Magnetoresistance of polycrystalline Fe_3O_4 films prepared by reactive sputtering at room temperature

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The magnetic, structural, and transport properties of single-layer magnetite (Fe_3O_4) films prepared by reactive sputtering were investigated. Magnetoresistance (MR) was measured at various thicknesses and temperatures. The increase in MR with thickness is related to grain crystallinity and size, as confirmed by transmission electron microscopy. MR arises from intergranular tunneling, which is supported by the temperature dependence of resistivity ($\log \rho \sim T^{-1/2}$). Field-dependent MR correlates with the M curve. Magnetoresistance versus magnetization curves clearly show that the MR effects come from the surface spin arrangement near the grain boundaries. The dependence of MR on the magnetic field observed in polycrystalline Fe_3O_4 films can be attributed to a surface magnetization near the grain boundary, which will be discussed. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1847853]

Half-metallic materials having 100% spin polarization are very attractive in the light of applications for spin-based devices such as magnetic random access memory (MRAM), magnetic head, and magnetic sensor, because the magnetoresistance effect (i.e., the resistance change due to an applied magnetic field) depends on the spin polarization of the materials used.[1] Fe_3O_4 is one type of a half-metallic material, all of which have an energy gap in only one spin band at the Fermi level.[2] A negative magnetoresistance (MR) has been observed in polycryalline Fe_3O_4 films.[3–5] Coey *et al.* suggested that the negative MR at high fields in polycrystalline Fe_3O_4 films is due to the field-induced alignment of the magnetization of contiguous grains.[3] Ziese *et al.* attributed the high-field magnetoresistance in polycrystalline Fe_3O_4 films to spin disorder scattering at the grain boundaries.[4] These reports suggest that MR is associated with the spin-dependent transport phenomena between contiguous grains. However, the origin of the MR in Fe_3O_4 films remains unclear.

In this study, we show that MR in reactive sputtered polycrystalline Fe_3O_4 films can be attributed to the spin-dependent tunneling between contiguous grains that is only determined by the relative alignment of the surface magnetization of the contiguous grains.

Single-layer thin films of Fe_3O_4, with thicknesses in the range of 17–200 nm, were deposited on oxidized silicon substrates by using a rf/dc sputtering system. The base pressure was 3×10^{-7} Torr. The deposition pressure and temperature were 5 mT and room temperature, respectively. The magnetite layer was fabricated by reactive sputtering of Fe in flowing oxygen. Oxygen and argon gases were introduced through the top of the chamber and their flow rates were 6.8 and 27 SCCM (standard cubic centimeter per minute), respectively. The phase identity and microstructure of the films were investigated by transmission electron microscopy (TEM) and x-ray diffraction (XRD). The magnetic properties of the samples were measured using a vibrating-sample magnetometer (VSM). The in-plane MR of the films was measured by a four-point measurement in fields up to 5500 Oe.

The in-plane XRD patterns for films at different thicknesses are shown in Fig. 1. All of the peaks can be assigned to magnetite. As the thickness decreases, the full width at half maximum (FWHM) increases, which indicates that the grain size is decreased. This is consistent with the TEM results shown in Fig. 2. It is important to note that Fe_3O_4 has almost the same lattice parameter as γ-Fe_2O_3. In a randomly oriented polycrystalline γ-Fe_2O_3 film, there are several peaks (near 40° and 50°) which have similar intensity to that of the (222) peak at 37°.[5] These peaks are absent in our films, indicating a pure Fe_3O_4. Details of this analysis were explained in the paper by Liu *et al.*[5]

To investigate the microstructural dependence of the reactive sputtered Fe_3O_4 on the thickness, plan-view images of films of different thicknesses were taken, and are shown in Fig. 2. The grain size increases from ~15 to ~25 nm as the film thickness increases from 17 to 100 nm. There are diffuse rings in the selected area diffraction (SAD) pattern of Fig. 2(a), indicating an amorphous phase in the 17-nm Fe_3O_4 film. The plan-view images in Figs. 2(a), 2(c), and 2(e) show

