Fabrication and properties of heteroepitaxial magnetite (Fe_3O_4) tunnel junctions

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Micron-size magnetic tunnel junctions consisting of ferromagnetic Fe_3O_4 electrodes, with MgO as a barrier layer, have been fabricated on (100) MgO substrates. Reflection high-energy electron diffraction and transmission electron microscopy studies reveal that the Fe_3O_4/MgO/Fe_3O_4 trilayers grown by pulsed laser deposition are heteroepitaxial with abrupt interfaces. To achieve different coercivities for the top and bottom Fe_3O_4 layers, the trilayers are grown on MgO substrates with a $CoCr_2O_4$ buffer layer. The junctions exhibit nonlinear current–voltage characteristics and changes in junction resistance with applied field corresponding to the coercivities of the two magnetic layers. However, the observed magnetoresistance (~0.5% at 300 K, ~1.5% at 150 K) is much lower than would be expected for a highly spin-polarized system. Possible reasons for the reduced magnetoresistance are discussed.
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Spin-dependent transport in the doped manganite system results in a large low-field magnetoresistance (MR) being observed in grain boundary samples[1–3] and in heteroepitaxial manganite/insulator/manganite tunnel junction structures.[4–7] These results have generated interest in studying the MR properties of other magnetic systems exhibiting a high degree of spin polarization.[8–11] Band structure calculations have shown that the well-known magnetic oxide material magnetite (Fe_3O_4) contains a gap in the majority spin band at the Fermi level but there is no gap in the minority spin band.[12] A large negative value of spin polarization (~40%) has been measured at 0.5 eV below the threshold in spin-polarized photoemission experiments.[13] In spite of the numerous studies related to Fe_3O_4,[14] the magnetotransport behaviors of this material have only been recently investigated.[10,11,15,16] Large negative MR has been observed around and below the Verway transition in single crystals[15] and epitaxial films.[16] Low-field negative MR associated with intergranular transport of spin-polarized electrons has also been reported in polycrystalline thin films and powder compacts of Fe_3O_4 at higher temperatures.[10,11] However, the magnitude of the MR (~1%–2% at 0.5 T) is significantly smaller than what has been observed in the manganites.

In this letter we report on the fabrication and low-field MR properties of heteroepitaxial magnetic tunnel junction structures in the form of Fe_3O_4 (top electrode)/MgO (barrier)/Fe_3O_4 (bottom electrode) on (100)-oriented MgO substrates. In order to achieve switching at different coercive fields for the two electrodes, the trilayer structures have been grown on substrates buffered by a thin layer of the $CoCr_2O_4$ spinel material. The fabricated tunnel junctions exhibit low-field MR with resistance changes corresponding to the switching fields of the Fe_3O_4 electrodes. However, as in the case of polycrystalline samples, the observed magnitude of the MR is much smaller (~0.5% at 300 K and ~1.5% at 150 K) than expected based on the spin polarization.

The mangnetite heterostructures have been grown on single crystal (100) MgO substrates using the pulsed laser deposition technique.[4,16] Both cubic Fe_3O_4 ($a = 8.397$ Å) and MgO ($a = 4.213$ Å) have their oxygen atoms in a face-centered-lattice structure with a small mismatch of about −0.3%. The buffer layer material $CoCr_2O_4$ is a paramagnetic insulator at room temperature and has the same spinel structure as Fe_3O_4, with a slightly smaller lattice parameter (lattice mismatch = +0.3%).[17] A focused KrF excimer laser (248 nm) beam is used for ablation, with a repetition rate of 4 Hz and a fluence of ~2–3 J/cm^2 at the target. The substrate is placed on a heater that can be rotated and translated for proper positioning of the azimuth and incidence angle for reflection high-energy electron diffraction (RHEED) measurements. Heteroepitaxial Fe_3O_4/MgO/Fe_3O_4 films have been grown both with and without the $CoCr_2O_4$ buffer layer. The buffer layer is grown at 475 °C, whereas the Fe_3O_4 bottom and top layers and the MgO barrier layer are deposited at a substrate temperature of 350 °C, all under vacuum conditions (~10^{-6} Torr).

