Effects of buffer layer on the electronic properties of half-metallic Fe_3O_4

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We have investigated in a systematic way the effect of buffer layer materials on the metal-insulator transition and also on the $I-V$ characteristics of half-metallic Fe_3O_4 films. Using an electron-beam deposition technique, we have grown 150 nm of Fe_3O_4 films directly on Si(001) substrate, on 20-nm Fe_2O_3 and 20-nm SiO_2 buffer layers. We observed that for a fixed Fe_3O_4 film thickness, the metal-insulator transition is strongly dependent on the buffer layer materials. From the $I-V$ characteristics, we observed an insulator-like gap structure in the density of states below the transition temperature which disappears gradually with increasing temperature. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1855205]

INTRODUCTION

Half-metallic ferromagnetic materials, characterized by 100% spin polarization and having only one spin subband at the Fermi level, have been the subject of interest for more than a decade.[1–4] Several materials such as NiMnSb, CrO_2, $La_{0.7}Sr_{0.3}MnO_3$, and Fe_3O_4 are classified as half metals.[5,6] Among these, Fe_3O_4 has gained enormous attention due to the high Curie temperature (T_C) of 850 K as compared to other half-metal oxides and is therefore a suitable candidate for tunneling magnetoresistance devices.[6] The order–disorder transition at Verwey point for Fe_3O_4 is known to take place at ~120 K.[7] This metal-insulator transition of Fe_3O_4 makes its magnetoelectronics properties very interesting to investigate.

Several attempts have been made to characterize the bulk properties of Fe_3O_4 at low temperatures. Wei *et al.*[8] have studied the half-metallic properties of epitaxially grown Fe_3O_4 films on MgO substrates using scanning tunneling spectroscopy. In another study, Ziese and Bluthe[9] investigated the resistivity dependence of temperature for single-crystal Fe_3O_4 films deposited on MgO substrates using pulsed laser deposition. They established the relationship of conductivity with Arrhenius Law as a function of temperature below the metal-insulator transition. Recently, Hui *et al.*[10] reported a grain-boundary dominated electron tunneling mechanism for the change in resistivity as a function of temperature for polycrystalline Fe_3O_4 films prepared by reactive sputtering.

In this paper, we have investigated the correlation between metal-insulator transition temperature of Fe_3O_4 films and the buffer layer materials. We deposited Fe_3O_4 films directly on Si(001) substrates, on 20 nm of Fe_2O_3 and on 20-nm SiO_2 buffer layers using electron-beam deposition technique. The metal-insulator transition temperature in Fe_3O_4 is strongly dependent on the type of buffer layer materials. This may be due to the stress imposed by the buffer layer or by impurity conduction. We have also investigated the $I-V$ characteristics of Fe_3O_4 as a function of temperature for each of the buffer layers. The effect of fixed magnetic field applied during cooling has been investigated in detail. We observed a shift in the metal-insulator transition temperature due to the presence of strong magnetic field during cooling.

EXPERIMENTAL DETAILS

Fe_3O_4 films were deposited using the electron-beam deposition from Fe_3O_4 pellets. The base pressure was maintained at 4×10^{-7} Torr. The Si(001) substrates were first precleaned in acetone followed by isopropanol before loading in the deposition chamber. We deposited 150-nm-thick Fe_3O_4 films at a rate of 0.8 Å/s on Si(001) substrates, on 20-nm Fe_2O_3 and on 20-nm SiO_2 buffer layers. The deposition rate for Fe_2O_3 was 0.1 Å/s and for SiO_2 the rate was 0.3 Å/s. Low-temperature measurements were carried out in Janis Research Cryostat in the temperature range from 10 to 300 K.

RESULTS AND DISCUSSION

The evolution during metal-insulator transition has been investigated by analyzing the variation in the film's resistance as a function of temperature. Shown in Fig. 1 is the

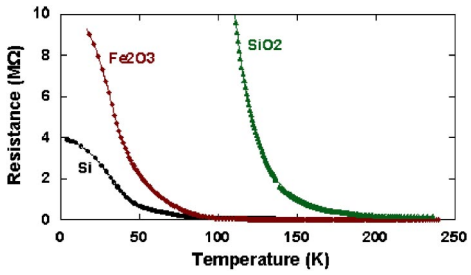

FIG. 1. Resistance vs temperature plot for 150-nm Fe_3O_4 deposited directly on Si(001) substrate and on 20-nm of Fe_2O_3 and SiO_2 buffer layers.

