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Microstructure of epitaxial α -Fe₂O₃ grains in Ba-ferrite thin films grown on sapphire (001)

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We revealed the existence of epitaxial α -Fe₂O₃ grains in Ba-ferrite thin films on sapphire (001) using synchrotron x-ray scattering. The antiferromagnetic α -Fe₂O₃ grains were formed during the crystallization of amorphous Ba-ferrite films grown on sapphire (001) by radio frequency sputtering deposition. The crystal domain size of the α -Fe₂O₃ grains was about 250 Å in the film plane, similar to that of the Ba-ferrite grains. The in-plane crystalline axis of the α -Fe₂O₃ was aligned to that of sapphire, while the Ba-ferrite film was rotated by 30° in the film plane. We confirm that the existence of these antiferromagnetic α -Fe₂O₃ grains greatly degraded magnetic properties of the Ba-ferrite films. © 1999 American Institute of Physics. [S0003-6951(99)03414-2]

BaFe₁₂O₁₉ (Ba-ferrite) thin films are considered to be attractive high-density recording media due to their excellent chemical stability, high mechanical durability, and large uniaxial anisotropy.¹⁻³ The microstructure of Ba-ferrite thin films has been extensively studied since it is necessary to enhance the magnetic property as well as to minimize the grain size for high-density recording media.^{4,5} Controlling the microstructure of magnetic grains and nonmagnetic impurities is one of the important issues.

The composition of the Ba-ferrite films that are grown with the stoichiometric Ba-ferrite target in sputtering methods is slightly Ba deficient due to the scattering loss.⁶⁻⁸ Ba-deficient bulk Ba-ferrites phase separates into Ba ferrite and α -Fe₂O₃.⁹ Similarly, during the deposition of thin Ba-ferrite films, the existence of α -Fe₂O₃ has been reported.¹⁰ The microstructure of α -Fe₂O₃ grains, however, has not been well characterized. Since antiferromagnetic α -Fe₂O₃ grains might affect the magnetic qualities of high-density recording media, it is important to elucidate their microstructure.

In this letter, we report the existence of epitaxial α -Fe₂O₃ grains in Ba-ferrite thin films grown on sapphire (001) using synchrotron x-ray scattering measurements. Synchrotron x-ray scattering with very high flux and high resolution is one of the best probes to study the out-of-plane and the in-plane structure of epitaxial thin films. We reveal that the crystal domain size of the α -Fe₂O₃ grains, similar to that of the Ba-ferrite grains, is about 250 Å in the film plane. The existence of these antiferromagnetic α -Fe₂O₃ grains greatly degraded magnetic properties of the Ba-ferrite films.

Ba-ferrite films were grown on sapphire (001) substrates at room temperature by radio frequency (rf) magnetron sputtering of a stoichiometric Ba-ferrite target. As a carrier gas, a mixture of Ar-10% O₂ was used. The deposition rate of the film was about 4.0 Å/min. The as-deposited films were amorphous, and were crystallized by annealing at 750 °C for 5 h

in air. The thickness of the postannealed films was determined by x-ray reflectivity measurements.¹¹ The typical as-deposited film composition measured by Rutherford backscattering spectroscopy (RBS) was Ba_{0.8}Fe₁₂O₂₀, somewhat Ba deficient with respect to the stoichiometric Ba-ferrite phase. The magnetic properties of the Ba-ferrite films were measured using a vibrating sample magnetometer (VSM).

The synchrotron x-ray scattering experiments were performed at beamline 5C2 at the Pohang Light Source (PLS) in Korea. The incident x rays were vertically focused by a mirror, and monochromatized to the wavelength of 1.447 Å by a double bounce Si (111) monochromator. The monochromator also focused the x rays in horizontal direction. A typical momentum transfer resolution was controlled by two pairs of slits in front of the detector, and was set at 0.001 Å⁻¹ in this experiment.