We initially grew a number of Fe_3O_4/MgO/Fe_3O_4 trilayers directly on (100) MgO substrates, with the thickness of both the Fe_3O_4 electrodes in the range of 400–500 Å, and the MgO barrier varying between 10 and 50 Å. Figure 1 shows the typical RHEED patterns obtained during growth of such a heterostructure along the ⟨011⟩ azimuth. The diffraction

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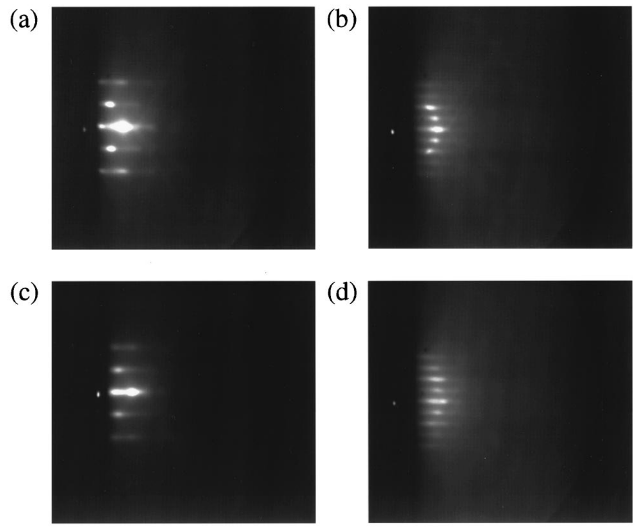

FIG. 1. RHEED patterns of: (a) cleaned MgO (100) substrate, (b) after 400 Å growth of bottom Fe_3O_4 layer, (c) after 40 Å growth of MgO barrier layer, and (d) after 400 Å growth of top Fe_3O_4 layer. All the patterns have been taken along the ⟨011⟩ azimuth at an electron beam energy of 20 kV.

pattern for the bare MgO substrate in Fig. 1(a) shows lattice rods and radial Kikuchi lines indicative of a well-ordered and flat surface. Upon growth of Fe_3O_4 the pattern remains streaky with the development of half-order streaks, reflecting the double periodicity of the unit cell of Fe_3O_4 as compared to MgO [Figs. 1(b)]. As expected, when a thin layer of the barrier MgO is deposited on top of the Fe_3O_4 film, the half-order streaks disappear as seen in Fig. 1(c). They subsequently reappear upon growth of the top Fe_3O_4 electrode [Fig. 1(d)]. The RHEED results suggest that the trilayer structure grows heteroepitaxially and the surface remains atomically smooth as a result of the two-dimensional growth mode of all the layers.

Further confirmation of the heteroepitaxial growth has been obtained from microstructural investigations of the films using transmission electron microscopy and electron diffraction. Figure 2 shows the high-resolution cross-

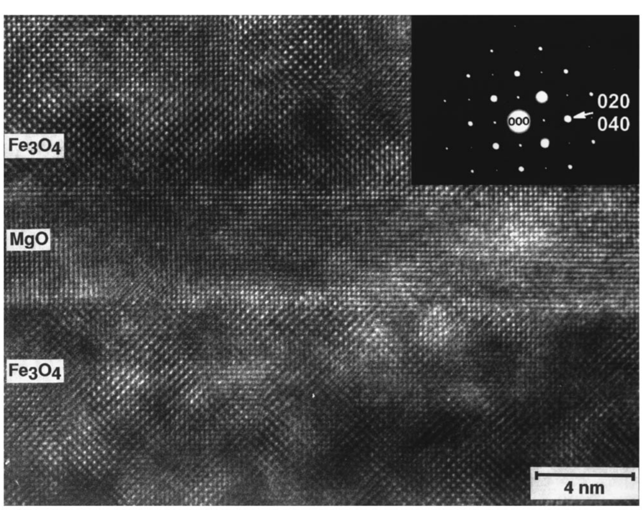

FIG. 2. High-resolution transmission electron micrograph of a cross-sectional lattice image obtained from a heteroepitaxial Fe_3O_4/MgO/Fe_3O_4 film. Inset shows the electron diffraction pattern from the heterostructure. The marked spot is the overlap of the MgO (020) and Fe_3O_4 (040) spots.

