Microstructure and magnetotransport properties of Cu doped Fe₃O₄ films

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A systematic and study on the microstructure and magnetotransport properties of Cu doped Fe₃O₄ films prepared by cosputtering is presented. Structural investigations reveal that the Cu doped films are polycrystalline in nature with a preferred growth direction and retain the cubic spinel structure of Fe₃O₄. Another characteristic feature of the Cu doped films is the transport mechanism being dominated by spin dependent tunneling across grain boundaries. The magnetic properties of the doped films are markedly sensitive to the doping concentration, with both saturation magnetization and coercivity increasing with increasing Cu doping concentration. In-plane magnetoresistance (MR) measurements show a reduction in MR ratio as the Cu doping concentration is increased. © 2008 American Institute of Physics. [DOI: 10.1063/1.2828504]

Magnetite (Fe₃O₄) is one of the most extensively studied ferrimagnetic oxides due to its unique and interesting set of magnetic and spin dependent transport properties.[1–4] It is extremely attractive for spintronics applications due to its high Curie temperature ($T_c = 860$ K) and a predicted fully spin polarized state at the Fermi level.[5] Fe₃O₄ exists in a cubic inverse spinel structure in which iron cations occupy the interstitial sites of a face centered cubic closed packed frame of oxygen anions. The tetrahedral *A* sites are occupied by Fe^{3+} ions, while the octahedral *B* sites are shared by Fe^{2+} and Fe^{3+} ions. The magnetic moments of the Fe^{3+} ions on octahedral and tetrahedral sites are aligned opposite to each other, and the net moment arises only from the Fe^{2+} ions.[6] The high T_c of Fe₃O₄ is explained by coexistence of ferromagnetic exchange interactions between *B-B* ions and strong antiferromagnetic interactions between *A-B* ions. The presence of Fe^{2+} and Fe^{2+} ions on octahedral sites also leads to a low electrical resistivity in Fe₃O₄ at room temperature due to carrier hopping between the Fe^{2+} and Fe^{3+} ions.

The magnetic and transport properties of Fe₃O₄ can be modified by carrier modulation at the interstitial sites. This is achieved by substitution of iron cations with transition metal cations.[7] The main factors influencing the site preference for cations are ion size (smaller ions go to tetrahedral sites), valency, and electronic configuration. Ishikawa *et al.*[8] have prepared epitaxial films of Mn doped magnetite using pulsed laser deposition technique and confirmed that as Mn concentration in the doped film was increased, carrier concentration became lower, thus indicating potential for field effect transistor or magnetization reversal by spin injection. Valence band studies of Zn doped Fe₃O₄ films have revealed that the density of states near the Fermi level was reduced with increasing Zn concentration.[9] These results indicate that such a system could serve as a tunable ferromagnetic semiconductor

with a strong electron correlation. Moreover, Co doped Fe₃O₄ films prepared by cosputtering technique have also been studied to investigate the high magnetic anisotropy of Co atoms in the spinel structure and its corresponding effects on the inherent properties of Fe₃O₄ films.[10,11]

The Cu doped Fe₃O₄ films were grown on precleaned Si(100) substrates by cosputtering Fe (dc) and Cu (dc) targets in an Ar+O₂ mixture at room temperature in a process pressure of 3×10^{-3} Torr. The base pressure of the chamber was better than 3×10^{-8} Torr before deposition. The doped films were then annealed at 300 °C for 60 min without breaking the vacuum to remove phases of paramagnetic FeO which may have been formed during reactive sputtering of Fe.[12] The thickness of the films was maintained at ∼60 nm for all doping concentrations.

The XRD patterns for the undoped and Cu doped Fe₃O₄ films with varying Cu doping concentrations are presented in Fig. 1. From the XRD patterns, it was observed that all peaks in both the undoped and Cu doped Fe₃O₄ films can be assigned to the inverse cubic spinel structure of Fe₃O₄. This indicates that the crystal structure of the Cu doped films is
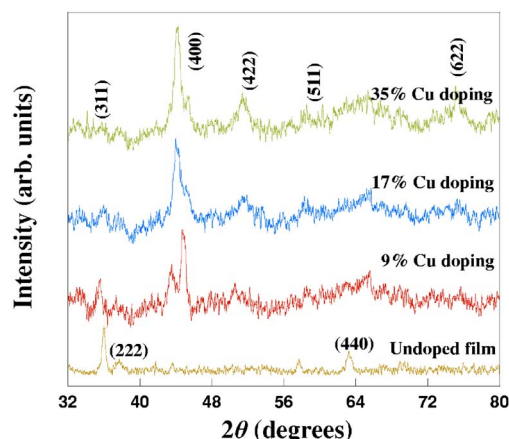

FIG. 1. (Color online) XRD patterns for Cu doped Fe₃O₄ films.

