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Direct observation of strain fields in epitaxial growth Fe_3O_4 thin films on MgO substrates

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Fe_3O_4 thin films with a thickness of about 140 nm have been deposited on MgO (001) substrates by reactive sputtering. Microstructural studies indicated that monocrystalline Fe_3O_4 thin films were epitaxially grown on the MgO substrates with a cubic-on-cubic orientation relationship with respect to the substrates. Strain field due to slight lattice mismatch between the films and substrates was observed. The saturation moment and the coercivity for in-plane magnetization hysteresis loop were 235 emu/cc and 500 Oe, respectively. The lower saturation moment value of the Fe_3O_4 thin film suggested that the strain field may play a role in the reduction of magnetization. © 2004 American Institute of Physics. [DOI: 10.1063/1.1682788]

The scientific and technological importance of spinel Fe_3O_4 has attracted much attention due to its high spin polarized nature, which is desirable for tunneling-magnetoresistance based device applications.¹ Much emphasis has been placed on the epitaxial growth of Fe_3O_4 single crystalline films on various substrates, such as SrTiO_3 , Al_2O_3 ,² and MgO ,^{3–5} etc. Epitaxial growth of Fe_3O_4 films has shown several anomalous magnetic properties, such as much larger saturation field and quasirandom zero-field magnetic moment distributions, and superparamagnetic behaviors, etc.^{4,6} These anomalous properties of epitaxial growth Fe_3O_4 thin films have been attributed to antiphase boundaries (APBs), across which the exchange coupling is altered. APBs have been observed on both single crystalline and nanocrystalline Fe_3O_4 thin films deposited on MgO (Refs. 4 and 5) and Si (Ref. 7) substrates, respectively.

In addition to APBs, the interfacial structure between the Fe_3O_4 thin films and the substrates may play an important role in the anomalous properties of the Fe_3O_4 thin films, since it is well known that two-dimensional thin films are in strain state due to the lattice mismatch between films and substrates.⁸ Lattice strain resulting from misfit dislocation may also has some effects on films' properties. Until now, very limited papers about interfacial structure of Fe_3O_4 thin films were found. In this study, we report the microstructure study and the magnetization hysteresis loop of Fe_3O_4 thin films deposited on MgO substrates using reactive sputtering method.

Reactive sputtering was done with a pure Fe target in a mixture of Ar and oxygen in a Shamrock system. The base pressure was lower than 1.0×10^{-7} Torr before the deposition took place. The Fe_3O_4 films were deposited on single

crystalline (001) MgO substrates. Before the Fe_3O_4 deposition, the MgO substrates were cleaned by ion milling for 1 min. The substrates had a planetary rotation during ion milling and sputtering. There was a magnetic field of 50 Oe, which rotated with the substrates, applied during film deposition. A protecting layer of Si_3N_4 was then deposited on all films in a PE4400 sputtering system. The films were then subjected to two annealing processes, the first at 200 °C for 3 h, and the second at 300 °C for 3 h, both in a magnetic field.

Cross-sectional transmission electron microscopy (TEM) samples were prepared using conventional method, including mechanical polishing, dimpling, and final ion milling. TEM observation was performed with a JEOL2010 transmission electron microscope. The magnetization was measured using a quantum design magnetic property measurement system parallel to the film plane at 300 K.

Figure 1(a) is a bright field TEM image showing cross-sectional growth of a Fe_3O_4 film on a MgO substrate. It can be seen from the image that the surface of the Fe_3O_4 film is very flat and smooth. The contrast is uniform through the whole film, indicating a good epitaxial growth of the Fe_3O_4 films on the MgO substrate. The thickness of the Fe_3O_4 thin films was measured to be 140 nm. Figure 1(b) is a selected area diffraction pattern (SADP) taken from the Fe_3O_4 film, which indicates a single crystal feature of the Fe_3O_4 thin films. Figure 1(c) is a SADP taken from the [100] MgO substrate. Figures 1(b) and 1(c) exhibit a cube-on-cube orientation relationship between the Fe_3O_4 films and the MgO substrate, i.e.,

$$[001]_{\text{Fe}_3\text{O}_4} // [001]_{\text{MgO}},$$

$$(010)_{\text{Fe}_3\text{O}_4} // (010)_{\text{MgO}}.$$

Fe_3O_4 is spinel-type structure with space group of $Fd\bar{3}m$ and lattice parameter of 0.8394 nm, whereas MgO is

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FIG. 1. (a) Bright field TEM image showing growth morphology of the Fe₃O₄ thin films on the MgO substrates. (b) and (c) are SADPs taken from the Fe₃O₄ thin film and the MgO substrate, respectively.

NaCl-type structure with space group of $Fm\bar{3}m$ and lattice parameter of 0.4213 nm. The lattice parameter of Fe₃O₄ is nearly twice of that of MgO. The O atoms in both Fe₃O₄ film and MgO substrate form sublattices of approximately face-centered cubic (fcc) lattices. The lattice mismatch between Fe₃O₄ and MgO can be calculated using equation

$$\delta = \frac{2(d_1 - d_2)}{d_1 + d_2}, \quad (1)$$

where d_1 and d_2 represent lattice parameters of the film and substrate, respectively. In the present case, however, since the Fe₃O₄ unit cell is nearly twice the size of the MgO unit cell, the lattice parameter d_2 in Eq. (1) should be taken as twice of the lattice parameter of MgO. Therefore, the lattice mismatch δ was calculated to be about 0.3%. The similar spacing of the O lattices in Fe₃O₄ and MgO makes MgO a good template for the epitaxial growth of single crystal Fe₃O₄. A cube-on-cube orientation relationship between Fe₃O₄ and MgO is therefore formed, since the fcc sublattices of O in both Fe₃O₄ and MgO crystals are of nearly the same size (δ is only about 0.3%).

