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Magnetic properties of *c*-axis oriented $Sr_{0.8}La_{0.2}Fe_{11.8}Co_{0.2}O_{19}$ ferrite film prepared by chemical solution deposition

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ABSTRACT

A $Sr_{0.8}La_{0.2}Fe_{11.8}Co_{0.2}O_{19}$ ferrite film has been prepared on a (0 0 1) sapphire substrate by chemical solution deposition. Structural characteristics indicate that the film is *c*-axis oriented and single-phase with space group $P6_3/mmc$. The grains are regular columnar with diameter between 50 and 100 nm as determined by atomic force microscopy. The sample possesses high saturation magnetization (130 emu/cm^3), high coercivity (6.9 kOe), and large squareness ratio (0.9) at room temperature, which makes it a promising recording material.

1. Introduction

For decades, M-type hexaferrites have attracted many attentions not only due to their high electromagnetic performance and excellent chemical stability of oxides at high temperature in air [1–5], but also due to high magnetocrystalline anisotropy, and high coercivity (H_c) in the form of thin film, which make them have potential applications in low-noise high-density digital recording media [6] and microwave devices due to high permittivity at high frequency [7]. In order to satisfy the requirements for high-density recording media, the films should behave high coercivity to record bits with narrow transition length and a moderate remnant magnetization (M_r) to achieve high signal to noise ratio [8].

Many groups have reported the magnetic properties and microstructure of pure M-type $SrFe_{12}O_{19}$ ferrites (SrM). However, SrM films with no substitution have met some difficulties for high-density magnetic recording, such as these films with a large positive temperature coefficient of coercivity and the overlarge grain size [9]. The improved intrinsic magnetic properties of SrM can be obtained by the partial substitution of Sr and Fe. But most of the substitutions, such as Co–Sn, Zn–Ti, and Co–Ti substitutions will reduce the magnetocrystalline anisotropy of SrM. As a result, the coercivities of the films are below 1 kOe. But future high-density recording media must have the coercivity above 3 kOe. It has recently been shown that La–Co substituted SrM have improved magnetic properties, and this improvement is associated with the increase of the coercivity and the magnetocrystalline anisotropy [10]. In addition, the magnetic properties of $Sr_{0.8}La_{0.2}Fe_{11.8}Co_{0.2}O_{19}$ (SLCFO) (x=0.2) bulks are superior to those of other substitution ratios of $Sr_{1-x}La_xFe_{12-x}Co_xO_{19}$ in previous studies [11].

In order to reduce the grain sizes of SrM films, some methods have been applied to fabricate SrM films, including the RF sputtering method [12], metal-organic chemical vapor deposition [13], and laser ablation [14]. However, most of the methods mentioned above cannot be commercially used on large-scale films on account of the requirements of high vacuum and high depositing temperature.

Based on the above considerations, in this article, the chemical solution deposition (CSD) method is introduced to synthesize SLCFO ferrite thin film on (0 0 1) sapphire substrate. The advantages of the chemical route are not only low annealing temperature in the crystallization process, but also the small size of the homogeneous grains fulfilling the need in high-density magnetic recording media.

2. Experimental

The M-type SLCFO hexagonal ferrite film was fabricated by the CSD method. The starting materials of high-purity strontium acetate [$Sr(CH_3COO)_2\cdot 1/2H_2O$, 99%, Alfa Aesar], lanthanum acetate [$La(CH_3COO)_3\cdot 5H_2O$, 99%, Alfa Aesar], cobalt acetate [$Co(CH_3COO)_2\cdot 4H_2O$, 99%, Alfa Aesar], and ferric citrate

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[$FeC_6H_5O_7 \cdot 5H_2O$, 99.5%, Alfa Aesar] were dissolved in 2-methoxyethanol at 70 °C and stirred at this temperature for 20 min. The transparent solution with brown color was further stirred at room temperature for 20 h in order to get well-mixed solution. The total concentration of the metal ions was 0.2 M. The film was synthesized by spin-coating method on *c*-cut (0 0 1) sapphire substrate using rotation speed of 4000 rpm and time of 50 s, and then dried at 300 °C for 5 min to expel the organisms. The spin-coating and dry procedures were repeated four times in order to obtain the film with desired thickness. The dried film was annealed at 900 °C in air for 20 min in order to get the crystallized film.

