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The magnetic properties of strained and relaxed $Fe_{3-x}Mg_xO_4$ ferrite films on MgO(001) and $SrTiO_3$(001) by molecular beam epitaxy

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The present study grows a series of $Fe_{3-x}Mg_xO_4$ $(0 \leqq x \leqq 1.5)$ films and systematically measure both structure and magnetization of these films. These films are grown on MgO and $SrTiO_3$ (STO), which have small (∼−0.3%) and large (∼7.5%) lattice mismatch in order to have either strained or relaxed films, by plasma-oxygen-assisted molecular beam epitaxy, respectively. X-ray diffraction (XRD) is carried out to analyze the crystalline structure. Saturation magnetization (M_s) of pure Fe_3O_4 $(x=0)$ on both substrates is $\sim 500\ \mathrm{emu/cm^3}$, which is consistent with the bulk value. However, M_s has a fast decrease with increasing x for the films grown on MgO(001), from 340 to $\sim 100\ \mathrm{emu/cm^3}$ in the region of $0.3 < x < 1.35$, and stays at $\sim 100\ \mathrm{emu/cm^3}$ for $x > 1.35$. On the other hand, M_s remains unchanged with x increasing from 0.3 to 1 for the film grown on STO. With $x > 1$, M_s drops abruptly to $\sim 100\ \mathrm{emu/cm^3}$, which is comparable to M_s of the film grown on MgO. The discrepancy in M_s of $Fe_{3-x}Mg_xO_4$ film grown on MgO and STO may imply that the cation distribution of these films may be fundamentally different. Possible cation distribution and the substrate strain effect will be discussed.
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I. INTRODUCTION

The study of magnetite (Fe_3O_4) and related ferrite thin films has recently attracted a lot of attention due to the half-metal property and possible application of these materials on spintronic devices.[1–4] However, some unexpected observations on the magnetization and electrical transport of the ferrite thin films, including metallic state and relatively high magnetization, have been reported.[5] These observations clearly indicate that different metastable phases may exist due to different fabrication processes in thin films of ferrite. In this paper, we fabricate a pure magnetite and a series of $Fe_{3-x}Mg_xO_4$ $(0 < x < 1.5)$ films on MgO(001) and $SrTiO_3$ (STO)(001), respectively. Instead of focusing on some specific configuration of Mg ferrites, we tend to systematically study the physical properties of these films with "continuously" varied Mg/Fe ratio. Two different substrates are used for the present study and the substrate effect is discussed. MgO has been frequently utilized for the growth of magnetite and ferrites due to small lattice mismatch (∼−0.3%) and epitaxial films are expected. On the other hand, STO substrate is included in this study because of its relatively large lattice mismatch (∼7.5%) and dissimilar oxygen sublattice to ferrites so a relaxed thin film may be obtained for comparison. Detailed studies including out of plane x-ray diffraction (XRD) and magnetization measurements are carried out for these films. XRD measured along the z direction reveals that these films are indeed epitaxial and strained for films grown on MgO but it shows two phases of crystalline orientation and thus relaxed for films grown on STO. The magnetic response of these films also shows difference especially in the range of $0.3 < x < 1.3$. Magnetization saturation (M_s) of films grown on STO is two to three times larger than that of the films grown on the MgO substrate.

II. EXPERIMENT

A series of $Fe_{3-x}Mg_xO_4$ films is grown on MgO(001) and $SrTiO_3$(001), side by side, by oxygen-plasma-assisted molecular beam epitaxy and the thickness of these films is all 1000 Å. Detailed description of the growth is similar to our previous study of oxide thin film and has been given elsewhere.[6] XRD at room temperature was carried out, with a Cu anode (θ-2θ, scan $\lambda = 1.5405$ Å), perpendicular to the film surface to analyze the crystalline quality of the films. Magnetic behaviors are measured using a vibrating sample magnetometer (VSM).

