Rectifying property and giant positive magnetoresistance of $Fe_3O_4/SiO_2/Si$ heterojunction

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

$Fe_3O_4/SiO_2/Si$ heterojunction was fabricated by growing Fe_3O_4 film on an *n*-typed Si wafer with the native SiO_2 buffer layer using the pulsed laser deposition. Transmission electron microcopic study shows the high quality of the heterojunction interfaces and the SiO_2 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 (Fe_3O_4) has attracted enormous attention due to its interesting properties,[1,2] such as its ferromagnetism with a high Curie temperature of 860 K, half-metallic state predicted by the band-structure calculations,[3] nearly 100% spin polarization indicated by the spin-resolved photoemission,[4] and various magnetoresistance (MR) effects,[5–9] which are very promising for the potential applications of magnetite in spintronics devices. Fe_3O_4 also shows a metal-insulator transition, known as the Verwey transition,[10] and the nature of this transition is still under debate.[1,2] Recently there are a few papers on Fe_3O_4-based heterojunctions, such as $Fe_3O_4/Nb:SrTiO_3$,[11,12] $Fe_3O_4/BaTiO_3$,[13] and $Fe_3O_4/GaAs$,[14] which show rectifying property and a few percent MRs were also demonstrated.[11,13]

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 SiO_2 layer with a suitable thickness is a good buffer layer between Si and $Pb(Zr,Ti)O_3$ or manganite.[15,16] So, it is interesting to see whether Fe_3O_4 thin film can form a good diode with Si by growing it on Si with the native SiO_2 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 $Fe_3O_4/SiO_2/Si$ 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 SiO_2 layer on the surface of the substrate. Fe_3O_4 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 SiO_2 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/cm^2 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 $Fe_3O_4/SiO_2/Si$ shown in Fig. 1(a) indicates a polycrystalline Fe_3O_4 film with (222) and (511) orientations. In-plane resistance of Fe_3O_4 film was measured by standard four-probe method. Gold pads with an area of about

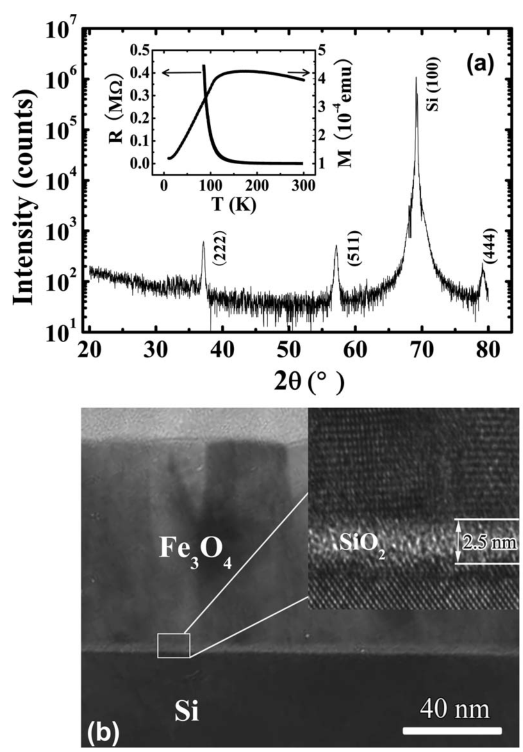

FIG. 1. (a) X-ray diffraction pattern for $Fe_3O_4/SiO_2/Si$ heterojunction. The inset shows the resistance and magnetization of Fe_3O_4 as a function of temperature. (b) TEM image of the cross-section morphology of the $Fe_3O_4/SiO_2/Si$ junction. The inset is the high-resolution TEM image near the SiO_2 layer.

