Rectifying property and giant positive magnetoresistance of Fe₃O₄/SiO₂/Si heterojunction

T. L. Qu, Y. G. Zhao, H. F. Tian, C. M. Xiong, and S. M. Guo
Department of Physics, Tsinghua University, Beijing 100084, China
J. Q. Li
Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100080, China

(Received 2 March 2007; accepted 7 May 2007; published online 1 June 2007)

Fe₃O₄/SiO₂/Si heterojunction was fabricated by growing Fe₃O₄ film on an n-type Si wafer with the native SiO₂ buffer layer using the pulsed laser deposition. Transmission electron microscopic study shows the high quality of the heterojunction interfaces and the SiO₂ layer is 2.5 nm thick. This junction shows a backward diodelike rectifying behavior and an anomalously giant positive magnetoresistance (MR) for the large reverse bias voltages. The temperature dependence of MR shows a peak around the Verwey transition temperature with a maximum MR of 87% under a −2 V bias voltage. The results were discussed by considering the band structure of the heterojunction and the effect of the reverse bias voltage. © 2007 American Institute of Physics. DOI: 10.1063/1.2743937

Magnetite (Fe₃O₄) has attracted enormous attention due to its interesting properties, such as its ferromagnetism with a high Curie temperature of 860 K, half-metallic state predicted by the band-structure calculations, nearly 100% spin polarization indicated by the spin-resolved photo-emission, and various magnetoresistance (MR) effects, which are very promising for the potential applications of magnetite in spintronics devices. Fe₃O₄ also shows a metal-insulator transition, known as the Verwey transition, and the nature of this transition is still under debate. Recently there are a few papers on Fe₃O₄-based heterojunctions, such as Fe₃O₄/Nb:SrTiO₃, Fe₃O₄/BaTiO₃, and Fe₃O₄/GaAs, which show rectifying property and a few percent MRs were also demonstrated.

Regarding spintronic device integration, growing magnetite on silicon substrates is very important because silicon is the most widely used material in modern semiconductor technology. To grow oxide thin films on Si, a buffer layer is usually needed due to the reaction and lattice mismatch between oxides and Si. It has been shown that a native SiO₂ layer with a suitable thickness is a good buffer layer between Si and Pb(Zr,Ti)O₃ or manganite. So, it is interesting to see whether Fe₃O₄ thin film can form a good diode with Si by growing it on Si with the native SiO₂ layer as a buffer layer. This will make the fabrication process of the diode simple. Up to now, there have been no reports on diode composed of magnetite and silicon. In this letter, we reported the fabrication of Fe₃O₄/SiO₂/Si heterojunction, its rectifying property and giant positive MR.

Electron-doped (n-type) (100) silicon was used as the substrate, whose resistivity is about 0.02 Ω cm. There is a native SiO₂ layer on the surface of the substrate. Fe₃O₄ film was grown by pulsed laser deposition. The substrate was first kept at 300 °C with an oxygen pressure of 100 Pa for 30 min in order to get a thicker SiO₂ layer, which acts as a buffer layer. Subsequently the oxygen pressure was set to 1 × 10⁻³ Pa and the substrate temperature was kept at 450 °C during deposition. The energy density of the laser pulse was about 1.5 J/cm² and the repetition rate was 2 Hz. After deposition, the sample was cooled down to room temperature with the same oxygen pressure as deposition. The x-ray diffraction pattern of Fe₃O₄/SiO₂/Si shown in Fig. 1(a) indicates a polycrystalline Fe₃O₄ film with (222) and (511) orientations. In-plane resistance of Fe₃O₄ film was measured by standard four-probe method. Gold pads with an area of about

![Graph and images](data:image/png;base64,iVBORw0KGgoAAAANSUhEUgAAAgAABAMAAQMAAABQAAAAAElFTkSuQmCC)
1 mm² were used as electrodes. The resistance versus temperature curve of Fe₃O₄ film in the inset of Fig. 1(a) shows the Verwey transition behavior, which is consistent with the previous report. The magnetic property of Fe₃O₄ film was also measured by using a quantum design magnetic property measurement system (MPMS-XL7). As shown in the inset of Fig. 1(a), the magnetization increases abruptly with the increase of the temperature near the Verwey transition \( T_V \approx 120 \text{ K} \), consistent with the previous report.

We firstly performed a structural examination of this heterojunction by using a Tecnai-F20 (200 kV) transmission electron microscope (TEM). Samples for TEM observations were prepared using the conventional method consisting of gluing, cutting, mechanical polishing, dimpling, and finally ion thinning. Figure 1(b) is a bright-field TEM image for a typical Fe₃O₄/SiO₂/Si junction, illustrating the cross-section morphology and the orientation relationships among the structural layers along the (001) direction of silicon. The inset of Fig. 1(b) shows a high resolution TEM image clearly exhibiting the atomic structural features across the SiO₂ layer. The essential columnar structural features in Fe₃O₄ film, as well as an interfacial amorphous SiO₂ layer (bright band), are evidently recognizable as a remarkable contrast alternations. This film is uniform, and the thicknesses of the Fe₃O₄ film and SiO₂ as measured from the TEM images are about 80 and 2.5 nm, respectively. The interfaces on either side of the SiO₂ are clean and sharp.