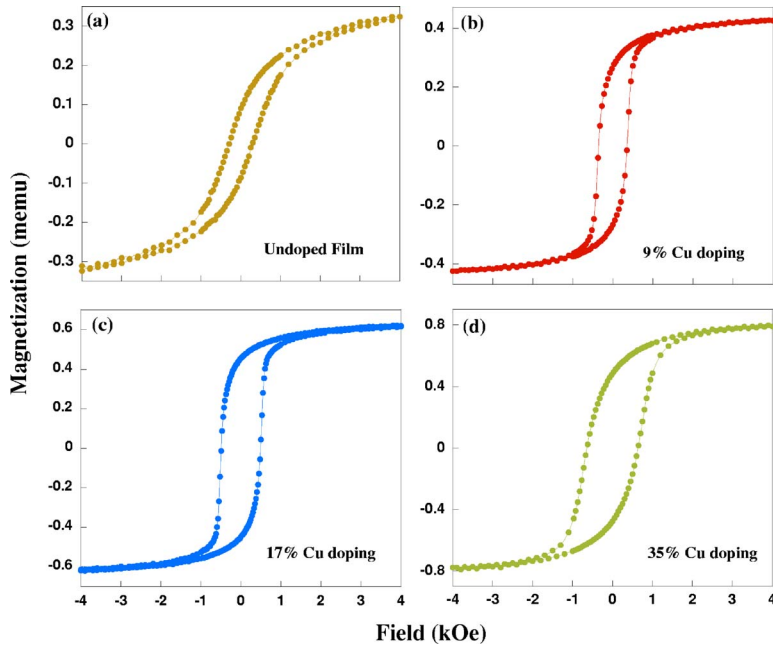a)Author to whom correspondence should be addressed. Electronic mail: eleaao@nus.edu.sg.

FIG. 2. (Color online) Room temperature in-plane magnetization curves for Cu doped Fe_3O_4 films as a function of Cu doping concentration.

similar to that of Fe_3O_4. Moreover, no crystal orientation corresponding to Cu was detected in any of the doped films. This suggests further that the Cu ions substitute Fe ions in the inverse spinel structure of Fe_3O_4, resulting in the formation of a polycrystalline Cu ferrite. It was also observed that with increasing Cu content, the intensity of the (311) peak decreases, while the (400) and (422) peaks become progressively stronger. These observations indicate a modification of the preferred growth direction for the Cu doped Fe_3O_4 films due to enhancement of the Cu/Fe ratio in the doped films. Moreover, a small shift in the peaks is also observed as the Cu doping concentration is increased. This may be attributed to a small change in the lattice constant which is caused by the larger ionic radius of the Cu^{2+} ions which substitute the Fe ions.[13]

Figure 2 shows the representative room temperature magnetization curves for the undoped and Cu doped Fe_3O_4 films with magnetic field applied parallel to the plane of the film. It was observed that the saturation magnetization increases with increasing Cu doping concentration. This behavior may be attributed to a complex cation arrangement in the Cu doped films. It has been previously suggested that Cu^{2+} ions can occupy both tetrahedral and octahedral sites in the spinel structure.[14] If a Cu^{2+} ion migrates to the tetrahedral site, the structural formula changes in such a way that the number of Fe^{3+} ions at the octahedral sites increases at the cost of same ions on the tetrahedral sites. The imbalance of spins on the two sublattices will result in an increase in the net magnetization. The Cu doped Fe_3O_4 samples may be expressed as

$$(Cu_y^{2+}Fe_{1-y}^{3+})[Cu_{\beta-y}^{2+}Fe_{1-\beta}^{2+}Fe_{1+y}^{3+}]O_4^{2-}, \tag{1}$$
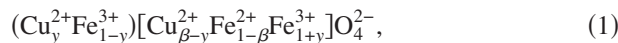
where ( ) denotes the tetrahedral lattice sites, [ ] denotes the octahedral lattice sites, β is the Cu doping concentration, and y is the fraction of Cu^{2+} ions migrating to the tetrahedral sites. The magnetic moment μ per formula unit can be represented as

$$\mu = (4 - 3\beta + 8y), \tag{2}$$

where $\mu(Fe^{2+})=4\mu_B$, $\mu(Fe^{3+})=5\mu_B$, and $\mu(Cu^{2+})=1\mu_B$, respectively. Hence, as the Cu doping concentration in the films increases, a larger fraction of the Cu^{2+} ions migrates to the tetrahedral sites and thus an increase in saturation magnetization occurs in accordance with Eq. (2).

