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Microstructure and magnetic properties of strained Fe_3O_4 films

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A comparable study of the microstructure and magnetic properties was performed for magnetite films deposited on (100)-oriented MgO and $SrTiO_3$ (STO) substrates. The growth of strained high quality Fe_3O_4 films was confirmed by x-ray diffraction analysis and Raman spectroscopy measurements. The surface morphology and magnetic properties of the two films were found to be obviously different. Moreover, a stripelike magnetic domain structure was observed in the film on STO. Substrate-induced strain is believed to be responsible for these observations, which significantly affects the magnetic anisotropy and the magnetic coupling at the antiphase boundaries in the films. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2832305]

I. INTRODUCTION

Magnetite (Fe_3O_4) is a well-known ferrimagnet with an inverse spinel structure and an archetypal compound exhibiting charge ordering known as Verwey transition.[1] In recent years, magnetite has drawn intensive attention in spin electronics for its high Curie temperature of 858 K and its expected half-metallic property.[2,3] However, the observed behavior of the Fe_3O_4 films is rather puzzling, and the anticipated -100% spin polarization is scarcely experimentally detected.[4–6] Recently, the spin polarization of Fe_3O_4 was studied by several groups through analyzing the current-voltage characteristics of the $Fe_3O_4/SrTiO_3$:Nb interface, and a -80% spin polarization was extracted.[7–9] However, the magnetic properties and the magnetic microstructure of the Fe_3O_4 films on $SrTiO_3$ (Fe_3O_4/STO) or $SrTiO_3$:Nb substrates have rarely been reported, though the corresponding results in films on MgO substrates (Fe_3O_4/MgO) have been comprehensively studied. Considering that the physical properties of magnetite films would be significantly influenced by strain, stoichiometry, or defect states, and the occurrence of many unexpected behaviors in Fe_3O_4/MgO due to the growth defects known as antiphase boundaries (APBs),[10,11] the difference of the strained states between Fe_3O_4/STO (compressive strain) and Fe_3O_4/MgO (tensile strain) may lead to significant different growth defects, i.e., the APBs. Thus, it would be worthwhile to study the magnetic properties and magnetic microstructure of the magnetite films with different strains. In the present paper, a corresponding study was performed on Fe_3O_4/STO and Fe_3O_4/MgO. The difference in magnetic properties of the two films is obvious. Compared with Fe_3O_4/MgO, larger domain structure and significant out-of-plane magnetization components were observed in Fe_3O_4/STO as a consequence of the in-plane compressive strain.

II. EXPERIMENT

The Fe_3O_4 films were grown on (100) MgO and (100) $SrTiO_3$ substrates by the pulsed laser ablation technique from a stoichiometric polycrystalline target. The two samples were deposited at the same time to eliminate extrinsic factors. During the deposition, the substrate temperature and O_2 pressure were kept at ~480 °C and $\sim 5\times10^{-6}$ torr, respectively. For the high affinity of Fe^{2+} ions to oxygen, the pressure ambience was kept during the cooling process after deposition until the temperature was close to room temperature. The film thickness was about 100 nm. The high crystalline quality of the films was confirmed by x-ray diffraction using a Rigaku D/Max-2400 x-ray diffractometer with Cu $K\alpha$ radiation. Raman spectroscopy measurements were performed to confirm the single magnetite phase using a Renishaw in-Via Raman system in backscattering configuration. The surface morphology and the magnetic microstructure of the films were analyzed simultaneously by atomic force microscopy (AFM) and magnetic force microscopy (MFM) [Digital Instrument NanoScope IIIa], respectively. The magnetic properties of the films were measured with a Quantum Design superconducting quantum interference device magnetometer and a LakeShore vibrating sample magnetometer.

III. RESULTS AND DISCUSSION

X-ray θ-2θ diffraction measurements reveal that both films are highly (100) oriented. Since the lattice parameter of Fe_3O_4 ($a=0.8396$ nm) is approximately twice that of the MgO substrate ($a=0.4204$ nm), it is hard to distinguish the reflections of Fe_3O_4 from those of MgO. The narrow full width at half maximum for the rocking curve of the (400) Fe_3O_4 peak (~0.2° on MgO, ~0.7° on STO, better than the previous reports[12]) indicates the high quality of the films. The Fe_3O_4/MgO (mismatch of $\sim +0.3\%$) and Fe_3O_4/STO (mismatch of $\sim -7.5\%$) conserve an in-plane tensile and

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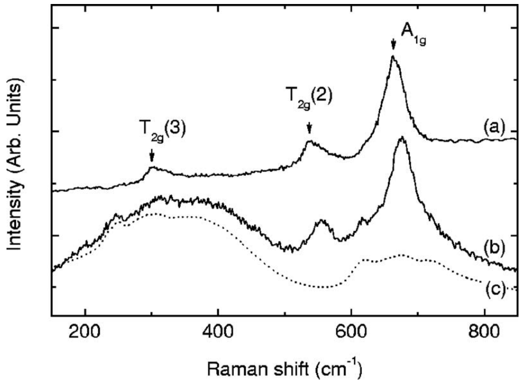

FIG. 1. Raman spectra for Fe_3O_4/MgO (a), Fe_3O_4/STO (b), and a bare $SrTiO_3$ substrate (c) at room temperature.

compressive strains, respectively, with the corresponding out-of-plane lattice parameters being 0.8385 and 0.8455 nm.

