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Barium ferrite thin films with faceted grains fabricated by using ethylenediaminetetraacetic acid

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ABSTRACT

Barium ferrite films were prepared by spin-coating of gels on sapphire (0 0 *l*) faces. Ethylenediaminetetraacetic acid was used to bind the metal ions. Thin films prepared by this method show faceted hexagonal grains with *c*-axis normal to the film plane and $[1\,1\,0]_{sapphire} \| [1\,0\,0]_{film}$. Needle-like grains, which have *c*-axis in the film plane, are minimized. Epitaxial growth of the film can be observed by the high resolution images. Reduction of the *a* and *c*-axis of the film compared with those of the bulk materials is confirmed both in real space and reciprocal space. Magnetic hysteresis loops were recorded in-plane and out-of-plane. The film shows uniaxial anisotropy as exemplified by branched domains with coercivity field of 87.6 kA/m along the in-plane direction and of 302.5 kA/m along the out-of-plane direction.

1. Introduction

M-type barium ferrite (BaM) thin films are candidates in MicroElectro-Mechanic Systems and magnetic recording media [1,2]. Recently they were proposed to be the key materials for thin film non-reciprocal microwave devices [3]. The films can be also integrated with piezoelectric films, so that these microwave devices can be tuned electrically or magnetically [4]. In all these applications, morphologies of the films play an important role in determination of the performances of devices. For example, the morphology of the films is crucial to the signal-to-noise ratio in magnetic recording media [5]. The line-width of microwave devices is sensitive to the perfection of the crystallization [6]. When integrated with the piezoelectric thin films epitaxial films of BaM are highly desired to maximize the coupling of the two materials [4]. It was widely reported [7–9] that barium ferrite crystallized into two different shapes: plate-like and needle-like. The plate-like grains are normal because the growth rate in the plane of the hexagonal grains is much higher than that in the normal direction, while the needle-like grains are developed because one of the faster growth direction is limited by space (e.g. the substrate) [10]. Moreover, plate-like crystallites in the films are usually found to be rounded, which means that the crystallization is incomplete. In our previous work using sol–gel methods, we found that the citric acid influences the morphology of the films greatly: reduction of the citric acid decreases the needle-like grains [11,12]. The reason is that the autocombustion process was slowed down with the decrease of the citric acid. The nucleation rate was also slowed down. This is essential to control the morphology of the crystallites. Citric acid, with ethylenediaminetetraacetic acid (EDTA) added in sol–gel methods, was reported to be able to produce faceted grains [13]. Using EDTA to bind other metal ions was able to grow films with high quality. The process is so-called polymer assistant deposition (PAD) [14,15]. In this process the soluble polymer plays at least two roles: controlling the viscosity of the sols and binding the metal ions to prevent premature precipitation. In this work, EDTA was used to prepare hexagonal barium ferrite thin film. Results show that hexagonal faceted platelets epitaxially grew on the sapphire, which indicated excellent crystallization.

2. Experimental

$Ba(NO_3)_2$ and $FeCl_3 \cdot 6H_2O$ with the mole ratio 1.0:10.5 were dissolved into distilled water, the concentration of Ba^{2+} was about 0.1 mol/L. EDTA (AR, 3 g) was dissolved into $NH_3 \cdot H_2O$ (6 mL) and added into the above solution, and was stirred for 2 h at 70 °C. At the same time, $NH_3 \cdot H_2O$ was dropped into the solution to adjust the pH between 6 and 7. Glycol with twice the volume of the above solution was added and a suitable mass of polyvinyl pyrrolidone (PVP, 2 wt.%) was added to adjust the viscosity of the solution. After stirred for 3 h at room temperature, a sol was obtained. The sol was spin-coated onto sapphire substrates at 3000 rpm for 30 s and the films were dried at 80 ° C for 15 min in air. The process of coating and drying were repeated 5 times. The films were annealed at 800, 900, 1000, and 1100 ° C respectively in a tube furnace in air up to 6 h.

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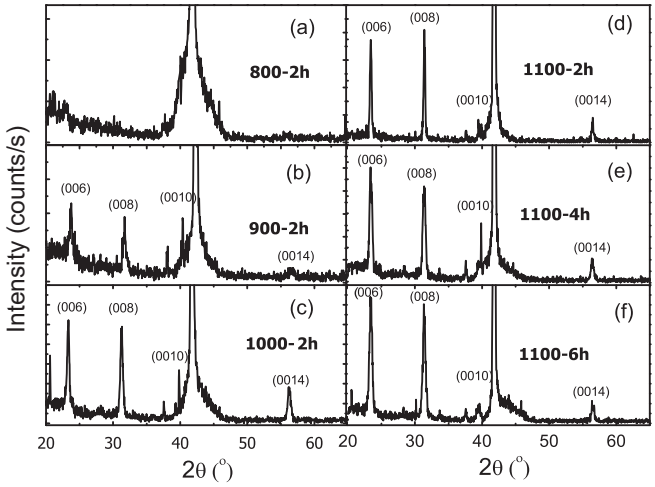

Fig. 1. XRD 2θ–ω scans of the films annealed under different time and temperatures. The legend "800-2h" means annealing at 800 ° C for 2 h and so in the figures. Four main peaks corresponding to the reflections from (0 0 l) crystalline planes are visible when the annealing temperature is above 800 °C. The XRD patterns of the samples annealed at 800 ° C are zoomed-in to show that there are no visible peaks from the films.