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temperature dependence of the resistance for 150-nm films of Fe_3O_4 deposited directly on a Si(001) substrates, on 20-nm Fe_2O_3 and on 20-nm SiO_2 buffer layers. We observed that above 100 K, the resistance of Fe_3O_4 films deposited on Si(001) and on the Fe_2O_3 buffer layer is low. As the temperature decreases, the resistance increases drastically, nearly becoming an insulator. From the *R-T* curve, we have determined the metal-insulator transition temperature (T_v) for the Fe_3O_4 film deposited on the Si(001) substrate to be 65 K. T_v for Fe_3O_4 deposited on Fe_2O_3 buffer layer is deduced to be 75 K. These metal-insulator transition points are very low when compared with the transition temperature proposed by Verwey (~120 K).[7] This decrease in T_v may be due to the impurities present at the interface between the buffer layer and the Fe_3O_4 film; thus making conduction possible even at such low temperatures. For Fe_3O_4 films deposited directly on the Si(001) substrates, however, weakly coupled phases of Fe, like FeO and Fe_2O_3 are present at the interface between Si and Fe_3O_4. This has been shown in our previous work,[11] where the weakly coupled phases affect the magnetic properties of Fe_3O_4. Chando *et al.*[12] have also observed similar results using TEM.

Surprisingly, for Fe_3O_4 film deposited on SiO_2 buffer layer, T_v increases to 142.5 K. The resistance shows a sharp jump at the transition temperature for the SiO_2 buffer layer, making a structural transition from a cubic high-temperature to a monoclinic low-temperature phase.[13] Another possible explanation for the marked increase in T_v could be due to the stress imposed by the buffer layer film.[14] To get a better understanding of the Fe_3O_4/SiO_2 interface, we characterized the growth mechanism of Fe_3O_4 using TEM. We clearly observed a columnar growth of Fe_3O_4 when deposited on SiO_2 buffer layer in direct contrast with the noncolumnar growth of Fe_3O_4 when deposited on Fe_2O_3 buffer layer as well as when deposited directly on Si(001) substrate. The exact conduction mechanism is still not known but it is suggested that this columnar growth of Fe_3O_4 on SiO_2 buffer layer may be responsible for the high transition temperature observed.

To further understand the conduction mechanism in Fe_3O_4 films, we have analyzed the temperature dependence of resistivity (ρ). Measurements were performed with and without 1-T magnetic field during cooling. Shown in Fig. 2 are the plots of $\ln \rho$ vs T^{-1} for the entire temperature range. For 150 nm of Fe_3O_4 deposited directly on Si(001) substrate, the difference in transition temperature is not very significant when a magnetic field is applied during cooling, as shown in Fig. 2(a). We observed that the temperature-dependent Arrhenius law ($\ln \rho \; \alpha \; T^{-1}$) (Ref. 15) is not obeyed above or below the transition. Instead, we attributed a $T^{-1/4}$ dependence of resistivity below the transition to a variable range hopping mechanism.

Figure 2(b) shows the plot of $\ln \rho$ vs T^{-1} for 150-nm Fe_3O_4 deposited on 20-nm Fe_2O_3 buffer layer. We clearly observed that there is no change in the resistivity of Fe_3O_4 when a magnetic field is applied during cooling. In the temperature range of 100–50 K, resistivity increases by a factor of 50. The slope of this rise was found to be 75 K which is the transition temperature. The resistivity plot below T_v clearly follows the T^{-1} dependence (Arrhenius law).

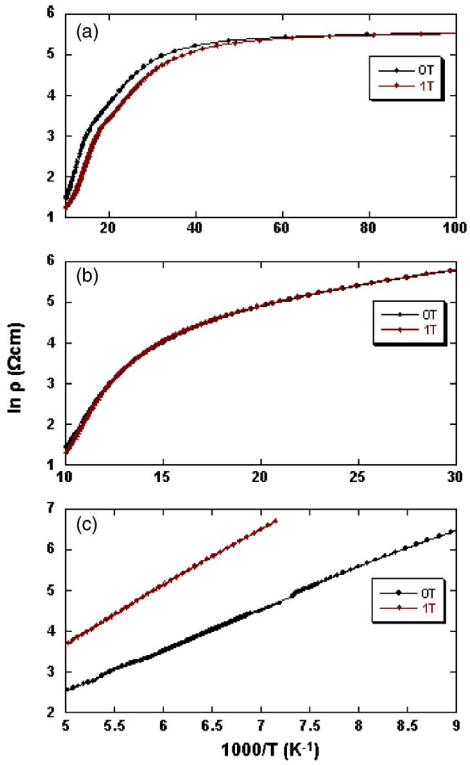

FIG. 2. Resistivity vs temperature plots for 150-nm Fe_3O_4 deposited on (a) Si(001) substrate, (b) 20-nm Fe_2O_3 buffer layer, and (c) 20-nm SiO_2 buffer layer, in the presence of 1-T magnetic field and without any field.