The laser Raman spectroscopy was then used to further investigate the single phase and the strained state of the magnetite films. For a single crystal Fe_3O_4, five Raman active modes at around 670 cm^{-1} (A_{1g}), 410 cm^{-1} (E_g), 193 cm^{-1} [$T_{2g}(1)$], 540 cm^{-1} [$T_{2g}(2)$], and 300 cm^{-1} [$T_{2g}(3)$] are predicted at room temperature according to group theory. While generally, only the three modes at around 670, 540, and 300 cm^{-1} are experimentally observed.[13,14] Figure 1 shows the Raman spectra of the Fe_3O_4 films in the range of 150–850 cm^{-1} at room temperature. For comparison, the spectrum of a bare STO substrate is also shown (dotted line). As shown in the figure, three modes around 666, 539, and 300 cm^{-1} are observed in Fe_3O_4/MgO, close to the values of bulk Fe_3O_4 and consistent with the reported results.[14] As for the Fe_3O_4/STO, similar features are observed when the contribution from the substrate is subtracted. Thus, both films exhibit a single Fe_3O_4 phase behavior, without the presence of any other iron oxide phase.[13] It should be mentioned that the Raman modes of the Fe_3O_4/STO show an obvious blueshift in contrast to the bulk ones, which is ascribed to the compressive strain. This is consistent with the x-ray results referred above. The substrate-induced strain significantly affects the magnetic properties of the magnetite films as addressed below.

The stoichiometric Fe_3O_4 undergoes a structure change from cubic to monoclinic below the Verwey transition near $T_V \sim 121$ K, which is accompanied by a sharp decrease in the magnetization.[1] The temperature dependence of magnetization for the Fe_3O_4/STO, under a magnetic field of 50 Oe applied parallel to the film plane, is shown in the inset (a) of Fig. 2. It is obvious that the magnetization shows an abnormality at $T_V \sim 110$ K, which should be due to the Verwey transition. The reduction of the transition temperature in the present film should be mainly attributed to the strain effects as reported previously.[12,15,16] In addition, it has been found that a sharper dM/dt curve indicates a higher quality and stoichiometry of the Fe_3O_4 film,[12] while the dM/dt curve of the present film is not as sharp as that of the reported films with similar thickness,[12] which may indicate a slight deviation from stoichiometry for our films. For that even a slight deviation from stoichiometry, generally associated with Fe^{2+} vacancies on the B sites as that in γ-Fe_2O_3, could produce a significant decrease of T_V for bulk samples,[17] the T_V decrease in the present film may also result from the presence of a small fraction of vacancies.

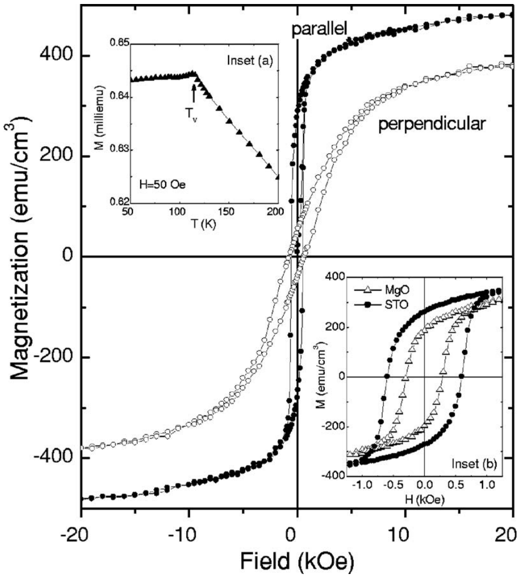

FIG. 2. The hysteresis loops of Fe_3O_4/STO with magnetic fields applied parallel and normal to the film plane, respectively. Inset (a): The temperature dependence of magnetization for Fe_3O_4/STO. Inset (b): Parts of the in-plane hysteresis loops of Fe_3O_4/MgO and Fe_3O_4/STO.

The magnetic hysteresis loops of the two films were measured at room temperature with fields of up to 20 kOe applied parallel and normal to the film plane, respectively. The films on different substrates exhibit principally similar characteristics. The in-plane hysteresis curves display an almost rectangular shape with high remanence and small coercivity, implying that the domain nucleation dominates the magnetization reversal process (the results of the Fe_3O_4/STO are shown in Fig. 2 with subtraction of the substrate contributions). The magnetization of both films seems to be unsaturated at a field of up to 20 kOe, with a slight residual slope extending to larger magnetic fields. The saturation magnetization (M_s) values obtained are ~480 and ~460 emu/cm^3 for Fe_3O_4/STO and Fe_3O_4/MgO, respectively. Meanwhile, the coercivity of Fe_3O_4/STO (~600 Oe) is obviously larger than that of Fe_3O_4/MgO (~280 Oe), as shown in the inset (b) of Fig. 3. In addition, the out-of-plane hysteresis loops exhibit obvious effects due to demagnetization. The estimated shape anisotropic field of 5.5 kOe is approximate to the expected value of 6 kOe ($4\pi M_s$). Considering the same deposition conditions, the magnetic property difference of the two films should be mainly related to the substrate, thus the strain. The larger coercivity of Fe_3O_4/STO may result from the formation of more pinning centers induced by the compressive strain.