The experimental data also show that the coercivity of the Cu doped Fe_3O_4 films increases monotonically from 375 to 620 Oe as the Cu doping concentration is increased from 9% to 35%. This behavior is expected due to the increased magnetic anisotropy and modifications in microstructure of the doped films with increasing Cu doping concentration. The anisotropic nature of the Cu doped Fe_3O_4 films was further confirmed by the out-of-plane magnetization curves. It was observed that the Cu doped films possess a strong out-of-plane magnetization component. Moreover, the coercivity and saturation magnetization of the out-of-plane magnetization curves also increase with increasing Cu doping concentration.

The resistances of the Cu doped Fe_3O_4 films have been investigated as a function of temperature for varying Cu doping concentrations. Figure 3 clearly shows that the resistivity of the films decreases with increasing Cu doping concentration. This may be due to improved crystallinity of the films as the doping concentration is increased. Moreover, both the undoped and Cu doped films exhibit a smooth resistivity versus temperature curve in which the resistance of the samples increases with decreasing temperature. The inset of Fig. 3 shows the temperature dependence of resistivity as $\log \rho$ versus $T^{-1/2}$. It was observed that the resistivities approximately follow the relation of $\rho=\rho_0 \exp[(1/T)]^{1/2}$. This linear relation between $\log \rho$ and $T^{-1/2}$ is expected for systems in which tunneling occurs through grain boundaries separating adjacent grains.[4,11,15,16]

Shown in Fig. 4 are the room temperature in-plane MR curves for the undoped and Cu doped Fe_3O_4 films as a func-
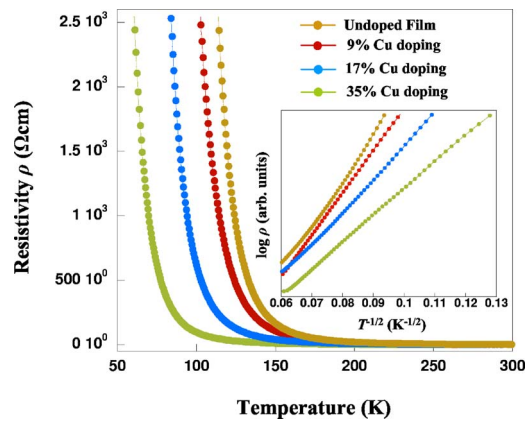
FIG. 3. (Color online) Temperature dependence of resistivity for Cu doped Fe_3O_4 films as a function of Cu doping concentration. The inset shows the corresponding logarithmic resistivity as a function of $T^{-1/2}$.

tion of Cu doping concentration. The MR ratio is defined as

$$\frac{\Delta R}{R}\% = \frac{R_H - R_{H=3\ \text{T}}}{R_{H=3\ \text{T}}} \times 100, \tag{3}$$

