Unconventional magnetization of Fe_3O_4 thin film grown on amorphous SiO_2 substrate

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High quality single crystal Fe_3O_4 thin films with (111) orientation had been prepared on amorphous SiO_2 substrate by pulsed laser deposition. The magnetization properties of the films are found to be unconventional. The Verwey transition temperature derived from the magnetization jump is around 140K, which is higher than the bulk value and it can be slightly suppressed by out-plane magnetic field; the out-of-plane magnetization, which is unexpectedly higher than the in-plane value, is also significantly increased as compared with the bulk value. Our findings highlight the unusual magnetization of Fe_3O_4 thin film grown on the amorphous SiO_2 substrate.
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I. INTRODUCTION

Magnetite (Fe_3O_4) is one of the well-known ferrimagnetic materials, which has been attracting a lot of attention due to its unique electrical and magnetic properties, such as low electrical resistivity at room temperature, high Curie temperature (858 K), 100% spin polarization.[1–4] These properties make Fe_3O_4 a promising candidate for spintronic devices.[5,6]

Magnetite has a cubic inverse spinel structure that is based on a face-centered cubic (fcc) lattice of oxygen anions. The cubic unit cell of Fe_3O_4 contains 32 oxygen anions and 24 iron cations, *i.e.* 8 Fe^{2+} and 16 Fe^{3+} ions which occupy interstices of oxygen ions; 8 tetrahedral (A) sites solely occupied by Fe^{3+} ions whereas 16 octahedral (B) sites equally shared by Fe^{3+} and Fe^{2+} ions. The magnetization of magnetite can be viewed as that the magnetic moments within the A and the B sublattices are ferromagnetically aligned while the two sublattices are antiferromagnetic with respect to each other.

At the room temperature, electrons continuously rapidly hop between Fe^{2+} and Fe^{3+} cations at B sites, leading to a fairly low electrical resistivity. Upon cooling, bulk Fe_3O_4 undergoes a metal–insulator transition termed as the Verwey transition.[1,4] Below 120 K, the hopping action is frozen and consequently the resistivity is increased by two orders of magnitude with a concomitant decrease in the magnetic moment. This transition is generally from a disordered phase to a charge ordered phase of Fe^{2+} and Fe^{3+} cations.[7–11]

Epitaxial Fe_3O_4 thin films have some physical properties that differ significantly from those of bulk single crystals, such as distinct transition temperatures on different substrates.[12,13] Fe_3O_4 thin films grown on single crystalline substrates naturally form antiphase boundaries (APBs),[14,15] which always produce anomalous properties, for instance, a lower Verwey transition temperature (T_V), and the out-of-plane magnetization is smaller than the in-plane magnetization at the same magnetic field, while thin films grown on buffer layers can result in polycrystalline or amorphous phases.

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II. FILM GROWTH

Thermal growth SiO_2 substrates are typical amorphous substrates, which do not provide preferred orientation for films grown on them. Hence, the films grow relaxed, leading to its lattice parameter very close to the bulk value.[16] In this paper, a single crystal Fe_3O_4 thin film with the (111) orientation on a 300nm thermal growth SiO_2 substrate is prepared. Experimental results show that T_V increases to 140 K and can be suppressed by out-plane magnetic field; moreover, the out-plane magnetization is larger than the bulk value and the in-plane magnetization.

The pulsed laser deposition technique (PLD) is an effective method to produce high quality thin films due to the high kinetic energy of atoms and ionized species in the laser-induced plasma. The thin film used was grown on an amorphous SiO_2 substrate using an α-Fe_2O_3 target, and a 300 nm amorphous SiO_2 substrate is grown on a Si (100) substrate. The target used for the ablation has been prepared by a standard solid-state reaction method. A KrF excimer laser source (λ=248 nm, pulse width=20 ns) was used to ablate the target at a pulse repetition rate of 10 Hz, and a fluence of 250 mJ pulses^{-1} was directed at a 45° angle of incidence on the target. The distance from the target to the substrate was maintained at 60 mm during deposition. Before the deposition, the chamber was evacuated to a pressure of 9.9×10^{-6} Pa and the deposition was carried out at a substrate temperature of 575 °C and in a vacuum of 6×10^{-3} Pa. During the deposition the target was rotated at a rate of 3 rpm to avoid excessive heating and erosion at a single spot on the target surface. At the end of the deposition, the film was cooled down to the room temperature at 3°C min^{-1} in the same environment as used during the deposition.