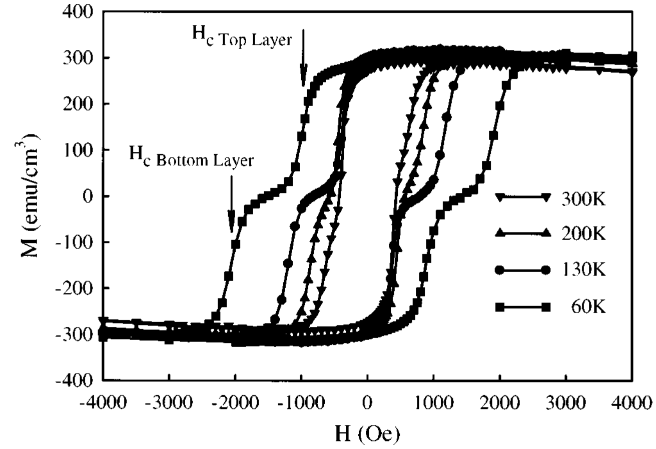

FIG. 3. Magnetization hysteresis loops at different temperatures for a heteroepitaxial Fe_3O_4 (400 Å)/MgO (40 Å)/Fe_3O_4 (400 Å) film grown on a 800-Å-thick $CoCr_2O_4$ buffer layer. Note that the separation in the coercivity of the two layers increases with decreasing temperature.

sectional transmission electron microscopy (TEM) lattice image of the interface region with the MgO barrier (50 Å) in one of the structures. All the layers are heteroepitaxially aligned and atomically smooth interfaces are observed between the Fe_3O_4 and MgO layers. The inset shows the electron diffraction pattern from an area containing all the layers. The diffraction spots from the MgO layer have essentially the same angular spacing as those of the Fe_3O_4 layers because of the small lattice mismatch. Lower resolution micrographs of the trilayers have shown the MgO barrier layer is flat and continuous over regions extending hundreds of nanometers. The interface region with the substrate has also been imaged and found to be atomically abrupt with the cubic ⟨100⟩ axes of Fe_3O_4 aligned exactly with the corresponding axes of the MgO substrate.

Magnetic measurements of the blanket trilayers show rounded hysteresis loops[16] with very similar coercivities (~200 Oe at 300 K) for the top and bottom electrodes. Because of the relatively high coercivity and nonsquare nature of the hysteresis loops, the induced shape anisotropy of the top electrode after patterning will not be sufficiently large to alter its coercivity significantly from that of the bottom electrode. Without independent switching of the two electrodes, junction MR would not be expected. In order to vary the coercivity of the layers we have experimented with different buffer layers. We have found that epitaxial growth of Fe_3O_4 on (100) MgO substrate buffered by a $CoCr_2O_4$ layer significantly improves the squareness of the hysteresis loop and increases its coercive field (~700 Oe at 300 K). Improvements in film crystallinity and saturation magnetization properties have been noted previously in epitaxial spinel ferrite thin films grown on $SrTiO_3$ and $MgAl_2O_4$ substrates buffered by $CoCr_2O_4$.[17] The changes in magnetic properties with the buffer layer may result from a decrease in the density of antiphase boundaries.[18]

Figure 3 shows the in-plane hysteresis loops at various temperatures for a Fe_3O_4/MgO/Fe_3O_4 film grown on top of a 800-Å-thick $CoCr_2O_4$ buffer layer, measured using a quantum design superconducting quantum interference device (SQUID) magnetometer. The field is applied along the cube axis direction for the single crystal MgO substrate. The dif-