where ΔR is the change in resistance, and R_H and $R_{H=3\ \text{T}}$ are the resistances of the Cu doped Fe_3O_4 films under magnetic field H and a magnetic field of 3 T, respectively. The undoped Fe_3O_4 films exhibit a MR ratio of 3.2% at room temperature. For the Cu doped Fe_3O_4 films, we observed that the magnitude of the MR ratio is smaller, and decreases from 0.76% to 0.25%, as the Cu doping concentration is increased from 9% to 35%. The MR in the Cu doped Fe_3O_4 films
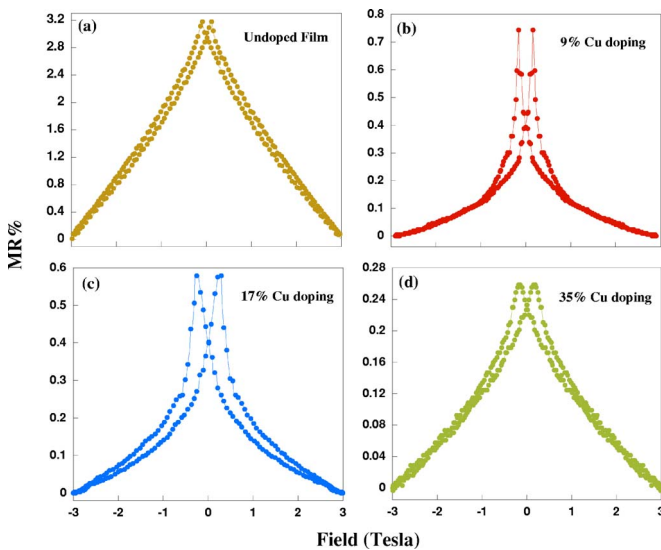
originates from the tunneling of spin polarized electrons across adjacent grains separated by grain boundaries. One of the primary reasons for the decrease in MR ratio is a reduction in spin polarization of the films with increasing Cu doping concentration. The magnitude of MR also depends on the degree of misalignment of magnetizations between neighboring grains, the grain boundary density, and the spin structure at the grain boundary. The MR at low field is due to the alignment of the magnetization between adjacent grains, while the MR at high field is caused from the change in spin structure near the grain boundaries.[12,17] A detailed examination of the evolution in the shape of the MR curves shows that the low field MR reduces while the high field MR increases with increasing Cu doping concentration. This suggests a weakening of the effect from the alignment of magnetizations in adjacent grains. In contrast, the influence of grain boundaries becomes increasingly dominant as Cu doping concentration in the films is increased. The corresponding increase in the high field MR may be attributed to a more disordered spin structure at the grain boundary.

FIG. 4. (Color online) Room temperature magnetoresistance curves for Cu doped Fe_3O_4 films as a function of Cu doping concentration.

[1]G. Q. Gong, A. Gupta, G. Xiao, W. Qian, and V. P. Dravid, Phys. Rev. B **56**, 5096 (1997).
[2]J. M. D. Coey, A. E. Berkowitz, L. Balcells, F. F. Putris, and F. T. Parker, Appl. Phys. Lett. **72**, 734 (1998).
[3]S. B. Ogale, K. Ghosh, R. P. Sharma, R. L. Greene, R. Ramesh, and T. Venkatesan, Phys. Rev. B **57**, 7823 (1998).
[4]D. Tripathy, A. O. Adeyeye, and C. B. Boothroyd, J. Appl. Phys. **99**, 08J105 (2006).
[5]Z. Zhang and S. Satpathy, Phys. Rev. B **44**, 13319 (1991).
[6]F. Walz, J. Phys.: Condens. Matter **14**, R285 (2002).
[7]J. M. Honig, J. Solid State Chem. **45**, 1 (1982).
[8]M. Ishikawa, H. Tanaka, and T. Kawai, Appl. Phys. Lett. **86**, 222504 (2005).
[9]J. Takaobushi, H. Tanaka, T. Kawai, S. Ueda, J. Kim, M. Kobata, E. Ikenaga, M. Yabashi, K. Kobayashi, Y. Nishino, D. Miwa, K. Tamasaku, and T. Ishikawa, Appl. Phys. Lett. **89**, 242507 (2006).
[10]D. Tripathy, A. O. Adeyeye, S. N. Piramanayagam, C. S. Mah, X. Gao, and A. T. S. Wee, Thin Solid Films **505**, 45 (2006).
[11]D. Tripathy, A. O. Adeyeye, C. B. Boothroyd, and S. N. Piramanayagam, J. Appl. Phys. **101**, 013904 (2007).
[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]C. M. Srivastava, S. N. Shringi, and R. G. Srivastava, Phys. Rev. B **14**, 2041 (1976).
[14]H. Ohnishi and T. Teranishi, J. Phys. Soc. Jpn. **16**, 35 (1991).
[15]P. Sheng, B. Abeles, and Y. Arie, Phys. Rev. Lett. **31**, 44 (1973).
[16]H. Liu, E. Y. Jiang, H. L. Bai, R. K. Zheng, and X. X. Xhang, Appl. Phys. Lett. **83**, 3531 (2003).
[17]M. Ziese, R. Hohne, H. C. Semmelhack, H. Rechentin, N. H. Hong, and P. Esquinazi, Eur. Phys. J. B **28**, 415 (2002).