III. FILM CHARACTERIZATION

The structural of the deposited film was characterized by x-ray diffraction (XRD) in θ-2θ geometry using a Cu Kα radiation (λ=1.54059 Å) (Rigaku, Japan). Phase purity of the film was

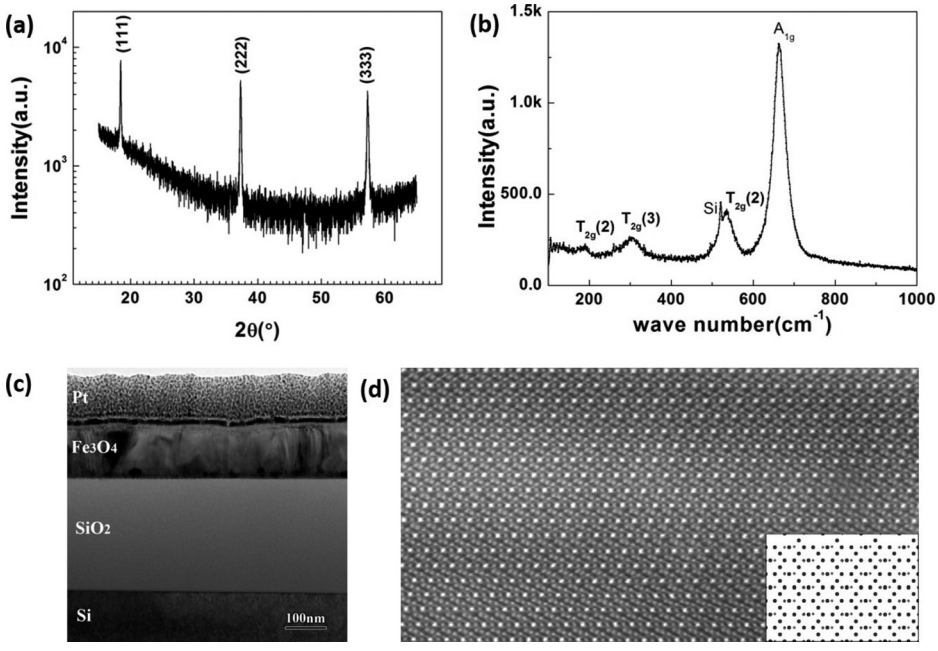

FIG. 1. (a) XRD spectrum of a Fe_3O_4 thin film on a SiO_2 substrate measured at the room temperature. (b) Raman spectrum of a Fe_3O_4 thin film on a SiO_2 substrate measured at the room temperature. (c) A bright-field TEM image displaying the cross section morphology of the $Fe_3O_4/SiO_2/Si$ film. The essential layered structural feature in the Fe_3O_4/SiO_2(amorphous)/Si hetero junction is clearly recognizable in the TEM image. The as-grown film with a uniform thickness of about 140nm is fully imaged in this micrograph. (d) HAADF image taken along the [1–10] zone axis direction of the Fe_3O_4 film. The inset gives the corresponding atomic structure projection of Fe_3O_4.

checked by performing laser Raman spectroscopy. Raman spectra was recorded using a HR800 Jobin-Yvon spectrometer employing He–Ne laser (λ=632.8 nm). The measured resolution of the spectrometer is 1 cm^{-1}. Both XRD and Raman measurements were performed at the room temperature. Aberration-corrected scanning transmission electron microscopy (STEM) was performed using a JEOL ARM 200F transmission electron microscope operated at 200 keV. Cross-sectional TEM specimens were prepared by mechanical polishing dimpling, and then focused ion beam milling. The film thickness was determined by STEM and estimated to be 140 nm. The magnetization measurements were carried out using a SQUID vibrational sample magnetometer (SVSM) and the R(T) measurements were performed in standard four-probe geometry using a Quantum Design PPMS.

Figure. 1(a) shows the XRD spectrum of a Fe_3O_4 thin film on a SiO_2 substrate, which clearly suggests that the film is grown with a preferred orientation in the (111) direction. No impurity or peak from other phase of iron oxide peaks is detected from the XRD patterns, suggesting that the film has a pure (111) orientation. The full width at half maximum for the rocking curve of the (111) peak of Fe_3O_4 is 0.1°, indicating a high degree of orientation quality. Analysis of the XRD peaks shows the presence of the Fe_3O_4 phase in the films. However, the possibility of the presence of γ-Fe_2O_3 cannot be totally ruled out since they have nearly the same lattice parameters