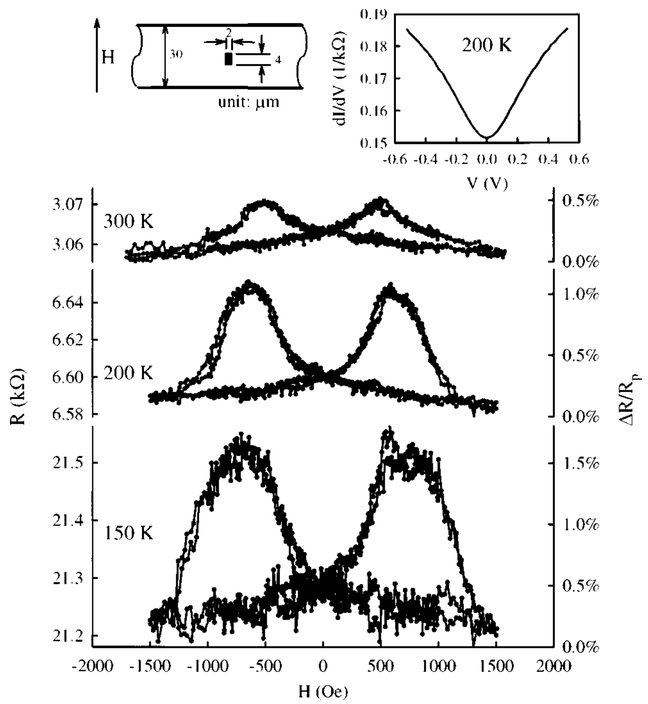

FIG. 4. Resistance and magnetoresistance ($\Delta R/R_p$) vs magnetic field at different temperatures for a tunnel junction with a rectangular 2×4 μm^2 top electrode. The insets show the junction geometry and the dynamic conductance vs bias voltage at 200 K.

ferences in the coercive fields for the bottom and top Fe_3O_4 layers are apparent, particularly at low temperatures. In the superposition of two hysteresis loops, the bottom layer displays the higher coercive field, similar to that of Fe_3O_4 deposited on $CoCr_2O_4$ buffer, while the top layer has a coercivity closer to that of a film grown directly on MgO substrate.

Figure 4 shows the field dependence of the tunneling resistance (R) and the MR ratio, $\Delta R/R_p$, at various temperatures of a tunnel junction fabricated from the Fe_3O_4/MgO/Fe_3O_4 trilayer deposited on $CoCr_2O_4$ buffer. Here R is measured at zero bias and R_p is the peak resistance. The junction has a rectangular top electrode of area 2×4 μm^2 and the magnetic field is applied along the easy axis of the rectangle. The inset shows that the dynamic conductance of the junction as a function of bias voltage is parabolic at low bias, indicative of electron tunneling. The changes in R in Fig. 4 are associated with the moment reversals of the two electrodes. The switching fields for the increase and decrease in R, at various temperatures, correspond closely with the magnetic coercivities of the top and bottom electrodes as observed in Fig. 3. At high fields, when the moments of the two electrodes are aligned along the field direction, R attains a low value. Whereas, in between the coercive fields for the two electrodes, R reaches the maximum value due to antiparallel orientation of the moments. The junction MR at 300 K is $\sim$0.5% and increases to about 1.5% at 150 K. For comparison, the MR of the Fe_3O_4 bottom electrode is negligible ($<$0.1% at 200 K) over the measured field range.

While the above results clearly demonstrate MR associated with field-induced switching of the Fe_3O_4 electrodes, the magnitude is very small considering the high degree of spin polarization expected in this system. At present we can only speculate about possible causes for the reduction. Since magnetotunneling is an interface effect, spin flip processes at the interface would certainly have a deleterious effect on the MR. A less-than-ideal insulating barrier containing impurities and defects would also lead to spin scattering. Various studies have indicated that the magnetic ordering near a region of 10–25 Å of the top surface or the interface region of Fe_3O_4 is modified resulting in a magnetically dead layer.[19,20] Besides a disordered spin structure at the interface due to termination,[19] it is possible that a reduced oxide, such as antiferromagnetic $Fe_{1-\delta}O$, is present at the interface due to interaction with the MgO barrier. This would certainly lead to a very large decrease in the spin polarization of the conduction electrons. Further studies are underway to understand the nature of the interface region in the heteroepitaxial structures.

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