Figure 1 shows a schematic illustration of the x-ray scat-

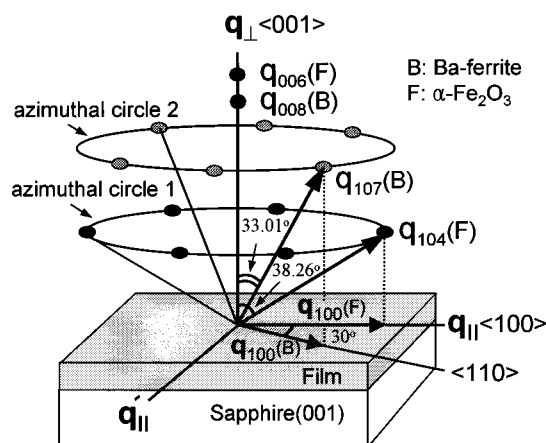


FIG. 1. The reciprocal lattice coordinate system of the x-ray scattering geometry. A conventional powder diffraction scan is obtained by measuring the scattering intensity along the specular q_{\perp} direction. The epitaxial relationship is investigated by the orientation of the nonspecular q_{104} (α -Fe₂O₃) and q_{107} (Ba ferrite) reflections of the film with respect to that of the substrate on the azimuthal circles.

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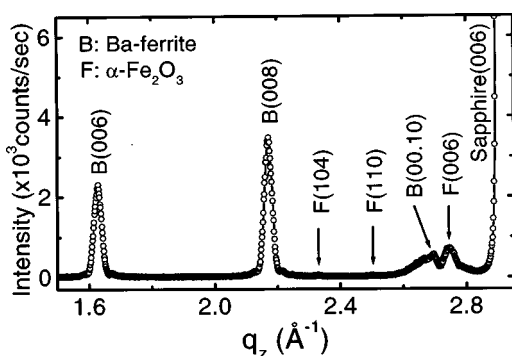


FIG. 2. The x-ray powder diffraction pattern taken on a 300-Å-thick Ba-ferrite film after annealing at 750 °C for 5 h in air. The Ba ferrite and the α -Fe₂O₃ grains are demonstrated to have the (00 l) preferred orientation on the sapphire (001).

tering geometry used in this experiment. From the Bragg's diffraction profile along the substrate normal direction in reciprocal space, one might obtain the crystal structure and the out-of-plane orientation of the film. However, to obtain the detailed information of the epitaxial relationship, one needs to observe additional Bragg reflections lying on nonspecular directions. The epitaxial relationship was investigated by observing the orientation of the nonspecular reflections of the film with respect to that of the substrate on the azimuthal circles shown in Fig. 1.

We first carried out powder diffraction measurements by varying the momentum transfer \mathbf{q} from 1.50 to 2.90 Å⁻¹ along the substrate normal direction in reciprocal space. Figure 2 illustrates the powder diffraction pattern taken on a 300-Å-thick Ba-ferrite film. The presence of the Ba ferrite (006), (008), and (00.10) reflections immediately shows that the Ba-ferrite film had the (00 l) preferred orientation on the sapphire (001). Since the direction of easy magnetization is along the hexagonal c axis, the (001) direction, in Ba ferrite, the data exhibit that the Ba-ferrite film is the perpendicular type; the easy c -axis magnetization direction is perpendicular to the film plane.

Besides the Ba-ferrite Bragg reflections, there exist additional Bragg reflections at $q_z = 2.34$, $q_z = 2.50$, and $q_z = 2.75$ Å⁻¹ that correspond to the α -Fe₂O₃ (104), α -Fe₂O₃ (110), and α -Fe₂O₃ (006), respectively. The existence of the α -Fe₂O₃ phase besides Ba-ferrite phase has also been reported in literature.¹⁰ It is attributed to the Ba deficiency that is caused by the scattering loss during the film growth process even with a stoichiometric Ba-ferrite target.⁶⁻⁸ Considering the relative structure factors of α -Fe₂O₃ ($f_{(104)} = 100$, $f_{(110)} = 50$, and $f_{(006)} = 2$, JCPDS 33-664), it is remarkable that the α -Fe₂O₃ (006) Bragg reflection with much smaller structure factor is much stronger than the α -Fe₂O₃ (104) and the α -Fe₂O₃ (110) reflections. This indicated that the α -Fe₂O₃ phase was grown with the strong (00 l) preferred orientation on the sapphire (001). The preferred orientation of the α -Fe₂O₃ in Ba-ferrite films has not been reported thus far.

