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Publisher's version / Version de l'éditeur:

<https://doi.org/10.1063/1.1952572>

Applied Physics Letters, 86, 25, pp. 252507-1-252507-3, 2005-05-16

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Effect of antiphase boundaries on electrical transport properties of Fe_3O_4 nanostructures

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(Received 3 February 2005; accepted 16 May 2005; published online 15 June 2005)

Fe_3O_4 nanowires have been fabricated based on Fe_3O_4 thin films grown on $\alpha\text{-Al}_2\text{O}_3$ (0001) substrates using the hard mask and ion milling technique. Compared with thin films, the Fe_3O_4 nanowire exhibits a slightly sharper Verwey transition but pronounced anisotropic magnetoresistance properties in the film plane at low magnetic field. Detailed bias-dependence study of both the conductance and magnetoresistance curves for both the thin films and nanowires suggests that the electrical conduction in magnetite near and above the Verwey transition temperature is dominated by a tunneling mechanism across antiphase boundaries. © 2005 American Institute of Physics. [DOI: 10.1063/1.1952572]

Recently, half-metals have received increasing attention because of its potential applications in spintronic devices.^{1,2} Among several different types of half-metallic materials, magnetite (Fe_3O_4) has been studied most intensively because of its highest known Curie temperature (858 K) and simplest chemical and crystalline structure, which allows for easy integration with existing metal-based giant magnetoresistance devices. Antiphase boundaries (APBs), as a kind of growth defect in Fe_3O_4 thin films, were reported in the literature by different groups with different substrates and growth techniques.^{3–5} It is commonly believed that APBs are intrinsic consequences of nucleation and a growth mechanism independent of preparation methods and substrates. From a practical application point of view, it is of great importance to obtain an understanding of how the APBs affect the electrical transport properties of the magnetite. Eerenstein *et al.* showed that epitaxial film with APBs has linear I/V curves and interpreted the transport properties across APBs in term of small polaron hopping.⁶ As the effect of APBs on the electron transport properties of thin films is very much dependent on the density of the APBs, it necessitates more detailed investigations through confining the APBs into a one-dimensional conduction channel. In this letter, we report a systematic study of the transport properties of both epitaxial Fe_3O_4 thin films and nanowires. The latter allow us to confine the APBs in a nanowire, which makes the effect of APBs more prominent as compared to the thin-film case, as

conduction paths through the host material are relatively reduced. The bias dependence of conductance and magnetoresistance (MR) suggests that the electron transport of Fe_3O_4 nanowires is well represented by a series of tunnel junctions made by APBs.

The Fe_3O_4 thin films (around 150 nm) were prepared on $\alpha\text{-Al}_2\text{O}_3$ (0001) single-crystal substrates using molecular-beam epitaxy with a background pressure of about 10^{-9} Torr. During the growth, iron metal was evaporated by an electron beam with an oxygen partial pressure of 1.0×10^{-5} Torr. The deposition rate was about 0.04 nm/s at a substrate temperature of 573 K. The structural, magnetic, and transport properties of the as-grown thin films were characterized by transition electron microscopy (TEM), superconducting quantum interference device magnetometer, and dc four-probe techniques, respectively. The nanowires were fabricated using electroplated Ni nanowires (average diameter of 200 nm and a length of 30 μm) as the hard mask. The typical fabrication processes involve dispersing the Ni nanowires on the as-grown Fe_3O_4 thin film, ion milling of uncovered film, removal of the Ni nanowires by ultrasonic cleaning, and electrode formation using a double-layer resist process. The location of nanowires, and the positioning and deposition of electrodes [Ti(20 nm)/Au(100 nm)] were performed with a laser writer and an e-beam evaporator, respectively. The finally finished Fe_3O_4 nanowire has a width of about 300 nm.

A dark-field TEM plane-view micrograph is shown in Fig. 1(a). The black lines are antiphase boundaries, which are irregular with an average size of ~ 100 nm. No other defects were found except the APBs, which is consistent with the

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FIG. 1. (a) Plane-view TEM images of Fe_3O_4 thin film. The black lines are antiphase boundaries. (b) Magnified APB as indicated by the arrow.

x-ray diffraction result (not shown here). Compared to the domain size of the sample by Moussy *et al.*,⁵ our sample shows a larger average domain size due to the thicker film. In Fig. 1(b), we can observe more clearly APBs by magnifying one of them along the arrow direction.

Figure 2(a) shows the temperature dependence of the resistance $R(T)$ normalized to the room temperature resistance $R(300\text{ K})$ for both a thin film and a nanowire. The resistivity of our film is $\sim 0.008\ \Omega\text{ cm}$, which is slightly higher than the bulk value of $0.005\ \Omega\text{ cm}$, and much less than $0.18\ \Omega\text{ cm}$ in the polycrystalline sample reported.⁷ A clear Verwey transition is seen in both curves at 120 K in the temperature-dependent resistance curve. Although it is not so obvious, the nanowire indeed shows a slightly sharper transition compared to the thin film, which is expected due to the decrease in randomness inside a smaller volume of sample. The magnetization versus temperature of zero-field-cooled (M_{ZFC}) and field-cooled (M_{FC}) thin film with 100 Oe field applied are shown in the inset of Fig. 2(a). We can clearly see a sharp decrease in the magnetic moment around 120 K. Both of them are strong indicators of good stoichiometry and high crystalline phase of the thin film.⁸

Figure 2(b) shows the typical magnetoresistance curves at 300 K. The in-plane MR is isotropic for thin films, but it is

FIG. 2. (a) Resistance as a function of temperature for both a thin film and a nanowire; Inset: ZFC and FC curves of the thin film with a magnetic field of 100 Oe. (b) Normalized MR curve for both thin films and nanowires at 300 K (nanowire_P: field parallel to the wire axis; nanowire_V: field perpendicular to the wire axis). Inset: high-field MR of the thin film at 300 K.