The crystal structure was characterized by X-ray diffractometer (XRD, Philips designed, X'pert PRO type) with CuK_α radiation (wavelength $\lambda = 1.54056$ Å) at room temperature. Field emission scanning electronic microscopy (FE-SEM, FEI designed, Sirion 200 type) was carried out to check the film thickness by the cross-section of the FE-SEM. Atomic force microscopy (AFM, Park Scientific Instruments designed, Autoprobe CP type) was used to characterize the crystallization and the orientation. Magnetic measurements were conducted with a SQUID magnetometer (MPMS, Quantum design).

3. Results and discussion

Fig. 1 shows the room temperature X-ray diffraction (XRD) pattern of SLCFO ferrite film. The peaks can be indexed to a single-phase hexagonal structure with the space group $P6_3/mmc$ apart from that of the substrate. And no additional phase is observed within the sensitivity of the experimental measurement. As seen in Fig. 1, the sample prepared by CSD shows prominent (0 0 1) lines, which indicates good *c*-axis orientation perpendicular to the film plane. This is a consequence of the fact that the *hcp* oxygen planes of the SLCFO ferrite is preferentially aligned parallel to the *hcp* oxygen plane in the *c*-plane of the sapphire [15]. The rocking curve of (0 0 $\underline{1\ 0}$) peak indicates that the film has preferential perpendicular orientation with a *c*-axis dispersion of only 2.66°. It can be explained from the viewpoint of lattice mismatch between sapphire (α-Al_2O_3) substrate and SLCFO hexaferrite. Because their lattice constants are very close and their structures are also same as hexagonal. Such a small lattice mismatch is a good prerequisite for the epitaxial film growth, which decreases the mismatch energy between the film and the substrate to a certain extent.

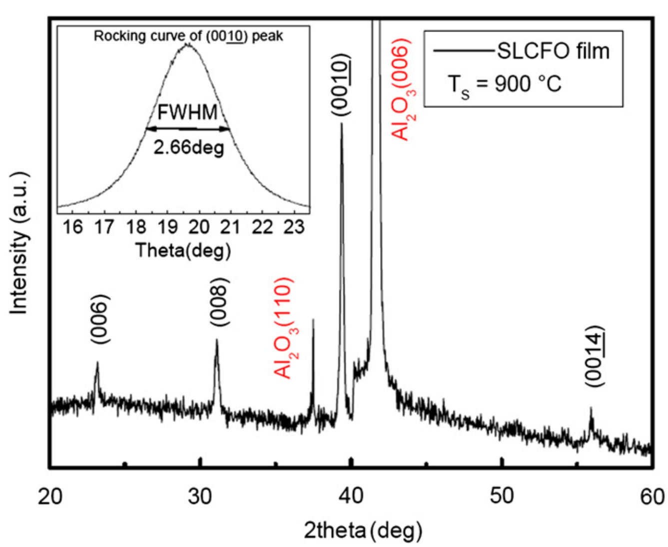

Fig. 1. XRD result of the SLCFO ferrite film annealed at 900 °C on sapphire (0 0 1) substrate. Inset: the rocking curve of (0 0 $\underline{1\ 0}$) peak of the SLCFO ferrite film.

AFM was used to measure the grain size and the surface morphology. Fig. 2(A) shows a view of 4 μm × 4 μm area of the surface of SLCFO ferrite film annealed at 900 °C on sapphire. Fig. 2(B) is taken from the Fig. 2(A) on a larger scale. As seen from the Fig. 2, the AFM result shows that the grains are regular columnar. The sizes in length are estimated to be between 100 and 500 nm, and the ones in diameter between 50 and 100 nm. Root mean square (RMS) is a term used to measure statistically the roughness of a surface. The RMS surface roughness of SLCFO ferrite film is about 16 nm. The film thickness estimated is about 500 nm according to the cross-sectional SEM micrograph [Fig. 2(C)].

To investigate the magnetic properties of SLCFO ferrite film, the temperature dependence of magnetization $M(T)$ and the applied magnetic field dependence of magnetization $M(H)$, i.e., the magnetic hysteresis loop, were measured. Fig. 3 shows the temperature dependence of magnetization $M(T)$ of SLCFO/Al_2O_3 (0 0 1) ferrite film under both zero-field cooling (ZFC) and field cooling (FC) modes at $H = 100$ Oe. As is shown in Fig. 3, on the one hand, with increase in temperature, a slight drop in magnetization occurred under both ZFC and FC modes. This demonstrates that our film shows the characteristics of stable room-temperature ferrimagnetism.