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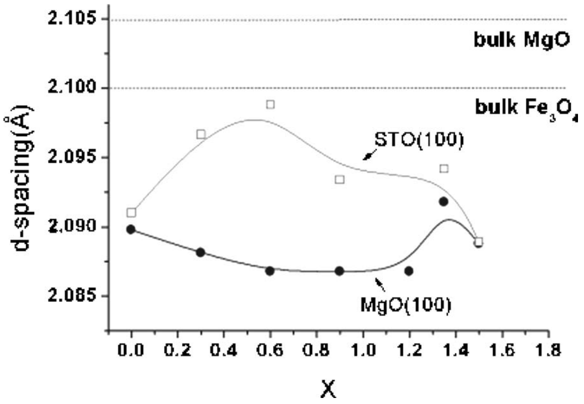

FIG. 1. The corresponding *d* spacing for a series of Fe–Mg–O oxide films with different Fe/Mg ratios on MgO and $SrTiO_3$ substrates.

III. RESULTS AND DISCUSSION

A. X-ray diffraction results

The atomic *d* spacings along the perpendicular direction are extracted from diffraction results. Figure 1 shows a plot of *d* spacing versus x and a comparison between MgO and STO grown films. Both curves show that *d* spacings for these films are lower than the bulk values, which are consistent with the study by Lind *et al.*[7] It is clear that the major difference of these films is that the *d* spacing for the films grown on STO tends upward and the *d* spacing of the film grown on MgO downward in the range of $0.3<x<1.3$. These discrepancies can be understood that for a strained film, in the case of the films grown on MgO, the lattice constant of Mg ferrite films tends to be enlarged in plane, which causes the reduction of the *d* spacing along the z direction. On the other hand, more relaxed film, in the case of the films grown on STO, shows a trend that *d* spacings are closer to the bulk value.

B. Magnetization measurement

Figures 2 and 3 show *M*-*H* curves of $Fe_{3-x}Mg_xO_4$ film on STO(001) and MgO(001) at RT including both parallel and perpendicular results. In Fig. 2(a), saturation magnetization (M_s) of Fe_3O_4 film on STO, H parallel to the film, is 500 emu/cm^3 and coercivity (H_c) ~ 314 Oe, which is consistent with the previous report on pure Fe_3O_4 film.[8] The magnetization remains ~400 emu/cm^3 and shows square loops in the range of $0.3<x<0.9$, then M_s quickly decreases with increasing x and becomes 100 emu/cm^3 at $x=1.35$. In Fig. 2(b), hysteresis loops are measured with the applied field along the direction normal to the surface. M_s basically follows the same trend as the results in Fig. 2(a) but the shape of these curves displays squareness, indicating that the easy axis is changed from in plane ($0<x<0.9$) to other unknown direction ($x>1.2$). On the other hand, Fig. 3 shows representative *M*-*H* curves of $Fe_{3-x}Mg_xO_4$ film on MgO (100) at RT including both parallel and perpendicular results. The shape anisotropy, the difference for the results of parallel to perpendicular, is basically similar to that of the films grown on STO. However, the saturation magnetization (M_s) linearly decreases with increasing Mg ratio in $Fe_{3-x}Mg_xO_4$ films.