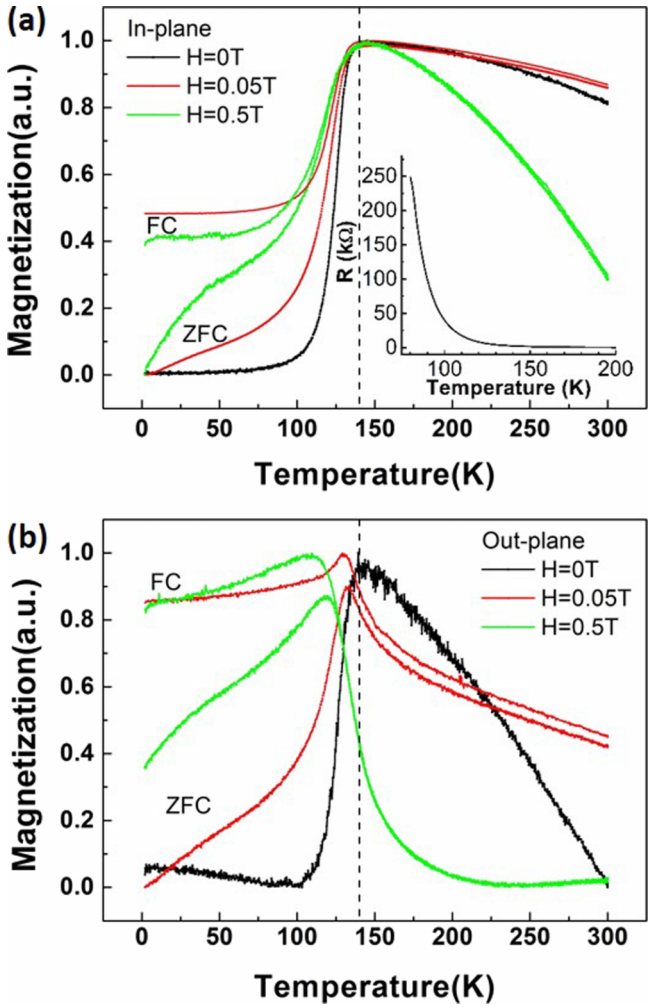

FIG. 2. Normalized ZFC and FC magnetization as a function of temperature with magnetic fields applied parallel (a) and perpendicular (b) to the thin film plane. The dash lines are guides to the eyes showing the critical temperature (140K) where the magnetization curves reach their maximum values. The inset in (a) shows the zero-field resistance as a function of temperature.

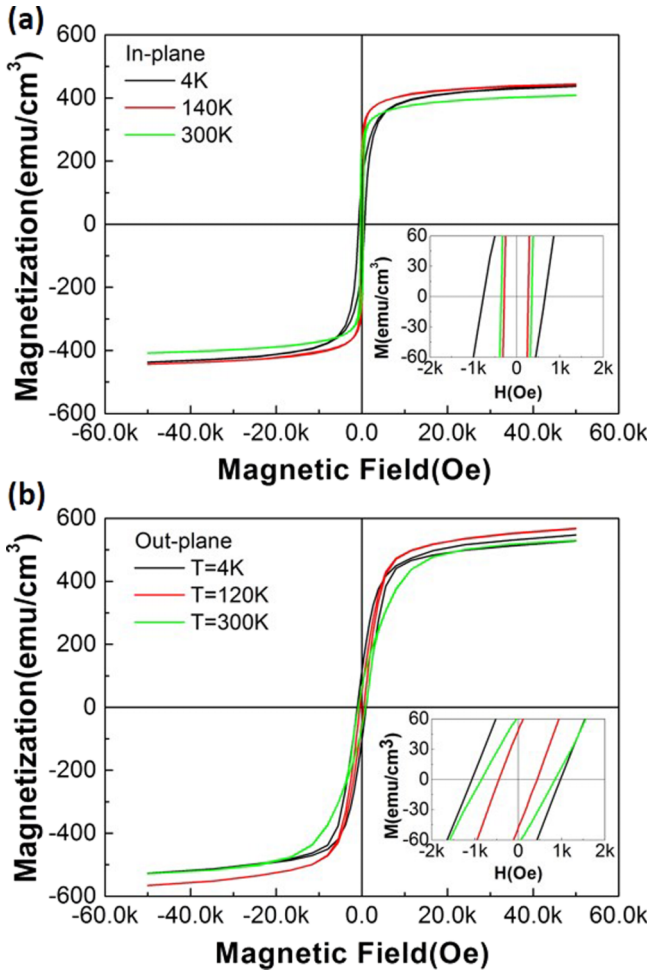

FIG. 3. Magnetization hysteresis loops measured at 4, 140 and 300 K with an in-plane (a) and out-of-plane (b) magnetic field up to ±50 kOe. The inset shows the low field magnetization.