A four-circle Bede D1 X-ray diffraction system with Cu-K_α radiation (40 kV and 30 mA) was used to identify the phases and textures of the films. The morphology and magnetic structures were measured by atom force microscopy (AFM) and magnetic force microscopy (MFM) (SPA-300HV) and transmission electron microscope (TEM) (JEM-3010). Magnetic properties of the films were measured at room temperature using SQUID (Quantum Design) with a maximum of applied field of 5 T.

3. Results and discussion

The texture of the films was characterized by 2θ–ω scans of the samples as shown in Fig. 1. Diffraction lines are clearly visible when the annealing temperature is 900 ° C and above. The intensity of the peaks is enhanced with increasing the annealing temperature as shown in the left panel of the figure. The strong (0 0 l) peaks show that the films have c-axis normal to the substrate. At 1100 ° C when the annealing time increased from 2 h to 6 h, the height of the peaks does not show significant increase. The full width at half maximum (FWHM) of the rocking curves decreases from 0.50° to 0.13° when the annealing process changes from 900 °C, 2 h up to 1100 °C, 6 h. The height of the peaks increases continuously with the increase of annealing temperature and time. The extreme narrow width (∼0.13°) of the rocking curve indicating excellent crystallization of our samples, comparable with that of the thin films with high crystalline quality prepared by pulsed laser deposition [6].

The surface morphology obtained by AFM of our sample annealed at 1100 ° C for 4 h are shown in Fig. 2 (a) and (c). The characteristic hexagonal platelets of M-type barium ferrites are clearly present. These platelets have lateral dimension of around 300 nm. Magnetic structure of the samples show bubble domains as shown in Fig. 2(b) which is the result of high magnetocrystalline anisotropy. In BaM, we have $Q = \frac{K_u}{K_d} \gg 1$, where K_u is the anisotropy coefficient, and $K_d = \frac{J_s^2}{2\mu_0}$ with J_s the saturation magnetic polarization and μ_0 the permeability in vacuum, which satisfies the criterion of bubble state [16]. The contrast is weak because of the limited thickness of the film, which produces rather weak magnetic signals to be detected.

The film and the interfaces between the film and the substrate were characterized by TEM images of the cross-section as shown in Fig. 3. The flat interface and surface of the film are clearly shown by the low magnification images in the upper-left inset in the figure. Atomically flat surfaces are evidential by the images with layer-by-layer stacking of the unit cell with total thickness of about 13.80 nm. Six layers of the unit cell is visible by the contrast of the image. The relaxation is within one unit cell of the BaM at the interface. The lattice constant in the c-axis is estimated to be about 22.996 Å from the TEM images, and 22.8 Å from the XRD diffraction peaks in Fig. 1. The value from TEM is about 0.88% smaller than the lattice constant of the bulk material with c = 23.2 Å. The lattice constant in the a-axis is about 5.65 Å, about 3.9% smaller than that of the bulk value of 5.88 Å. The selected area diffraction (SAD) patterns of the film and the substrate are shown in the bottom-right inset in the figure. The epitaxial relationship can be determined as $[0\,0\,1]_{\text{sapphire}} \,|||\, [0\,0\,1]_{\text{BaM}}$, and $[1\,1\,0]_{\text{sapphire}} \,|||\, [1\,0\,0]_{\text{BaM}}$.

Magnetic properties measured by SQUID show strong anisotropic magnetic hysteresis loops in the directions normal and parallel to the film plane as shown in Fig. 4. In the directions parallel to the film plane, the samples are not saturated even at field as high as 5 T. This is a consequence of the large magnetocrystalline anisotropy and almost perfect alignment of the hexagonal grains in this film. The extra large magnetocrystalline anisotropy may come from the diffusion of Al in the substrate

