathin Fe$_3$O$_4$ nanocrystalline films by rapid thermal annealing at 800 °C for 120 s in pure nitrogen. These authors all used passive annealing process to prevent the surfaces or interfaces from oxidation.

We have previously reported that polystyrene (PS) coated magnetite nanoparticles exhibit drastically enhanced intergranular TMR. The large TMR results from the better protection of the surfaces of Fe$_3$O$_4$ from oxidation by the PS coating. However the PS has low melting point (240 °C) and softening temperature (95 °C), which will limit its potential applications.

In this article, the investigation of the MR and spin polarization of the surface of Fe$_3$O$_4$ in a magnetite/organic hexabromobenzene (C$_6$Br$_6$) nanocomposite is discussed. The melting point of C$_6$Br$_6$ is relatively high (>320 °C) among oxygen-free organic materials. C$_6$Br$_6$ can also be deposited as molecular films, so it has the potential to be applied to spin polarized thin film system for spintronic studies.

II. RESULTS AND DISCUSSION

Powders of C$_6$Br$_6$ and α-Fe$_2$O$_3$ nanoparticles (1:2 in weight ratio) were mixed together by first dissolving C$_6$Br$_6$ in chloroform, then adding Fe$_3$O$_4$ particles and stirring, and finally evaporating the solvent. After powders were annealed at 250 °C in pure hydrogen flow, the weight ratio of C$_6$Br$_6$ and iron oxide nanoparticles changed to about 1:15 owing to the sublimation of C$_6$Br$_6$. Further annealing at 250 °C does not change the weight ratio significantly. The annealed powders were then pressed into pellets under a pressure of 5 × 10$^8$ N/m$^2$. The samples were annealed again in pure hydrogen flow. For the samples used in the transport measurement, contacts were made on the pellets and a PS layer was coated on the surface to protect the pellet before annealing. X-ray diffraction (XRD) patterns were collected with a Philips X’Pert diffractometer using Cu Kα radiation. Transmission electron microscopy (TEM) was done with a JEOL 2010 TEM. Samples destined for TEM analysis were prepared by ultrasonic dispersion of the annealed pellets in water, and a drop of suspension solution was placed on a holey carbon film grid. The resistance (R) and MR of the pellet samples were measured with a standard four-point method using a Quantum Design physical property measurement system. A magnetic field of up to 5 T was applied perpendicular to the current.

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Figure 1 is the XRD pattern of the sample annealed at 250 °C in hydrogen. The pattern shows that there exist Fe₃O₄ (or γ-Fe₂O₃) and a small amount of α-Fe₂O₃. The rest of the peaks do not fit the published pattern of monoclinic C₆Br₆. However, it may be possible that the structure of C₆Br₆ thin layer coated on the iron oxide is different from the bulk molecular crystals. There have been reports that the structure of C₆Br₆ films grown on graphite is hexagonal. Figure 2 is the TEM image of the sample annealed at 250 °C. It shows that Fe₃O₄ (or γ-Fe₂O₃) particles are nearly spherical and their sizes are between 10 and 30 nm.

The samples before annealing were insulators. After annealing in pure hydrogen, the samples became conducting. Knowing that γ-Fe₂O₃ is an insulator, the α-Fe₂O₃ should transform to magnetite after reduction in hydrogen. The magnetization M of the samples also shows the unique character of the Verwey transition (a sudden drop in M at the transition), which supports that the sample has transformed from α-Fe₂O₃ to Fe₃O₄.

The temperature dependence of the resistance for an annealed sample is shown in Fig. 3(a). In Fe₃O₄, the Verwey transition is characterized by an increase in resistivity by about two orders of magnitude at the transition temperature Tᵥ around 120 K. In our samples the change in the resistance at Verwey transition is not as sharp as those observed in single crystal samples. In Fig. 3(b), R is plotted on a logarithmic scale as a function of T⁻¹/². The good linear behavior suggests intergranular tunneling is the mechanism of transport.

Figure 4 shows the MR= (R_H−R₀)/R₀ of the sample annealed at 250 °C. Giant negative MR was observed at room temperature (280 K) and the MR ratio is 13.4% in an applied field of 5 T. The MR ratio is 21.5% at 130 K; however it slightly decreases to 19.4% at 85 K. Although the existence of α-Fe₂O₃ should decrease MR effect, these MR values are higher than reported data in pressed Fe₃O₄ powders and polycrystalline films which have MR ratios typically near 4%–5% at room temperature. It is well known that the surface state of Fe₃O₄ is different from the bulk. X-ray photoelectron spectroscopy study indicates that the top two layers of surface are rich in Fe III compared to the bulk in molecular beam epitaxy–grown Fe₃O₄ film. In our sample, a reasonable explanation of enhanced MR is that a thin layer of C₆Br₆ is perhaps coated on the surface of Fe₃O₄, which may help to prevent the oxidation of the surface of Fe₃O₄. The latter may have altered half-metallic state at its surface. We have previously mentioned that after primary sublimation of C₆Br₆, further annealing will not change the weight ratio between C₆Br₆ and Fe₃O₄. This implies that there may be some sort of binding between C₆Br₆ and the surface of iron oxide. Further investigation of the morphology of C₆Br₆ on iron oxide will be performed.
FIG. 5. Temperature dependence of the MR ratio in an applied field of 5 T for the sample annealed at 250 °C.

Figure 5 shows the temperature dependence of MR ratio in an applied field of 5 T. In our samples, MR ratios before and after Verwey point do not show significant change, implying that Verwey transition does not change the spin polarization of Fe₃O₄ significantly.

Our investigation suggests that C₆Br₆ can improve the MR performance of Fe₃O₄. Since this organic material has been successfully applied to growth of molecular films, it is possible that it can be used on Fe₃O₄ thin film systems and to improve their spin polarized characteristics.

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