On the other hand, in ZFC/FC curves an irreversible behavior is observed, that is to say, a divergence between ZFC and FC magnetization curves. This irreversibility originates from the anisotropy barrier blocking of the magnetization orientation in the particles under ZFC mode. The magnetization direction of the particles is frozen as the initial status at high temperature [16]. A ferrimagnetic to paramagnetic transition (the Curie temperature, T_C) cannot be observed during the whole measured temperature range, which might be at higher temperature above 380 K [17].

Fig. 4 shows magnetization loops of SLCFO ferrite film grown on sapphire. Both hysteresis curves were measured using a SQUID magnetometer with the field applied parallel and perpendicular to the film plane. The remanence and saturation magnetization (M_s) and coercivity were determined after the diamagnetic background from the sapphire substrate was subtracted out. As seen from Fig. 4, the perpendicular loop shows large hysteresis, whose H_c, M_r, and M_s are equal to 6.9 kOe, 117 and 130 emu/cm^3, respectively, whereas the in-plane remanence magnetization is 89 emu/cm^3 with the coercivity of 4.5 kOe and saturates at 128 emu/cm^3. That is to say, our SLCFO ferrite film exhibits the high orientation of perpendicular magnetic anisotropy [18]. This is in agreement with the XRD result seen in Fig. 1 because the *c*-axis of the (0 0 *l*) oriented SLCFO ferrite grains is perpendicular to the film surface. It could be explained that the *c*-axis of SLCFO hexaferrite film is the magnetic easy axis, and the magnetocrystalline anisotropy field H_k (about 17 kOe) is larger than the maximum demagnetizating filed of 6.9 kOe. It is well known that the squareness ratio (SQR) is denoted by the ratio of M_r/M_s. The value is an essential measure of squareness of the hysteresis loop. Generally, large SQR value is preferred in many applications such as magnetic recording media of high density and permanent magnets. When applied magnetic fields are parallel to the film surface, that is, for H parallel to the film surface, SQR=0.7; for H perpendicular to the film surface, SQR=0.9. The values including H_c, M_r, M_s, and SQR are superior to previously reported ones [19]. These observed results indicate that our SLCFO ferrite film prepared by the CSD method might be suitable for high-density recording media and microwave and millimeter wave devices.

4. Conclusions

In conclusion, the CSD method has been used to prepare SLCFO ferrite thin film successfully. The study of XRD indicates the film is single-phase with the *c*-axis orientation perpendicular to the