The surface morphologies of the two films exhibit obvious different characteristics. As shown in Fig. 3, the surface of Fe_3O_4/MgO is relatively flat, with a root mean square surface roughness of ~0.8 nm. Interestingly, some isolated holelike defects scatter on the surface, with the size of ~50 nm in diameter and ~3 nm in depth. Surprisingly, the holes form a pattern that seems to be quite similar to the

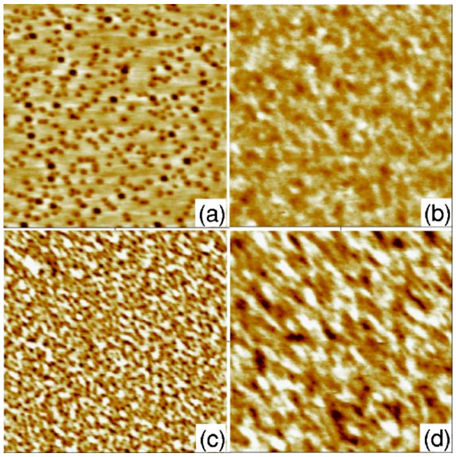

FIG. 3. (Color online) The AFM and MFM images with an area of $2 \times 2\ \mu m^2$ for Fe_3O_4/MgO [(a) and (b)] and Fe_3O_4/STO [(c) and (d)] at room temperature.

APB arrangement observed in such films by transmission electron microscopy.[10,11] In contrast, a granular surface is obtained for Fe_3O_4/STO, with an average grain size of around 60 nm and a surface roughness of ~1.2 nm. The unambiguous difference in the morphology of the two films may result from the difference in the atomic mobility during growth, associated with the lattice mismatch between Fe_3O_4 and the underlying substrates. The larger density of intergranular regions in Fe_3O_4/STO, where the pinning centers are expected to be located to impede the domain wall motion in the process of magnetization or demagnetization, may account for its larger coercivity, as shown in Fig. 2.

The MFM images under zero magnetic field are shown in Figs. 3(b) and 3(d) for Fe_3O_4/MgO and Fe_3O_4/STO, respectively. As can be seen, the magnetic domains in Fe_3O_4/MgO are rather irregular with the domain width of ~60 nm. In contrast, the magnetic microstructure of Fe_3O_4/STO exhibits a "stripe"-like pattern, with the domains of ~100 nm in length and ~60 nm in width. Meanwhile, more and stronger out-of-plane magnetic domains are observed for Fe_3O_4/STO. It is interesting that the domains of Fe_3O_4/STO show a tendency to be stripe domains as observed in an annealed Fe_3O_4/MgO.[18]

Similar magnetic microstructure results have been observed in films with different thicknesses on MgO substrates, where a larger density of APBs leads to a smaller domain structure in the thinner films resulting from the antiferromagnetic superexchange interactions near APBs.[12] Since the lattice mismatch is larger in Fe_3O_4/STO than that in Fe_3O_4/MgO, the shift or rotation of nearby islands will be much severe in Fe_3O_4/STO. Thus, a higher density of APBs is expected in Fe_3O_4/STO, which explains the appearance of rougher morphology and larger coercivity as discussed above, while a larger density of APBs in Fe_3O_4/STO would lead to a smaller domain structure if the situation is similar to that in Fe_3O_4/MgO. This seems to conflict with the observed phenomena. A possible explanation is that the characteristics of magnetic coupling at the APBs in Fe_3O_4/STO are considerably different from that in Fe_3O_4/MgO. The deactivation of the antiferromagnetic coupling in the vicinity of the APBs in Fe_3O_4/STO induced by the compressive strain may account for the stripelike domains. In fact, the domain structure forms due to the complicated competition between the exchange, magnetostatic, and magnetic anisotropy energies. The MFM detected the out-of-plane component of the magnetic stray field along the [100] direction, whereas the easy magnetization direction of bulk Fe_3O_4 is along the [111] axis at room temperature. In Fe_3O_4/MgO, the tensile strain would pull the [111] axis toward the in-plane direction. In contrast, the in-plane compressive strain in Fe_3O_4/STO will push the [111] axis toward the out-of-plane direction. As a result, more out-of-plane magnetization components would be anticipated in the compressively strained films. Moreover, the compressive strain can lead to a uniaxial perpendicular magnetic anisotropy sometimes, such as that in $La_{1/3}Sr_{2/3}MnO_3$ films on $LaAlO_3$ substrates[19] or annealed $Fe_{65}Ti_{13}Co_8Ni_7B_6Nb_1$ films on glass substrates.[20] It is inspiring that the magnetic domains observed in Fe_3O_4/STO show a tendency to have uniaxial perpendicular magnetic anisotropy.

ACKNOWLEDGMENTS

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