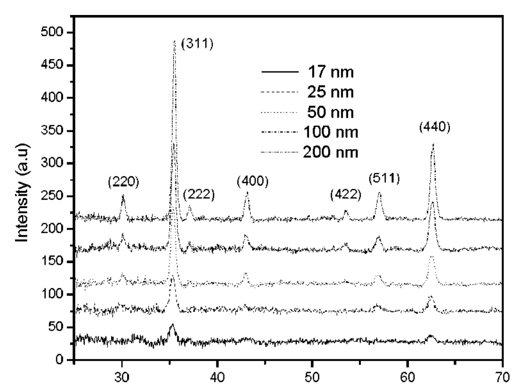

FIG. 1. In-plane XRD patterns as a function of film thickness at an oxygen flow rate of 6.8 SCCM and Ar flow rate of 27 SCCM.

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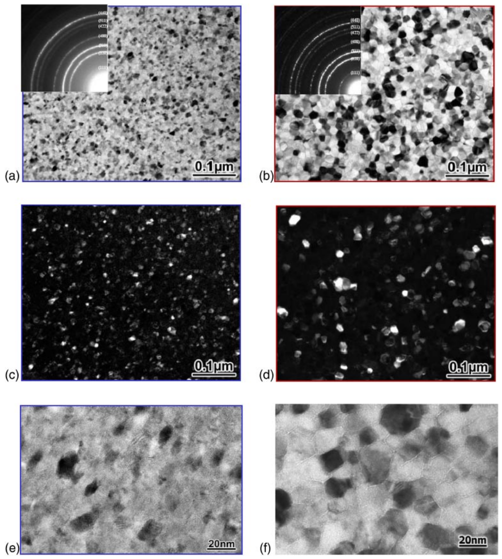

FIG. 2. (a) Bright field, (c) dark field, and (e) magnified images of 17 nm, and (b) bright field, (d) dark field, and (f) magnified images of a 100-nm Fe_3O_4 film. SAD is shown in the upper corner of the bright field image.

that small grains seem to be embedded in the amorphous matrix, while well-defined grains and grain boundaries are displayed in the 100-nm Fe_3O_4 film [Figs. 2(b), 2(d), and 2(f)]. As seen in the magnified images shown in Fig. 2(f), the grain boundaries have a uniform width and consist of an amorphous Fe-oxide phase. The analysis of the grain boundaries has been described previously.[6]

The resistivity versus temperature for the Fe_3O_4 films at different thicknesses is plotted in Fig. 3. Resistivity increases exponentially with decreasing temperature, which is the typical electrical property of Fe_3O_4 film.[7,8] However, none of the Fe_3O_4 films showed a clear Verwey transition, in which the resistance jumps by two orders of magnitude.[8] Room-temperature resistivities of the 17-nm and 100-nm film are

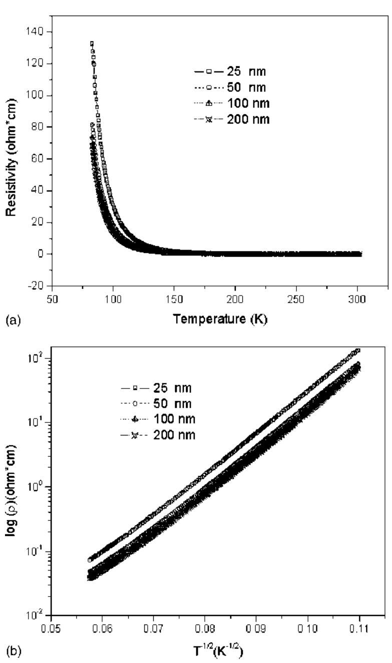

FIG. 3. Resistivity vs (a) temperature and (b) $T^{-1/2}$ for the films grown at room temperature as a function of thickness.