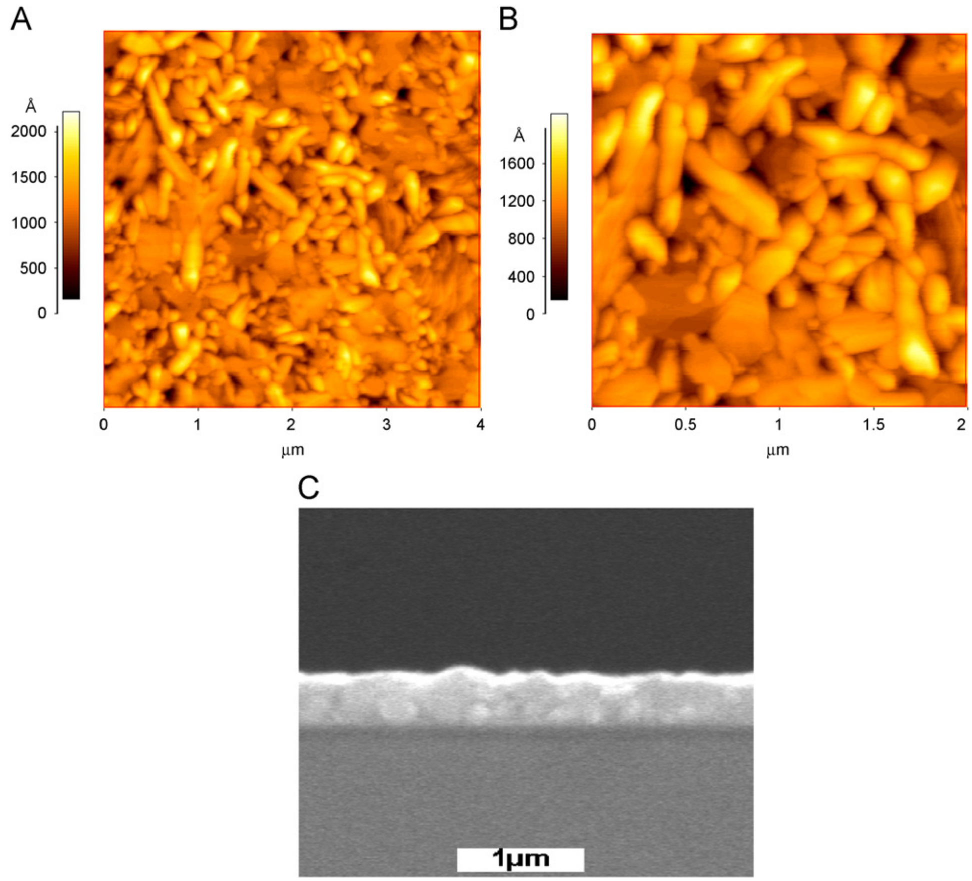

Fig. 2. Micrograph of the SLCFO ferrite film on sapphire annealed at 900 °C: (A) and (B) are 4 μm × 4 μm and 2 μm × 2 μm AFM images, respectively; (C) is the cross-sectional FE-SEM micrograph of film.

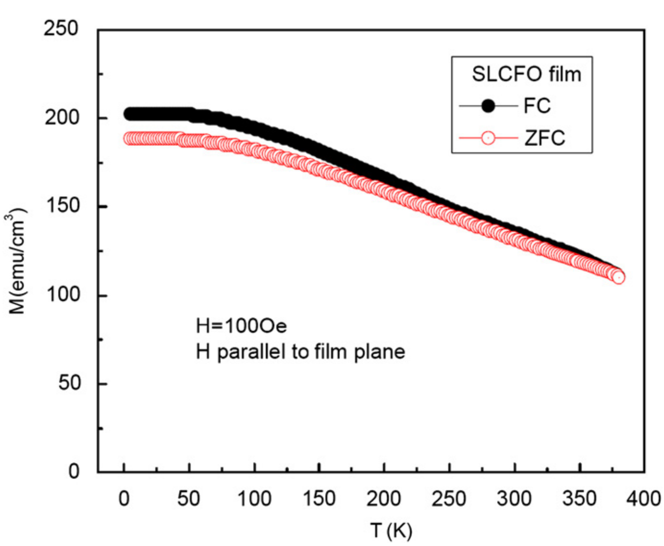

Fig. 3. Temperature dependence of magnetization $M(T)$ measured at an applied magnetic field H = 100 Oe under the measuring mode of ZFC and FC for SLCFO ferrite film annealed at 900 °C on sapphire, and H parallel to the SLCFO ferrite film surface.

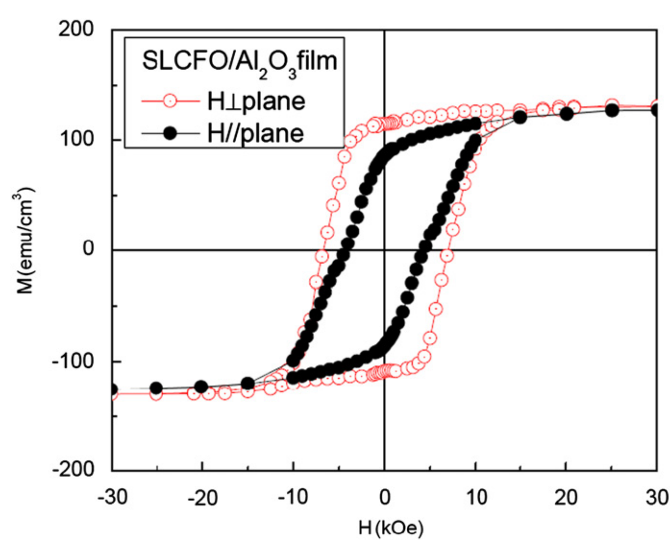

Fig. 4. Room-temperature magnetization hysteresis for magnetic fields parallel and perpendicular to the SLCFO ferrite film surface.

film. FE-SEM result shows that the thickness of the film is about 500 nm. Perpendicular-to-plane M_r and M_s values are higher than in-plane values, indicating the preferred *c*-axis orientation of magnetization in the film. The results of magnetic properties prove that the SLCFO film is perpendicular magnetic anisotropic in nature and exhibits large saturation magnetization as well as high coercivity (6.9 kOe) and large SQR (0.9), which might make it a potential candidate for use in magnetic recording media and self-biased microwave and millimeter devices.

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