The current to voltage \((I-V)\) curves at different temperatures, measured by a Keithley voltage source are shown in Fig. 2(a). The left inset schematically illustrates the electrode settings in which the forward bias corresponds to the application of a positive voltage to the Fe₃O₄ film. The right inset is the \( I-V \) curves within 250–300 K. It is interesting to note that the \( I-V \) curves exhibit a good backward diodelike rectifying property. The junction current increases dramatically with increasing reverse bias voltage. In contrast, the current remains low for the forward bias voltage even when the voltage reaches 2 V. Figure 2(b) shows the temperature dependence of the junction resistance defined as \( R = V/I \) with different reverse bias voltages. It can be seen that \( R_j \) increases with decreasing temperature, similar to the temperature dependence of the in-plane resistance of Fe₃O₄ film (the inset of Fig. 1). The inset of Fig. 2(b) shows \( \log[|I|] \) curves for the reverse bias within 100–140 K. The \( \log[|I|] \) curves for different temperatures are nearly parallel.

The most interesting characteristic of the junction is that, for the large reverse bias voltages, the junction exhibits giant positive MR under a magnetic field of \( 7 \text{ T} \), particularly for the large reverse bias voltages. From Fig. 3(b), it can be seen that the temperature dependence of the positive MR of Fe₃O₄/SiO₂/Si junction under different reverse bias voltages shows an extremum around \( T_V \). Interestingly, the negative MR of Fe₃O₄ polycrystalline samples, single crystals, and thin films also shows an extremum around \( T_V \). To account for the MR extremum in Fe₃O₄, Gridin et al. proposed a model based on their Fe₃O₄ single crystal data and thermodynamic arguments. According to this model, the MR extremum in Fe₃O₄ is proportional to the discontinuous change in the magnetization at \( T_V \), where a first-order phase transition occurs. It is expected that the positive MR extremum of Fe₃O₄/SiO₂/Si is related to the Verwey transition induced dramatic variation of electronic transport across the junction interface.

Figure 4 is the density of states (DOS) of Fe₃O₄ and the schematic band diagram for Fe₃O₄/SiO₂/Si heterojunction. It has been shown that Fe ions occupying the octahedral sites (Feoct) of Fe₃O₄ dominate the DOS around the \( E_F \), as shown in Fig. 4(a), which consists of the majority spin-up band and the minority spin-down band split by an exchange energy. The fivefold \( d \) levels of the Feoct ions are split into three degenerate \( t_{2g} \) levels and two degenerate \( e_g \) levels because of the crystal field splitting. The majority spin band is located below \( E_F \) and is occupied by five spin-up electrons. The extra electron of the Feoct ion occupies the \( t_{2g} \) level of the spin-down band, which is the only band located at \( E_F \), giving rise to the half-metallic behavior. The Fermi level of the \( n \)-type Si is located below the bottom of the conduction band.
band. The work functions of Fe$_3$O$_4$ and Si are 5.3 (Ref. 20) and 4.4 eV (Ref. 21), respectively. Thus, some electrons in Si will flow into the spin-down $t_{2g}$ band of Fe$_3$O$_4$ to make the two sides have the same Fermi level. From Fig. 4(b), it can be seen that when a forward bias voltage is applied, the electrons can only transport from Si to Fe$_3$O$_4$ by thermionic emission because tunneling of electrons is forbidden due to the gap on Fe$_3$O$_4$ side, thus the current is low. For the large reverse bias voltages, however, the bands of Si move downward so electrons can transport from Fe$_3$O$_4$ to Si by both tunneling effect and thermionic emission. This can account for the backward diodelike behavior of the Fe$_3$O$_4$/SiO$_2$/Si heterojunction. The tunneling scenario is consistent with both the ultrathin thickness of SiO$_2$ and the result shown in the inset of Fig. 2(b) that the log(I)-V curves for different temperatures are nearly parallel. For the anomalous positive MR of the Fe$_3$O$_4$/SiO$_2$/Si heterojunction, the mechanism may be similar to that of the giant positive MR for the reverse bias voltage observed in the Au/GaAs Schottky diode.\textsuperscript{22} In this scenario, the magnetic field weakens the impact ionization process of carriers leading to a giant positive MR. Since MR of the Fe$_3$O$_4$/SiO$_2$/Si heterojunction shows a peak at $T_p$, it is expected that Fe$_3$O$_4$ plays an important role in the anomalous positive MR. It should be pointed out that for magnetic heterojunctions, because of the splitting of the spin-up and spin-down bands, their contributions to the characteristics of the heterojunctions are different and this difference changes with the bias voltage. In contrast, for the nonmagnetic semiconductor heterojunctions, the contributions of the spin-up and spin-down bands to the characteristics of the heterojunctions are the same. The giant positive MR of our Fe$_3$O$_4$/SiO$_2$/Si heterojunction is different from the few percent negative MRs observed in Fe$_3$O$_4$/Nb–SrTiO$_3$;\textsuperscript{11} in that the negative MR was attributed to the Zeeman splitting effect. Our work demonstrates that Fe$_3$O$_4$/SiO$_2$/Si heterojunction shows some interesting properties, which will stimulate further studies as well as possible applications of the magnetic based spintronics devices.

This work was supported by the National Science Foundation of China (Grant Nos. 50425205, 10674079, and 50272031) and 973 project (Grant Nos. 2002CB613505 and 2006CB921502).