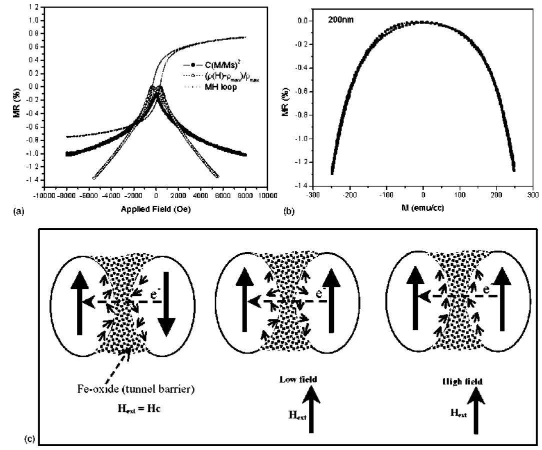

FIG. 4. (a) Magnetoresistance, hysteresis, and $-(M/Ms)^2$ curves vs applied field, (b) magnetoresistance vs magnetization for a 200-nm Fe_3O_4 film, and (c) schematic model for the MR behaviors. The measurement was conducted at 300 K.

0.07321 and 0.04183 Ω cm, respectively, which are much higher than the value (0.004 Ω cm) of the 150-nm epitaxial film without grain boundaries.[7] Thus, we believe that the large density of grain boundaries causes the disappearance of the Verwey transition. The temperature dependence of the resistivity shown in these films has the form $\rho \sim \exp(1/T^{1/2})$. This is the form expected for a granular system where tunneling occurs through the grain boundary between the grains.[9–11] This means that the amorphous phase in the grain boundaries acts as a tunnel barrier for in-plane current conduction. These results are consistent with other recent reports.[10,11]

Room-temperature magnetoresistance and $-(M/Ms)^2$ curves are shown in Fig. 4(a). The maximum MR occurs near the coercive field because of the randomly oriented grains. If no interaction occurred between the grains, the tunneling conductance between adjacent grains would be proportional to $\cos(\phi_{ij})$, where ϕ_{ij} is the relative angle between the magnetizations of the grain i and grain j. Averaging over the grains, $\mathrm{MR} \propto \langle \cos(\phi_{ij}) \rangle \propto \langle \cos(\theta) \rangle^2 \propto (M/Ms)^2$, where θ is the angle between the magnetization direction of a grain and applied field.[4,12] Therefore the MR has a quadratic dependence on M for noninteracting grains. As seen Fig. 4(a), MR

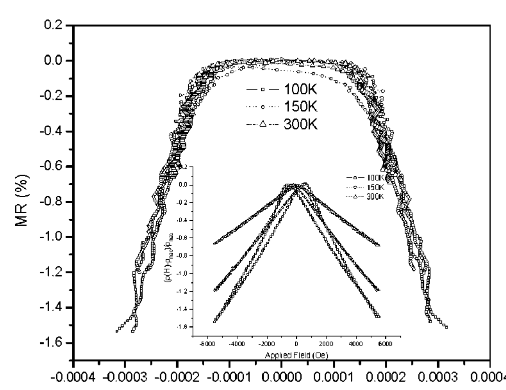

FIG. 5. Magnetoresistance vs magnetization of a 17-nm Fe_3O_4 film at various temperatures. The inset shows the magnetoresistance as a function of field.

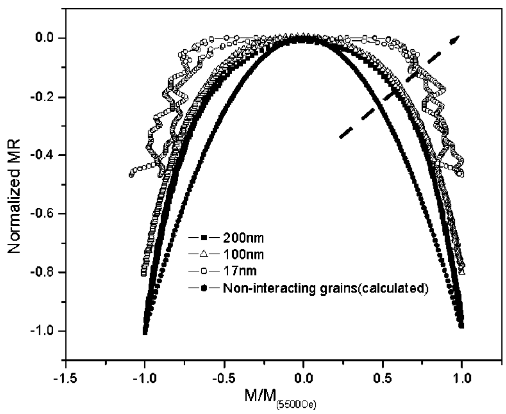

FIG. 6. Magnetoresistance curve measured at room temperature for Fe_3O_4 films at different thicknesses. Magnetization is normalized by magnetization at 5500 Oe.