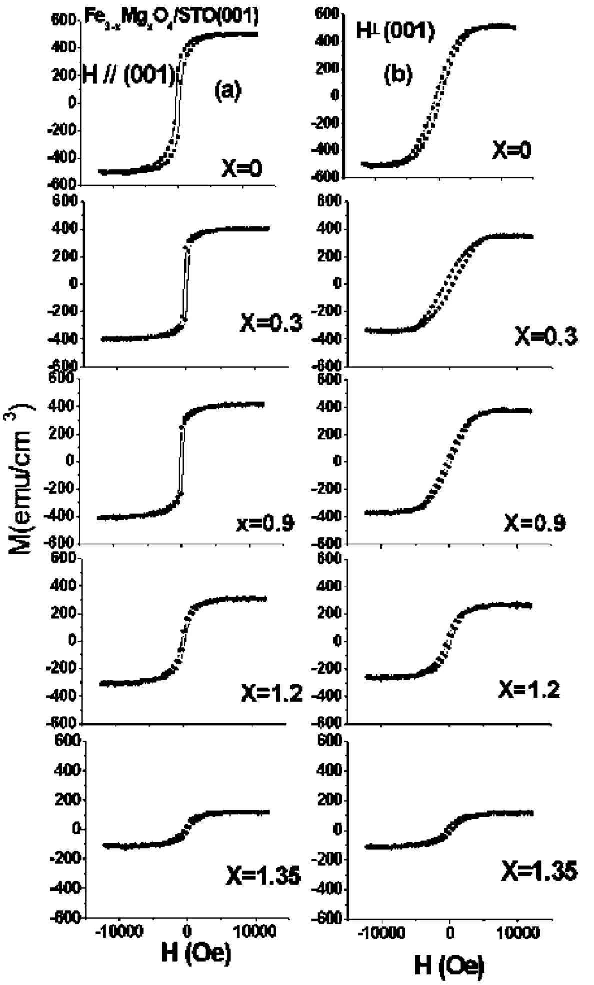

FIG. 2. Hysteresis loops at magnetic field applied (a) parallel to the film plane and (b) normal to the film plane at 300 K for the $Fe_{3-x}Mg_xO_4$ films on STO(001).

In Fig. 4(a) we summarize M_s vs x for the films grown on STO and MgO and also show both high and low limits of M_s based on a simple local moment assumption. It is well known that the magnetization of ferrites is due to the incomplete compensation (antiparallel) of magnetic moment between A and B sites. While varying x in $Fe_{3-x}Mg_xO_4$ ($0<x<1$), because Mg ion does not have magnetic moment, M_s increases if Mg replace Fe in the A site and decreases if Mg replace Fe in the B site. Depending on the distribution of Mg cation, the net moment can, in principle, vary from 0 to $10\mu_B$ (Bohr magnetron) at Fe_2MgO_4 ($x=1$) and the extreme of M_s vs x follows linearly. On the other hand, for $x>1$, it becomes more complicated because the valence state of Mg ion needs to be 3+ to satisfy neutrality constrain or Fe needs to be +4 state (see below).

For our experimental data, the major difference in M_s between films grown on MgO and STO is in the range of $0.3<x<1.35$. It is shown that M_s gradually drops from 500 to ~100 emu/cm^3 for the film grown on STO(001), but M_s ~ 400 emu/cm^3 at $x=0.3$, remains unchanged at $0.3<x<1$, and then gradually merges to the M_s of films grown on MgO at $x=1.35$. The cation distribution corresponding to the experimentally observed M_s is plotted in Fig. 4(b), which shows the variation of Fe in the B site versus x (note that the

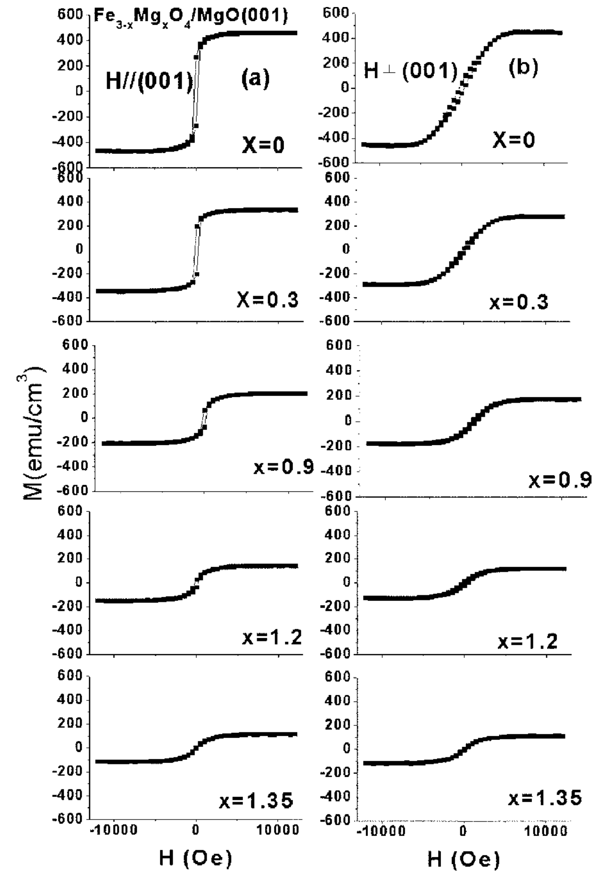

FIG. 3. Hysteresis loops at magnetic field applied (a) parallel to the film plane and (b) normal to the film plane at 300 K for the $Fe_{3-x}Mg_xO_4$ films on MgO(001).