(a = 0.8397 nm for Fe_3O_4; a = 0.8342 nm for γ-Fe_2O_3; and a = 0.840 nm for the thin film as calculated from XRD) and all diffraction peaks of Fe_3O_4 and γ-Fe_2O_3 appear at nearly the same 2θ values.

To confirm the phase purity of Fe_3O_4 in the film, Raman spectroscopy measurements have been performed since the Raman technique is very sensitive to the different phases of iron oxides on account of the vibrational frequencies of different compositions.[17] Figure. 1(b) shows a Raman spectrum of a Fe_3O_4 thin film on a SiO_2 substrate. We can see an acceptable consistency of the $T_{2g}(1)$, $T_{2g}(3)$, $T_{2g}(2)$ and A_{1g} modes corresponding to the Fe_3O_4 phase at 193, 306, 540 and 669 cm^{-1}, respectively. These values are close to that observed in a magnetite single crystal.[18] We note that none of the Raman spectra reveal any signature of the corresponding modes of γ-Fe_2O_3 normally seen at 350, 500, and 700 cm^{-1}. Thus, Raman studies further confirm the pure single phase of our Fe_3O_4 thin film.

To further confirm that the film is a single crystal, we present the STEM data of our film in Fig. 1(c) and 1(d). It can be seen that the high angle annular dark field (HAADF) image taken along the[1–10] zone axis direction of the Fe_3O_4 film shows a clear and well ordered atomic structure, demonstrating the single crystal nature of the film. Meanwhile, we also estimate the grain size to be around 60nm from the low resolution TEM image.

Thin films can usually be very different from the bulk materials due to its interaction with the substrate and the reduced dimenonality. Here we especially focus on the magnetization properties of the magnetite thin film. Figure. 2 shows the normalized zero-field-cooled (ZFC) and field-cooled

TABLE I. Temperature dependence of M_{5T} and H_c of the Fe_3O_4 film obtained in the H-parallel and H-perpendicular cases with respect to the film plane.

	Field	4K	140K	300K
M_{5T}	In-plane	437	442	409
(emu cm^{-3})	Out-plane	528	567	530
H_c	In-plane	−766/664	−274/250	−359/359
(Oe)	Out-plane	−1071/974	−445/432	−847/848

(FC) magnetization as a function of temperature with magnetic fields applied parallel and perpendicular to the film plane, respectively. The ZFC spontaneous magnetization curves exhibit a spontaneous magnetization jump in the vicinity of 140 K. It coincides with the metal-insulator transition from the transport measurement as shown in the inset of Fig. 2(a). Both of the measurements are consistent with the Verwey transition T_V. Thin films of Fe_3O_4 are known to usually exhibit suppressed T_V (<120K) that could originate from a variety of other reasons, like strain or APB. However, the measured results on our films show that the transition temperature of Fe_3O_4 is enhanced. More interestingly, the magnetization derived T_V is unchanged as the in-plane applied field increases, while the transition temperature decreases for out-plane magnetization.

The magnetization hysteresis loops of our thin film also exhibits interesting behaviour. Figure. 3 shows ZFC magnetization hysteresis loops with magnetic fields parallel and perpendicular to the film plane at different temperatures. We observe that the magnetization of the Fe_3O_4 film is unsaturated at 50 kOe, with a slight residual slope extending to larger magnetic fields. The in-plane hysteresis curves display an almost rectangular shape with higher remanence and smaller coercivity than that of out-of-plane case at the same temperature, indicating that the magnetic moments lie in plane, which is in accordance with the assumption that the easy axis of the films lies in the film plane. The magnetization values measured at 50 kOe field and the coercivities at different temperatures are listed in Table I. At 50 kOe, the out-plane magnetization is about 530 emu cm^{-3} and not saturated even at such a high field at room temperature. This value is higher than the saturation magnetization of 471 emu cm^{-3} measured at 300 K for bulk Fe_3O_4. It implies that the strain or APBs in the films may play little role since strong anti-ferromagnetic coupling within APBs reduces the magnetization.[19,20] Moreover, through the comparison of the values of magnetizations with 50 kOe field parallel and perpendicular to the film plane, the out-plane magnetization is even higher than the in-plane magnetization. This is very striking as the shape anisotropy is expected to confine the magnetic moments to the plane of the film. Considering that the Verwey transition can lead to a negative jump of the magnetization while the out-plane magnetic field can supress the Verwey transition for our film, this unusual magnetization anisotropy actually resonates with our previous observations in certain senses. Here we also note that at 4K both the in-plane and out-plane magnetizations exhibit exchange bias, which is believed to be induced by the Verwey transiton.[21]