initially follows the values predicted by this model and deviates later, indicating nonuniform magnetization in the grains. Figure 4(b) shows the MR dependence of magnetization. The MR does not change much until the magnetization approaches the saturation value. As confirmed by the resistivity measurement in Fig. 3, conduction occurs by tunneling between adjacent grains. These results suggest that the MR is most likely associated with the alignment of the surface spins near the grain boundaries because tunneling is an interface effect. Therefore, the spin at the grain boundaries determines the tunneling, while the contribution from these spins to the total magnetization is small. The MR measurement (Fig. 4) indicates that the surface spins of the Fe_3O_4 grains at room temperature are probably above "the blocking temperature." Thus, the surface spins of the grains at room temperature are randomized. They can be aligned by a high field (forced surface magnetization), resulting in a significant reduction of in-plane resistance. Based on the above results, we draw the following conclusion as shown in Fig. 4(c): when a magnetic field is applied, the spins in the central regions of the grains are oriented first, while the spins at the surface are only slightly affected. As the magnetic field is increased above the field at which the spins at the surface start to become aligned, the resistance decreases abruptly because it is only the spins at the surface which determine the tunneling probability.

Figure 5 shows the magnetoresistance versus magnetization of a 17-nm Fe_3O_4 film at various temperatures. The magnetoresistance of a 17-nm Fe_3O_4 film at 5500 Oe increases with decreasing temperature. The MR behavior as a function of field is different at various temperatures. However, the dependence of the resistance upon the magnetization is the same at different temperatures. The magnetization of the 17-nm Fe_3O_4 film at 5500 Oe decreases with increasing temperature. The increase in magnetization (20%) is much smaller than the increase in MR (200%). The noise in Fig. 5 arises from the small signal from the *MH* loop measurement because the 17-nm Fe_3O_4 film is so thin (17 nm). However, as Fig. 5 shows, the MR for the 17-nm Fe_3O_4 film significantly deviates from this quadratic relation. A similar MR behavior has been reported for core-shell Fe–Fe oxide system where the core consists of α-Fe and the shell of Fe oxide.[13] This result is consistent with our model shown in Fig. 4(c).

Figure 6 shows a magnetoresistance curve measured at room temperature for the Fe_3O_4 films. As the thickness increases and the mean grain size increases, the MR increases. The MR curve of a 200-nm film starts to change even at a low field while the MR curve of a 17-nm film starts to change at a high field. Note that as thickness decreases, the deviation increases between the experimental MR curve and the calculated MR curve of the noninteracting grains with uniform magnetization. This indicates that the large grains have more uniform magnetization than the small grains. Therefore, the magnetization in a thicker film is slightly larger than in a thinner film, resulting in a larger MR. This type of MR behavior clearly shows that the significant resistance change at high fields is the result of the alignment of surface spins (forced surface magnetization).

The quality and size of the grains in films of Fe_3O_4 are critically dependent on the thickness of the reactive sputtered Fe_3O_4 film. It is found that the crystallinity of the Fe_3O_4 grains in the thinner film (17 nm) is relatively poor with significant presence of an amorphous phase (Fe oxide) in between Fe_3O_4 grains. Such microstructure results in a significantly lower *Ms* than the bulk value. The amorphous phase in the grain boundaries acts as a tunnel barrier for in-plane current conduction. At small grain sizes, this magnetization-dependent resistance varies significantly from the quadratic dependence assuming uniformly magnetized grains, indicating that the surface spins of the Fe_3O_4 grains at room temperature are above the "blocking temperature" thereby, randomized. The significant resistance change at high fields is the result of the alignment of surface spins (forced surface magnetization). The implication of this finding is important for successfully using Fe_3O_4 as electrodes for magnetic tunnel junctions. The grain size of the Fe_3O_4 electrode needs to be sufficiently large so that the blocking temperature of the surface spins is sufficiently above room temperature for spin-dependent tunneling.

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