For perpendicular Ba-ferrite films, the c -axis alignment of the Ba ferrite, the mosaic distribution, greatly affects to the magnetic qualities of high-density recording media.¹² The mosaic distributions of the α -Fe₂O₃ (006) and the Ba ferrite (008) were very small as 0.273° and 0.326° full width

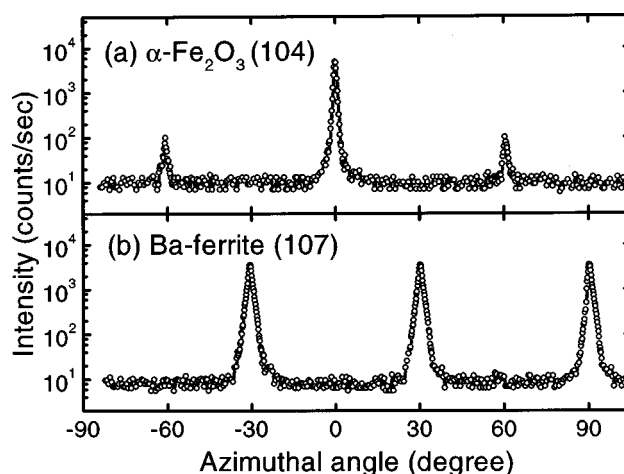


FIG. 3. The intensity profiles of (a) the α -Fe₂O₃ (104) and the Ba-ferrite (107) nonspecular reflections on the azimuthal circles. The sharp scattering features of sixfold symmetry show that the α -Fe₂O₃ and the Ba-ferrite grains were grown epitaxially on the sapphire (001), with 30° off each other.

at half maximums (FWHM), respectively, (data not shown), indicating that they were very well aligned to the substrate normal direction. The small mosaic distribution, compared with the reported value of 1° FWHM,¹² is worth noting since the smaller mosaic distribution of the easy c -axis magnetization direction is indispensable in producing high quality, high-density magnetic recording media.³

The α -Fe₂O₃ was epitaxial to the sapphire substrate. To examine the orientational relationship, we investigated the α -Fe₂O₃ (104) Bragg reflection lying on a nonspecular direction, 38.26° away from the specular rod, and performed the azimuthal circle scan 1 as illustrated in Fig. 1. The well-defined peaks on the azimuthal scan 1 illustrated in Fig. 3(a) indicated that the distribution of the in-plane crystalline axis of the α -Fe₂O₃ grains was sharply peaked with the FWHM of 1.1°. This showed that the α -Fe₂O₃ was in fact grown epitaxially to the substrate. The epitaxial relationship can be revealed by the direction of the momentum transfer at the peak projected to the film plane relative to the in-plane orientation of the sapphire substrate. From the relative directions of the α -Fe₂O₃ and the substrate crystalline axes it was found that the epitaxial relationship of the α -Fe₂O₃ grains was α -Fe₂O₃ (00 l)//sapphire (00 l), and α -Fe₂O₃ (100)//sapphire (100).

The Ba-ferrite grains were also epitaxially grown. This was revealed by the Ba-ferrite (107) reflection, which was located 33.01° away from the surface normal direction. Figure 3(b) shows the scattering profile along the azimuthal scan 2 shown in Fig. 1. As indicated by the well-defined peaks on the azimuthal circle 2, the in-plane crystalline axis of the Ba-ferrite grains was distributed along the substrate crystalline axis direction with the FWHM of 1.5°, indicating that the Ba-ferrite phase was also grown epitaxially to the substrate. To obtain the epitaxial relationship of the Ba-ferrite phase with the sapphire substrate, we projected the \mathbf{q}_{107} (Ba ferrite) on the film plane in reciprocal space as illustrated in Fig. 1. Interestingly, the projected \mathbf{q}_{100} (Ba ferrite) was along the sapphire [110] direction. This implies that the Ba-ferrite (100) direction is parallel to the sapphire (110) direction. From the relative directions of the Ba ferrite and

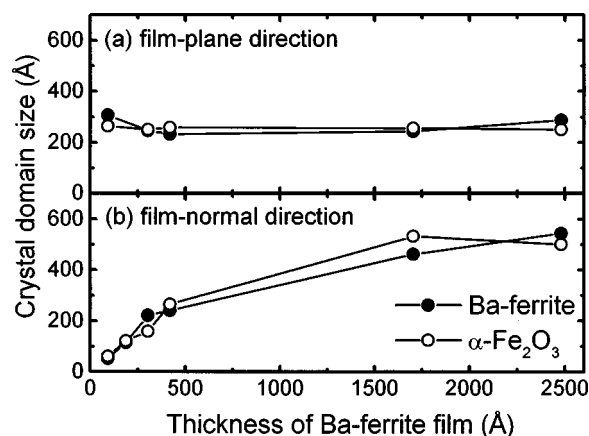


FIG. 4. The crystal domain sizes of the α -Fe₂O₃ and the Ba-ferrite grains in (a) the film-plane direction, and in (b) the film-normal direction as a function of film thickness. The crystal domain sizes of the α -Fe₂O₃ grains are very similar to those of the Ba-ferrite grains.