total number of Fe ions equals $3-x$). At this moment, we could not find any previous M_s results for Mg ferrite except in the bulk phase that Fe_2MgO_4 has $M_s \sim 1\mu_B$, which corresponds to a mixed spinel structure (0.1 Mg in the A site and 0.9 Mg in the B site).[9] A dash line, indicating a 1:2 ratio of Mg ion in A and B sites, is plotted for the discussion below. This 1:2 ratio of cation distribution for the film growth has been suggested in the study of Ni ferrite films.[10] The reason for 1:2 is plausible regarding the film growth [a two-dimensional (2D) growth process], since along the [001] direction a 2D growth has to be consistent with the ion ratio of A to B site which is 1:2. This simple argument of the ionic distribution of ferrite film needs further experimental evidence for the test.

IV. CONCLUSIONS

The structure and magnetic response of $Fe_{3-x}Mg_xO_4$ ($0 < x < 1.5$) films, which are grown on MgO(001) and STO(001) substrate by oxygen-plasma-assisted molecular beam epitaxy, are compared. The films grown on MgO show single crystalline quality, while the films grown on STO show polycrystalline quality, which are revealed by x-ray diffraction. The magnetization measurement indicates that the easy axis is in the (001) plane if $0 < x < 1$ for both films. The magnetic easy axis changes to an unknown direction, maybe [111], for $x > 1$. The saturation magnetization (M_s) for films grown on MgO reduces from 500 emu/cm^3 roughly linearly from $x=0$ to $x=1.5$. However, M_s remains ~ 400 emu/cm^3 in the range of $0.3 < x < 0.9$ for the films grown on STO. The difference in M_s can be attributed to cation distribution. For the low M_s state found in the film grown on MgO (strained case), Mg mostly replace Fe in the B site. However, for the high M_s state found in films grown on STO (relaxed case), Mg replace Fe both in the A and B sites with a ratio of $\sim 1:2$. The mechanism for the high M_s or the 1:2 distribution may be related to the thin film layer-by-layer growth characteristic.

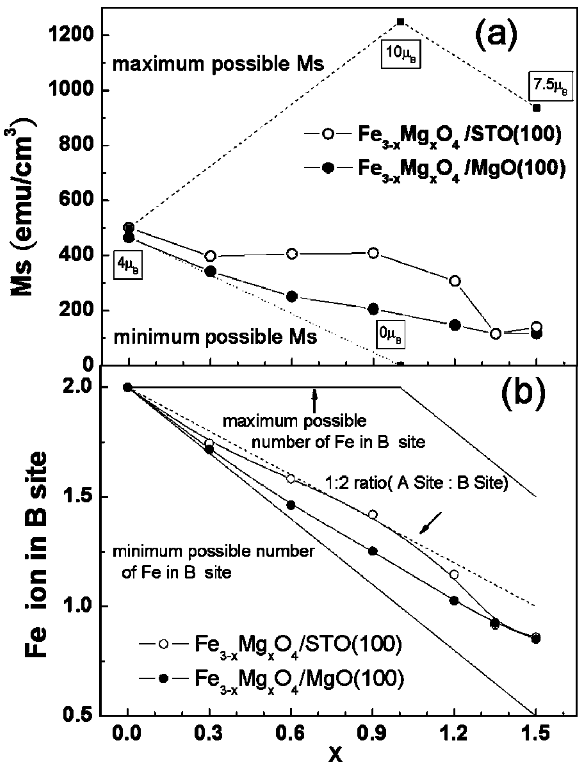

FIG. 4. (a) M_s vs x for the film grown on STO and MgO. (b) The variation of Fe in the B site vs x.

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