The corresponding $\ln \rho$ vs T^{-1} plot for 150-nm Fe_3O_4 on 20-nm SiO_2 buffer layer is shown in Fig. 2(c). From the plot we did not observe any change in resistivity near T_v. The conductivity remains isotropic throughout the temperature range and indicates that a thermally assisted process is involved. The major change observed for SiO_2 buffer layer was the effect of magnetic field. The transition temperature increases to 170 K during field cooling. This is in direct contrast with the decrease in transition temperature observed for other two samples. This suggests that there exists a different conduction mechanism in Fe_3O_4 when it is deposited on SiO_2 buffer layer.

In order to have a comprehensive understanding of the electrical properties of Fe_3O_4 at low temperatures, we have investigated the conductivity of Fe_3O_4 by studying the current–voltage ($I-V$) characteristics. It has been reported by Hibma *et al.*[16] that Fe_3O_4 has antiphase boundaries (APB) with Fe grains surrounded by oxide shells. At low temperatures, tunneling of electric charge into the grains increases the Coulomb energy by a charging effect. This opens the Coulomb gap and strongly enhances the tunneling resistance. The $I-V$ characteristics of such a configuration display a current step known as the Coulomb gap or an insulating gap which increases in width with decreasing temperature.

Shown in Fig. 3 are the $I-V$ characteristics for 150-nm Fe_3O_4 films deposited on 20-nm Fe_2O_3 buffer layer as a function of temperature. At temperatures above T_v, Fe_3O_4 shows a linear relation between voltage and current. However, as the temperature is decreased, the conductivity of Fe_3O_4 also decreases as seen by the increasing nonlinear behavior in current–voltage loops at 90 K in Fig. 3(a). The

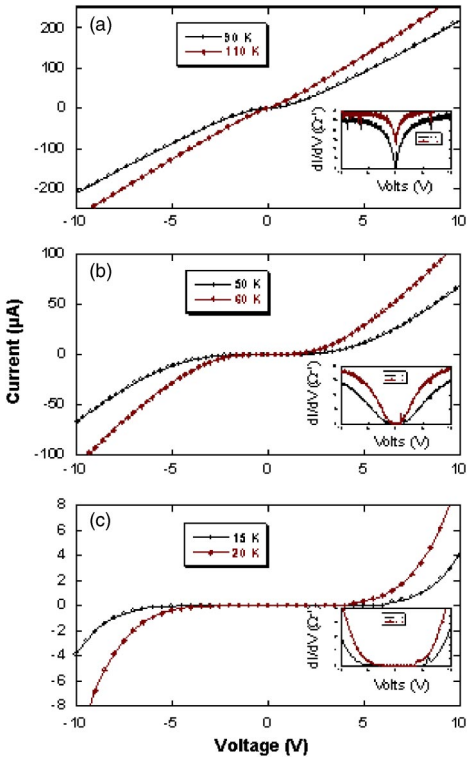

FIG. 3. $I-V$ characteristics for 150-nm films of Fe_3O_4 deposited on 20-nm Fe_2O_3 buffer layer at temperatures (a) 90, 110 K, (b) 50, 60 K, and (c) 15, 20 K.