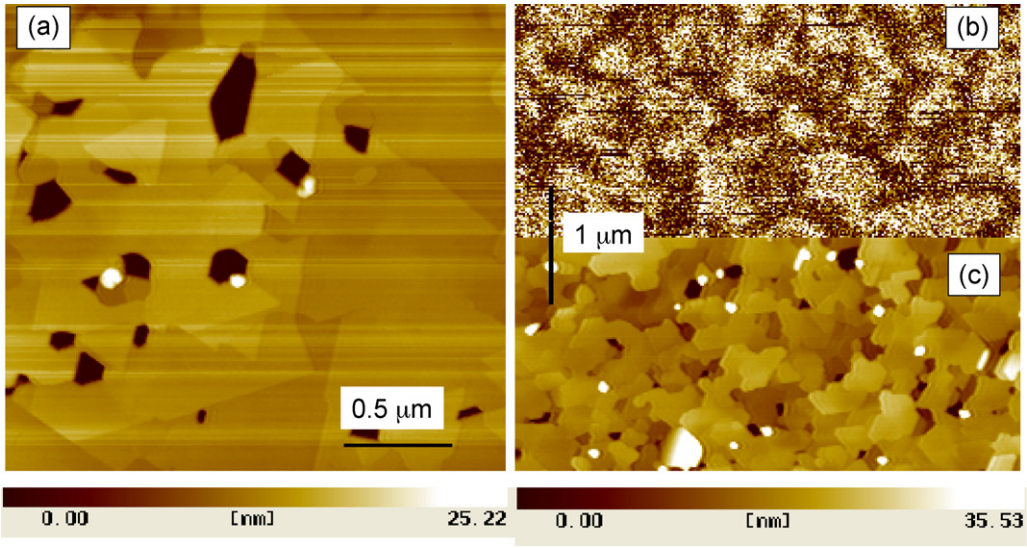

Fig. 2. Surface morphology and magnetic structure of the samples. (a) is in a smaller scale of the surface than (c). The magnetic structure of the same area of (c) is shown in (b).

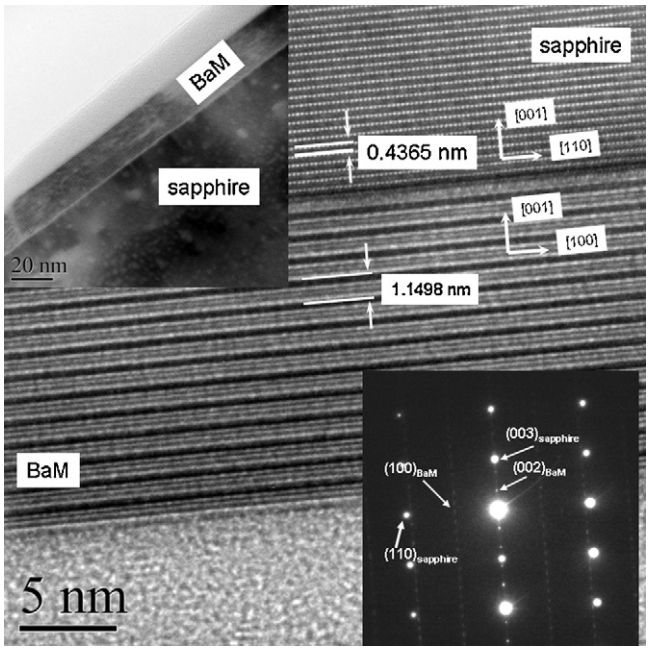

Fig. 3. TEM image of the cross-section of the samples. The upper-left inset has a lower magnification, and the bottom-right inset is the selected area diffraction (SAD) from the sample.

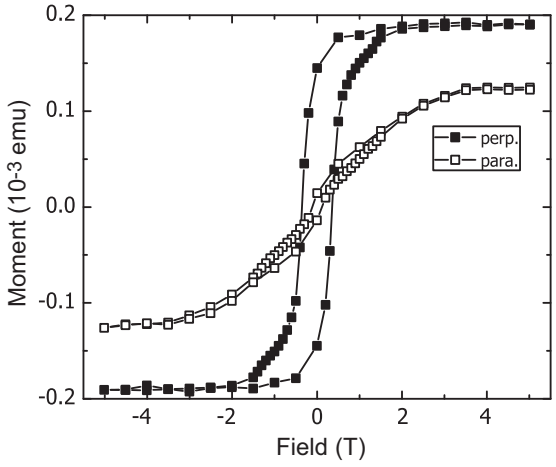

Fig. 4. Magnetic hysteresis loops in directions parallel (para.) and perpendicular (perp.) to the film plane.

under our high annealing temperature (over 1000 °C), which has been reported to be able to greatly enhance the magnetocrystalline anisotropy [17,18]. The similar behavior was also reported by other works, such as one in Ref. [6]. The intrinsic coercivity is about 302.5 kA/m in the out-of-plane direction and 87.6 kA/m in the in-plane direction.

Compared with our previous work [12] and other similar works using chemical solutions to fabricate BaM thin films [19,20], the most significance is that faceted crystallites are epitaxially grown on sapphire substrates. Platelet crystallites are the results of low nucleation rate and faster growth in the lateral directions than in the *c*-direction. The hexagonal faceted crystallites are formed when the crystal growth at or near equilibrium. In this process, the minimization of the surface energy determines the growth rate of the faces and the shape of the grains. In order to approaching the equilibrium growth, the distribution of the ions and the reaction rate must be carefully controlled. EDTA was shown to be able to bind Fe and Ba ions forming stable complexes. The distribution of the ions is expected to be homogenous.

4. Conclusion

In summary, it was shown that by using EDTA, faceted barium ferrite thin films can be grown on the sapphire (0 0 1) face. The epitaxial relationship is: $[0\,0\,1]_{\text{sapphire}} \| \| [0\,0\,1]_{\text{BaM}}$, and $[1\,1\,0]_{\text{sapphire}} \| \| [1\,0\,0]_{\text{BaM}}$. The lattice constants in both *a* and *c* directions are smaller than that of bulk crystals because of the smaller lattice constants of the sapphire. The film showed strong uniaxial anisotropy and bubble domains were formed at demagnetized state.

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