Figure 2 is a high resolution electron microscopy (HREM) image viewing along the [100] direction of the MgO substrate. The image exhibits interfacial features between the Fe₃O₄ thin films and the MgO substrates, where the dash line indicates the interface. From the image, it can be seen that the lattices in both sides of the interface are perfect. No intermediate layers were observed in the interfacial region, indicating a chemically clear interface. The dark contrast near the interface implies that a misfit dislocation may be present at the interface. A Burgers circuit was drawn around the dark contrast region. From the Burgers circuit, it can be seen that the Burgers vector of the misfit dislocation is $1/2[100]$ (denoted by a white arrow). The $1/2[100]$ is a Burgers vector of a partial dislocation in NaCl-type MgO

FIG. 2. HREM image viewing along the [100] direction of the MgO substrates, exhibiting interfacial features between the Fe₃O₄ thin films and the MgO substrates. A Burgers circuit was drawn around the dark contrast region.

structure. The actual Burgers vector of the misfit dislocation should be $1/2[110]$, which indicates that the misfit dislocation is of mixed type. The projection of $1/2[110]$ to (001) lattice plane is the edge part of the Burgers vector, i.e., $1/2[100]$. The lattice mismatch between Fe₃O₄ and MgO was accommodated by $1/2[100]$. The dark contrast at the interfacial region implies a lattice strain resulting from lattice distortion near the misfit dislocation.

It is well known that misfit dislocations should be arranged periodically in the interface to accommodate lattice mismatch, especially in epitaxial growth thin films. The misfit dislocation spacing can be calculated using the equation⁹

$$d = \left| \frac{1 + \delta}{\delta} \right| |b|, \quad (2)$$

where δ and b represent lattice mismatch and Burgers vector of misfit dislocation, respectively. Here, b is taken as $1/2[100]a_{\text{MgO}}$, the edge part of Burgers vector of the misfit dislocation, where a_{MgO} represents lattice parameter of MgO. It was therefore calculated that the misfit dislocation spacing is 70.2 nm. This value is much larger than the interfacial region shown in Fig. 2. Thus, the frequency for the misfit dislocations to be observed by HREM should be very low. In fact, we observed periodically arrayed strain contrasts along the interface caused by misfit dislocations with an average spacing of about 75 nm. It is thus concluded that calculated dislocation density along the interface is close to what we observed by TEM.

It was reported that the APB size was about 27.5 nm for monocrystalline⁴ and 5–15 nm for nanocrystalline⁷ Fe₃O₄ thin films. These values are much smaller than the spacing of periodically arranged misfit dislocations, i.e., 70.2 nm. It is thus expected that the effect of lattice strain resulting from the periodically arranged misfit dislocation on the high saturation field of the Fe₃O₄ thin films should be smaller than that of APBs.

Figure 3 exhibits the field in-plane [100] direction hysteresis loop of the Fe₃O₄ thin films. The saturation moment

FIG. 3. Magnetization hysteresis loop at 300 K for the Fe_3O_4 thin films with field in-plane $[100]$ direction up to 5 T.

(M_s) is about 235 emu/cc, less than the reported bulk value of 471 emu/cc.¹⁰ The coercivity (H_c) for the film is about 500 Oe. As shown in Fig. 2, strain field was directly observed in the Fe_3O_4 thin films resulting from lattice distortion near the misfit dislocation. Moreover, it is generally believed that the in-plane and out-plane thin films are in different strain states because of the lattice mismatch in heterostructure. In the present case, since the lattice parameter of MgO is larger than half of lattice parameter of Fe_3O_4 , it is expected that the in plane and out plane of the Fe_3O_4 thin films should be in expanded strain state and compressed strain state, respectively. The lower M_s value of the Fe_3O_4 thin films suggested that the strain field plays a role in the reduction of magnetization. It was reported that the strain in the Fe_3O_4 thin films played a role in the reduction of magnetization,³ in which the M_s was 415 emu/cc for 660 nm Fe_3O_4 thin films on the (001) MgO substrate and even lower magnetization was observed for the films with a thickness of 150 nm. In our 140 nm thin film, the reduction of magnetization is larger than usual Fe_3O_4 thin films. Until now, it is not fully understood how the strain induces considerable

magnetization reduction and how much it is reduced, because of the complexity between strain and magnetization in the Fe_3O_4 thin films. Further work about the effect of strain field on the magnetization reduction is in study.

In summary, the Fe_3O_4 thin films with a thickness of about 140 nm were epitaxially grown on the (001) MgO substrates by reactive sputtering. The Fe_3O_4 thin films were single crystal with a cubic-on-cubic orientation relationship with respect to the MgO substrates, i.e., $[001]_{\text{Fe}_3\text{O}_4} // [001]_{\text{MgO}}$, and $(010)_{\text{Fe}_3\text{O}_4} // (010)_{\text{MgO}}$. The misfit dislocations were observed at the interface between Fe_3O_4 thin films and MgO substrates. The lattice mismatch generated strain field at the interface. The saturation moment for the in-plane hysteresis loops was about 235 emu/cc, whereas, the coercivity of the in-plane hysteresis loops was 500 Oe. The lower M_s value of the Fe_3O_4 thin film suggested that the strain field plays a role in the reduction of magnetization.

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