FIG. 3. Bias dependence of differential conductance for a nanowire at 130 K with applied magnetic fields of 0 and 5 T, respectively. Solid curve: fitted data according to the Simmons equation; solid circles: experimental data at zero field; open circles: experimental data at 5 T. Inset: bias dependence of G' .

anisotropic for the nanowires. The MR ratio of thin film is about 1% at a magnetic field of 6000 Oe. The nanowire exhibits an almost the same MR as that of the thin film in the longitudinal direction, but a somewhat reduced MR in the transverse direction. The former shows a shape that is universal to almost all the Fe_3O_4 films grown by different techniques.^{6,7,9,10} We believe that the exchange coupling across APBs should be antiferromagnetic, as discussed in Refs. 6 and 9. Depending on the domain size, the spins at the center of the domains may switch earlier or easier than those at the boundaries. This may explain the difference in the MR curves at low and high fields. This argument is also supported by the slow change of transverse MR of nanowires at low field which can be understood as caused by the shape anisotropy in the center region of the domain, whereas in the high-field region the MR curve is almost the same as that in the longitudinal direction. The inset of Fig. 2(b) shows the thin film MR curve at a high magnetic field. It can be seen that the MR curve is unsaturated even at an applied field of 7 T, which is consistent with most observations that the Fe_3O_4 magnetization is difficult to saturate due to the existence of atomically sharp antiphase boundaries. It is interesting to note that the large MR at high fields does not correspond to a large change of magnetization in the same field range. In other words, the MR at high field is caused mainly by the spin alignment at the boundaries instead of the center region of the domains. As it will be discussed subsequently, the transport across the APBs is dominated by tunneling.

The typical differential conductance-voltage curve for a nanowire is shown in Fig. 3, which was measured at a temperature of 130 K. The curves at other temperatures ranging from 110 to 300 K exhibit almost the same parabolic shape except for the absolute values, which are dependent on temperature. As shown in Fig. 3, the conductance-voltage curve can be fitted almost perfectly to a parabola using $G(V) = \alpha V^2 + \beta V + G_0$, where α and β are constants and G_0 is the zero-bias conductance. Although it is not shown here, a similar degree of agreement between experimental and fitted curves has also been obtained for the conductance curves at all other temperatures which we have investigated. β is negligibly small compared to α in the entire temperature range, suggesting that the transport is dominated by tunneling across APBs. Also shown in the figure is the conductance curve taken at an applied field of 5 T. If we assume a rectangular shape of potential barrier with a height of ϕ and thickness d , then according to the Simmons model,¹¹ one has $G_0 \propto 1/d$ and $\alpha \propto d/\phi$. The increase of zero-bias conductance

FIG. 4. Bias dependence of MR for the nanowire at 110, 120, and 130 K. Inset: comparison of bias dependence of MR for the thin film (solid circles) and nanowire (open circles) at 110 K.

with an external field may be attributed to a decrease of barrier thickness. Shown in the inset of Fig. 3(a) is the bias voltage dependence of $G'_{(V)} = [G_{(H=0,V)} / G_{(H=0,0)}] / [G_{(H=5\text{ T},V)} / G_{(H=5\text{ T},0)}]$. Substituting $G_0 \propto 1/d$ and $\alpha \propto d/\phi$ into the equation, one finds $d^2(H)/\phi(H) < d^2(0)/\phi(0)$. As the potential barrier will either not change or will decrease with external field, it implies again that the barrier thickness decreases with the external field.

It is well known from the work on magnetic tunnel junctions that the MR ratio normally decreases with the bias voltage. Figure 4 shows the bias dependence of MR ratio $\Delta R/R_0 = (R_{(5\text{ T})} - R_0)/R_0$ at 110, 120, and 130 K for the nanowire sample. It was obtained by first measuring the I - V curve at zero field and then repeating the measurement at an applied field of 5 T. The MR shows a minimum value at 120 K which is consistent with other groups' results.¹²⁻¹⁴ The MR ratio increases with increasing the bias, which is a typical behavior of magnetic tunneling junctions. The thin film also shows the same bias dependence of MR, although it is not as obvious as the nanowire case (see the inset of Fig. 4). As it is

shown in the inset, we also observe a zero-bias MR anomaly at 110 K for the nanowire sample that is not well understood at present.

In summary, our systematic study of the transport properties of Fe_3O_4 thin films and nanowires suggests that APBs have a strong effect on electrical transport properties in Fe_3O_4 . Antiferromagnetic coupling across the APBs is responsible for the universal shape of the MR curves and the transport across the APBs is dominated by tunneling.

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