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1 mm^2 were used as electrodes. The resistance versus temperature curve of Fe_3O_4 film in the inset of Fig. 1(a) shows the Verwey transition behavior, which is consistent with the previous report.[17] The magnetic property of Fe_3O_4 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 =120 K), consistent with the previous report.[7]

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 $Fe_3O_4/SiO_2/Si$ 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 SiO_2 layer. The essential columnar structural features in Fe_3O_4 film, as well as an interfacial amorphous SiO_2 layer (bright band), are evidently recognizable as a remarkable contrast alternations. This film is uniform, and the thicknesses of the Fe_3O_4 film and SiO_2 as measured from the TEM images are about 80 and 2.5 nm, respectively. The interfaces on either side of the SiO_2 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 Fe_3O_4 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 $R_j = V/I$ 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 Fe_3O_4 film (see the inset of Fig. 1). The inset of Fig. 2(b) shows $\log|I|$-V curves for the reverse bias within 100–140 K. The $\log|I|$-V 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 T, particularly around T_V, as shown in the inset of Fig. 3(b). The large separation between the two I-V curves clearly indicates the giant positive MR of the junction. MR of the junction is defined as $100\%[R_j(B)-R_j(0)]/R_j(0)$. Figure 3(a) shows the voltage dependence of MR at different temperatures. Below T_v, MR shows a peak at a certain voltage. Above T_V, MR increases monotonically with increasing bias voltage. So the voltage dependence of MR shows different behaviors below and above T_V. Figure 3(b) shows the temperature dependence of MR at different bias voltages. There is a peak at T_V in all the MR curves. Under the bias of −2.0 V at 120 K, MR can reach a maximum of 87%. It should be mentioned that the giant positive MR of $Fe_3O_4/SiO_2/Si$ junction is different from the negative MR of Fe_3O_4.[5–7] Moreover, $Fe_3O_4/SiO_2/Si$ junction shows the giant positive MR only for the large reverse bias voltages. From Fig. 3(b), it can be seen that the temperature dependence of the positive MR of $Fe_3O_4/SiO_2/Si$ junction under different reverse bias voltages shows an extremum around T_V. Interestingly, the negative MR of Fe_3O_4 polycrystalline samples,[5] single crystals,[6] and thin films[7] also shows an extremum around T_V. To account for the MR extremum in Fe_3O_4, Gridin *et al.*[6] proposed a model based on their Fe_3O_4 single crystal data and thermodynamic arguments. According to this model, the MR extremum in Fe_3O_4 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 $Fe_3O_4/SiO_2/Si$ is related to the Verwey transition induced dramatic variation of electronic transport across the junction interface.

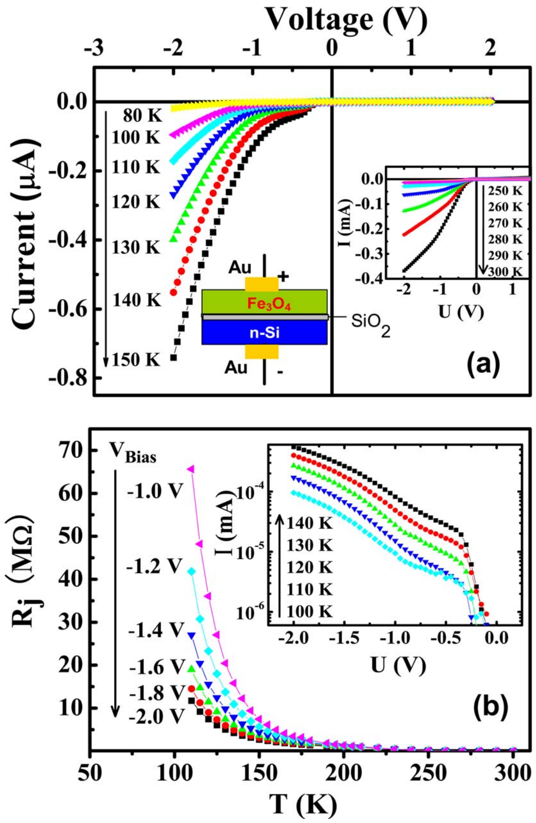

FIG. 2. (Color online) (a) I-V characteristics of $Fe_3O_4/SiO_2/Si$ heterojunction at different temperatures. Upper inset: I-V characteristic for 250–300 K. Bottom inset: the schematic illustration of the heterojunction. (b) Temperature dependence of R_j at different reverse voltages. The inset shows the $\log|I|$-V curves for the reverse bias in the temperature range of 100–140 K.