the substrate crystalline axes, we concluded that the epitaxial relationship of the Ba-ferrite grains was summarized as Ba-ferrite (001)//sapphire (001), and Ba-ferrite $\langle 100 \rangle$ //sapphire $\langle 110 \rangle$, as previously reported.¹³

Murdoch has estimated that recording at densities of 10 Gbit/in.² will require 100 Å grains that are magnetically decoupled from neighboring grains.¹⁴ However, the grain size is usually greater than the magnetic domain size, probably due to defects within grains. Also, the crystal domain size is directly related with defects. We estimate the crystal domain size of the α -Fe₂O₃ and the Ba-ferrite grains in the film normal direction and in the film plane direction by the FWHM of the scattering profile in the corresponding direction using Sherrer's formula.¹⁵ Although the scattering profile is anisotropic, we can still use the width of the profile to estimate the given direction.

Figure 4 shows that the crystal domain sizes of the α -Fe₂O₃ grains are very similar to those of Ba-ferrite grains. In the film plane, the α -Fe₂O₃ and the Ba-ferrite grains have comparable crystal domain size of about 250 Å irrespective of the film thickness, as illustrated in Fig. 4(a). We also observe, in the film normal direction, that the crystal domain sizes were very similar each other in α -Fe₂O₃ and Ba-ferrite grains, as shown in Fig. 4(b). As the film thickness increased to 2500 Å, the out-of-plane crystal domain sizes increased to about 500 Å in both phases. The plane view observed by field emission scanning electron microscope showed fine grains of about 600 Å in diameter, larger than the in-plane crystal domain size, 250 Å. This indicated that both Ba ferrite and α -Fe₂O₃ were grown in columnar-type on the sapphire (001).

The performance of high-density recording media is greatly affected by the magnetic properties of Ba-ferrite films. The Ba-ferrite phase is ferrimagnetic, while the α -Fe₂O₃ phase is antiferromagnetic. It is known that the saturation magnetization (M_s) of stoichiometric Ba-ferrite phase is 380 emu/cm³ at room temperature, while that of the α -Fe₂O₃ phase is very small.¹⁶ For Ba ferrites in the form of

aligned, spherical, single-domain particles, its intrinsic coercivity (H_c) was estimated as 17 kOe.¹⁶ In the 300-Å-thick Ba-ferrite film, however, the M_s and the H_c measured in the film normal direction were small at 223 emu/cm³ and 0.93 kOe, respectively. In all films studied, we also observe that the M_s and H_c decreased quite a lot, compared to those of the theoretical Ba ferrite. We attribute these severely degraded magnetic properties, especially H_c , to the existence of antiferromagnetic α -Fe₂O₃ grains as defects. The antiferromagnetic α -Fe₂O₃ grains among the neighboring ferrimagnetic Ba-ferrite grains might induce recording defects owing to poor intergranular interaction.¹⁴

In conclusion, we have first revealed the existence of epitaxial α -Fe₂O₃ grains in perpendicular Ba-ferrite/sapphire(001) thin films by synchrotron x-ray scattering measurements. The epitaxial relationship is summarized as α -Fe₂O₃ (006)[Ba-ferrite (001)]//sapphire (001), α -Fe₂O₃ $\langle 100 \rangle$ //sapphire $\langle 100 \rangle$, and Ba-ferrite $\langle 100 \rangle$ //sapphire $\langle 110 \rangle$. In the film plane, the α -Fe₂O₃ and the Ba-ferrite grains have comparable crystal domain size of about 250 Å in all the films studied. In the film normal direction, we also observe that the crystal domain sizes are very similar to each other in the α -Fe₂O₃ and the Ba-ferrite grains and increase to about 500 Å with the film thickness. We confirm by measuring the magnetization and the intrinsic coercivity that the existence of these antiferromagnetic α -Fe₂O₃ grains among the neighboring ferrimagnetic Ba-ferrite grains greatly degraded magnetic properties of the Ba-ferrite films. Further study is required to elucidate the detailed phase separation during the crystallization of amorphous Ba-ferrite films.

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