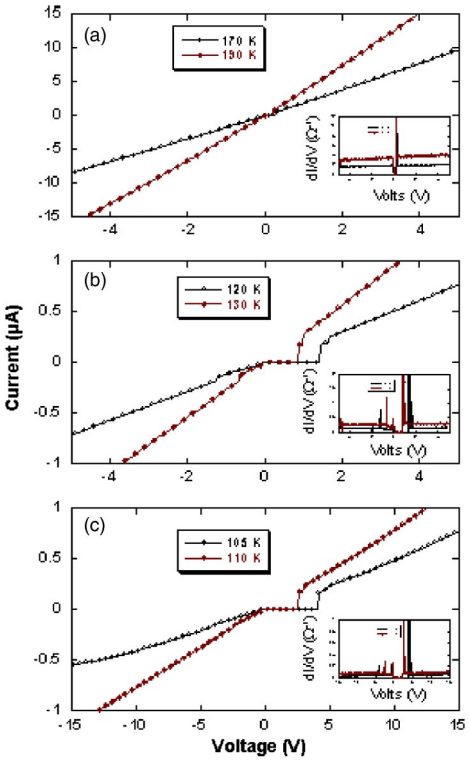

FIG. 4. $I-V$ characteristics for 150-nm films of Fe_3O_4 deposited on 20-nm SiO_2 buffer layer at temperatures (a) 170, 190 K, (b) 120, 130 K, and (c) 105, 110 K.

inset in Fig. 3(a) shows the peaklike structure above T_v around the Fermi level. This peak structure gradually opens up in the form of insulating gap as the temperature decreases. At the onset of T_v, the flat region around zero voltage becomes more pronounced, thus showing a sharp decrease in conductivity. From Fig. 3(b) the Coulomb gap is found to be 2 V at 50 K. Furthermore, a clear change in conductivity spectrum can be seen in the inset of Fig. 3(c). The threshold voltage for the Coulomb gap is found to be symmetric around zero voltage. The abrupt change in the tunneling spectra from a linear conductivity behavior above T_v to the region of low conductance below T_v is a manifestation of the metal-insulator transition in the film.

Shown in Fig. 4 are the corresponding $I-V$ curves as a function of temperature for Fe_3O_4 deposited on SiO_2 buffer layer. As seen from the figure, the Coulomb gap is asymmetric starting from zero voltage when compared to the symmetric behavior obtained for Fe_3O_4 films deposited on Si(001) substrates, on 20-nm Fe_2O_3 buffer layer. The asymmetric nature of the Coulomb gap may be due to the presence of impurities and voids in the grain structure. We observed a clear linearity in the current–voltage relationship at 190 K. As the temperature is decreased, the region of low conductance starts to set in from the zero voltage and keeps increasing until it purely becomes insulator. The Coulomb gap increases from 200 mV to 1 V when the temperature is decreased from 140 K to 120 K. Below T_v, the highest Coulomb gap of 4.8 V at 105 K was observed, as shown in Fig. 4(c).

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[1]R. A. Groot and F. M. Muller, Phys. Rev. Lett. **50**, 2024 (1983).
[2]P. G. van Engen, K. H. Buschow, and R. Jongebrever, Appl. Phys. Lett. **42**, 202 (1983).
[3]R. A. Groot and K. H. Buschow, J. Magn. Magn. Mater. **54–57**, 1377 (1986).
[4]V. Y. Irkin and M. I. Katsnel, Jr., Phys. Usp. **37**, 659 (1994).
[5]J. M. D. Coey and M. Venkatesan, J. Appl. Phys. **91**, 8345 (2002).
[6]P. Senesor, A. Fert, J.-L. Maurice, F. Montaigne, F. Petroff, and A. Vauress, Appl. Phys. Lett. **74**, 4017 (1999).
[7]E. J. W. Verwey, Nature (London) **144**, 327 (1939).
[8]J. Y. T. Wei, N. C. Yeh, R. P. Vasquez, and A. Gupta, J. Appl. Phys. **83**, 7366 (1998).
[9]M. Ziese and H. J. Bluthe, J. Phys.: Condens. Matter **12**, 13 (2002).
[10]H. Liu, E. Y. Jiang, H. L. Bai, R. K. Zheng, and X. X. Zhang, J. Phys. D **36**, 2950 (2003).
[11]S. Jain, A. O. Adeyeye, and D. Y. Dai, J. Appl. Phys. **95**, 7237 (2004).
[12]C. Park, Y. Shi, Y. Peng, K. Barmak, J.-G. Zhu, D. E. Laughlin, and R. M. White, IEEE Trans. Magn. **39**, 2806 (2003).
[13]B. A. Calhoun, Phys. Rev. **94**, 1577 (1954).
[14]D. T. Margulies, F. T. Parker, and A. E. Berkowitz, J. Appl. Phys. **75**, 6097 (1994).
[15]M. Pai and J. M. Honig, J. Phys. C **16**, L35 (1983).
[16]T. Hibma, F. C. Voogt, L. Niesen, P. A. A. van der Heijden, W. J. M. de Jonge, J. J. T. M. Donkers, and P. J. van der Zaag, J. Appl. Phys. **85**, 5291 (1999).