Figure 4 is the density of states (DOS) of Fe_3O_4 and the schematic band diagram for $Fe_3O_4/SiO_2/Si$ heterojunction. It has been shown[18,19] that Fe ions occupying the octahedral sites (Fe_{oct}) of Fe_3O_4 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.[19] The fivefold d levels of the Fe_{oct} 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 Fe_{oct}^{2+} 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-typed Si is located below the bottom of the conduction

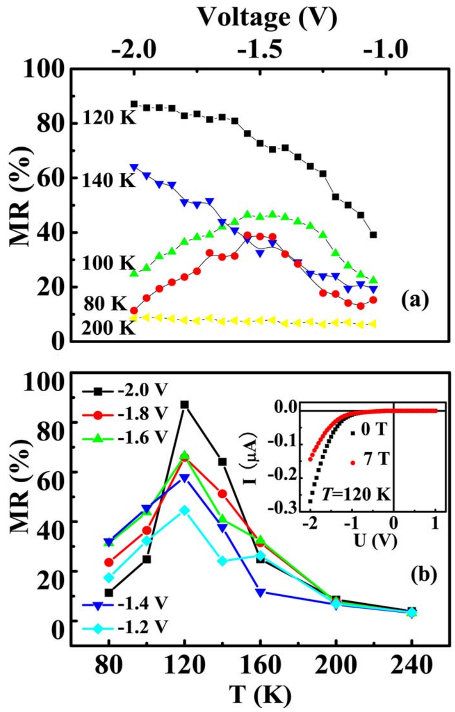

FIG. 3. (Color online) (a) Reverse bias voltage dependence of MR for $Fe_3O_4/SiO_2/Si$ heterojunction at different temperatures. (b) Temperature dependence of MR at different reverse bias voltages. Inset is *I-V* curves of the $Fe_3O_4/SiO_2/Si$ heterojunction, measured at 120 K with $B=0$ and 7 T, respectively.

band. The work functions of Fe_3O_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_3O_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_3O_4 by thermionic emission because tunneling of electrons is forbidden due to the gap on Fe_3O_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_3O_4 to Si by both tunneling effect and thermionic emission. This can account for the backward diodelike behavior of the $Fe_3O_4/SiO_2/Si$ 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 $Fe_3O_4/SiO_2/Si$ 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.[22] In this scenario, the magnetic field weakens the impact ionization process of carriers leading to a giant positive MR. Since MR of the $Fe_3O_4/SiO_2/Si$ heterojunction shows a peak at T_V, it is expected that Fe_3O_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 $Fe_3O_4/SiO_2/Si$ heterojunction is different from the few percent negative MRs observed in $Fe_3O_4/Nb-SrTiO_3$;[11] in that the negative MR was attributed to the Zeeman splitting effect. Our work demonstrates that $Fe_3O_4/SiO_2/Si$ heterojunction shows some interesting properties, which will stimulate further studies as well as possible applications of the magnetite based spintronics devices.

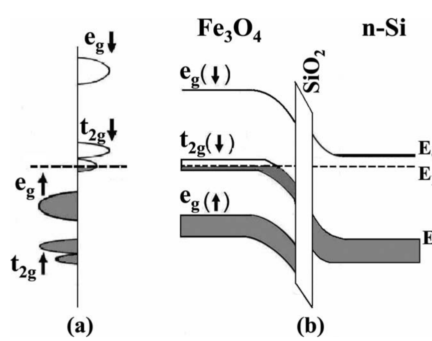

FIG. 4. (a) DOS of Fe_3O_4. (b) Schematic band diagram for $Fe_3O_4/SiO_2/Si$ heterojunction.

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).

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