IV. DISCUSSION AND CONCLUSION

The Verwey transition is usually viewed as a charge ordering of the Fe^{2+} and Fe^{3+} in the B sublattice due to local Coulomb correlation U,[7–11] and the magnetization is microscopically related with the effective ferrimagnetic exchange interaction J. Accordingly, the enhanced Verwey transition temperature and magnetization than those in bulk materials may suggest that both the U and J are strengthened in our film, while the suppression of the Verwey transition by out-plane magnetic field and unusual magnetization anisotropy may further indicate that U and J are uniquely out-plane directionally coupled. The microscopic mechanism of the enhancement and entanglement of U and J is still unclear based on our current data. We speculate that this may be related with the interaction between the Fe_3O_4 thin film and the amorphous SiO_2 substrate, and we believe a further systematic study on the magnetization of Fe_3O_4 films with different thickness would be helpful. We believe that the investigations on such novel magnetization properties not only have potential application

on spintronics, but also offer an exciting platform for future theoretical and experimental studies on the cooperation or competition behaviors of Coulomb interaction and ferrimagnetic coupling in this correlated system.

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[1] E. J. W. Verwey, Nature (London) **144**, 327 (1939).
[2] Z. Zhang and S. Satpathy, Phys. Rev. B **44**, 13319 (1991).
[3] V. I. Anisimov, I. S. Elfimov, N. Hamada, and K. Terakura, Phys. Rev. B **54**, 4387 (1996).
[4] Friedrich Walz, J. Phys.: Condens. Matter **14**, 285 (2002).
[5] Igor Žutić, Jaroslav Fabian, and S. Das Sarma, Rev. Mod. Phys. **76**, 323 (2004).
[6] S. A. Wolf, D. D. Awschalom, R. A. Buhrman, J. M. Daughton, S. von Molnár, M. L. Roukes, A. Y. Chtchelkanova, and D. M. Treger, Science **294**, 1488 (2001).
[7] J. P. Wright, J. P. Attfield, and P. G. Radaelli, Phys. Rev. Lett. **87**, 266401 (2001).
[8] Horng-Tay Jeng, G. Y. Guo, and D. J. Huang, Phys. Rev. Lett. **93**, 156403 (2004).
[9] Przemysław Piekarz, Krzysztof Parlinski, and Andrzej M. Oleś, Phys. Rev. Lett. **97**, 156402 (2006).
[10] D. J. Huang, H.-J. Lin, J. Okamoto, K. S. Chao, H.-T. Jeng, G. Y. Guo, C.-H. Hsu, C.-M. Huang, D. C. Ling, W. B. Wu, C. S. Yang, and C. T. Chen, Phys. Rev. Lett. **96**, 096401 (2006).
[11] J. Schlappa, C. Schüßler-Langeheine, C. F. Chang, H. Ott, A. Tanaka, Z. Hu, M. W. Haverkort, E. Schierle, E. Weschke, G. Kaindl, and L. H. Tjeng, Phys. Rev. Lett. **100**, 026406 (2008).
[12] D. T. Margulies, F. T. Parker, and F. E. Spada, Phys. Rev. B **53**, 9175 (1996).
[13] S. Soeya, J. Hayakawa, H. Takahashi, K. Ito, C. Yamamoto, A. Kida, H. Asano, and M. Matsui, Appl. Phys. Lett. **80**, 823 (2002).
[14] W. Eerenstein, T. T. M. Palstra, S. S. Saxena, and T. Hibma, Phys. Rev. Lett. **88**, 247204 (2002).
[15] S. K. Arora, R. G. S. Sofin, and I. V. Shvets, Phys. Rev. B **72**, 134404 (2005).
[16] Shailja Tiwari, Ram Prakash, R. J. Choudhary, and D. M. Phase, J. Phys. D: Appl. Phys. **40**, 4943 (2007).
[17] I. Chamritski and G. Burns, J. Phys. Chem. B **109**, 4965 (2005).
[18] R. Gupta, A. K. Sood, P. Metcalf, and J. M. Honig, Phys. Rev. B **65**, 104430 (2002).
[19] D. T. Margulies, F. T. Parker, M. L. Rudee, F. E. Spada, J. N. Chapman, P. R. Aitchison, and A. E. Berkowitz, Phys. Rev. Lett. **79**, 5162 (1997).
[20] W. Eerenstein, T. Hibma, and S. Celotto, Phys. Rev. B **70**, 184404 (2004).
[21] J. de la Venta, M. Erekhinsky, Siming Wang, K. G. West, R. Morales, and Ivan K. Schuller, Phys. Rev. B **85**, 134447 (2012).