

Growth of Textured CoFe₂O₄ Thin Films on Platinized Silicon Prepared by a Sol-Gel Method

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We fabricated textured polycrystalline CoFe₂O₄ thin films on Pt(111)/TiO₂/SiO₂/Si substrate through a sol-gel method. We varied the thickness of the films, by using precursor solutions with different concentrations of 0.1, 0.2, and 0.3 M, and by depositing 5, 8, or 10 layers on the substrate by spin-coating. X-ray diffraction spectra indicated that when the precursor concentration of the solution was higher than 0.1 M, the spin-coated films were preferentially oriented in the $\langle 111 \rangle$ direction. Inspection of the surface morphology by scanning electron microscopy revealed that CoFe₂O₄ thin films prepared with 0.2 M solution and 5-time spin-coatings had smoother surface, as compared to the other conditions. Each coating had an average thickness of about 50 nm. The magnetic properties measured by vibrating sample magnetometer showed magnetic anisotropy, as evidenced from the difference in the in-plane and out-of-plane hysteresis loops, which we attributed to the textured orientation of the CoFe₂O₄ thin films.

Keywords : Sol-gel, CoFe₂O₄, textured film, magnetic anisotropy

1. Introduction

Cobalt ferrite (CoFe₂O₄) is an inverse spinel material that has large magnetocrystalline anisotropy ($K_1 = +2 \times 10^6$ erg/cm³), high coercivity (5400 Oe), moderate saturation magnetization (about 80 emu/g), remarkable chemical stability, and mechanical hardness [1-4]. In the spinel CoFe₂O₄, the divalent Co²⁺ ions occupy the octahedral (B) site, while half of the Fe³⁺ ions occupy the tetrahedral (A) site, and the other half fill the octahedral (B) site. There is no net magnetic moment from the Fe³⁺ ions, because all spins of the Fe³⁺ ions in the A site and B site are parallel, but have opposite directions. Thus, the net magnetization is in particular caused by the Co²⁺ ions, which are parallel to one another.

Up to now, cobalt ferrites have been prepared in the form of nanoparticles, and of thin films. CoFe₂O₄ nanoparticles have been utilized for biological application, such as magnetically-activated drug delivery and hyperthermia [5], MRI contrast [6], and biomedicine for cancer cell [7]. A variety of methods have been employed to synthesize CoFe₂O₄ nanoparticles, such as co-precipitation

[8], hydrothermal [9], and sol-gel [10]. Moreover, CoFe₂O₄ thin films have been used for device applications, such as magnetic tunnel junction [11], anode material for Li-ion batteries [12], hybrid-data storage [13], and multiferroic magnetoelectric composite [14]. CoFe₂O₄ thin films have been prepared by several techniques, such as sol-gel methods [15-17], pulsed laser deposition [18-20], molecular beam epitaxy [21, 22], and magnetron sputtering [23]. Among these various methods, sol-gel processing has gained much interest, due to its many advantages, which include simplicity, ease of control of film composition, safety, and low cost of the apparatus and raw materials [15].

The magnetization behavior within crystalline materials can be dominated by the magnetic anisotropy. The magnetic anisotropy itself can be intrinsic, as a result of the crystal structure (magnetocrystalline anisotropy), and/or extrinsic, due to the shape anisotropy. In ferromagnetic materials, the magnetization tends to align along the easy axis, which is the preferred direction of domain magnetization. Normally, polycrystalline materials show no average magnetic anisotropy, due to random crystallographic orientation. But, conversely in textured polycrystal, it is possible to exhibit magnetic anisotropy, since the easy-axis orientation in all grains is approximately parallel [24]. Although the sol-gel method usually produce polycrystalline thin films, textured nickel and zinc ferrite thin films prepared

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using sol-gel have been reported recently [24-26]. In this work, we prepared textured CoFe_2O_4 polycrystalline thin films with preferred orientation of $\langle 111 \rangle$ on Pt(111)/ $\text{TiO}_2/\text{SiO}_2/\text{Si}$ substrates by a sol-gel method. By changing the solution concentrations as 0.1, 0.2, and 0.3 M, and the number of spin-coated layers as 5, 8, and 10, we investigate the morphology, structural property, and magnetic anisotropy of CoFe_2O_4 thin films.

2. Experimental Details

To prepare the CoFe_2O_4 thin films, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were first dissolved separately in 2-methoxyethanol, and then the two kinds of metal nitrate solutions were mixed in a molar ratio of $\text{Co} : \text{Fe} = 1 : 2$. The mixed solution was stirred for 4 h at room temperature. The concentration of the final solutions was adjusted to be 0.1, 0.2, and 0.3 M. Prior to deposition, the substrate were cleaned at 75°C in a mixture of ammonia and peroxide, and in a mixture of hydrochloric acid and peroxide for 15 minutes each, in order to improve the wetting property of the surface. The films were deposited by spin-coating, with a rotational speed of 3000 rpm for 30 s. After each coating, the films were first dried at 170°C for 10 min to evaporate the solvent, and then pre-annealed at 400°C for 10 min to exclude the organic residuals. The procedures from coating to pre-annealing were repeated up to 5, 8, and 10 times. Finally, the films were post-annealed at 700°C for 1 h in ambient air.

The crystalline structure of the films was characterized in the θ - 2θ mode by Rigaku x-ray diffraction (XRD) with $\text{Cu } K_\alpha$ radiation. The surface morphology and thickness of the films were observed by scanning electronic microscopy (SEM). Measurement of magnetization was carried out by vibrating sample magnetometer (VSM) at room temperature, with an external magnetic field of up to 1 Tesla.

3. Results and Discussion

Figures 1(a)-(f) show SEM images of the surface and cross-section of CoFe_2O_4 thin films prepared with 0.1, 0.2, and 0.3 M precursor solutions. The films were prepared with 5 time coatings. Figures 1(a)-(c) clearly show that the particle size increases as the concentration increases from 0.1 to 0.2 M, and then decreases for concentration of 0.3 M. The particle sizes are 50, 65, and 44 nm for films prepared with 0.1, 0.2, and 0.3 M, respectively. The photographic insets in Fig. 1(a)-(c) were taken after all 5 coatings and the final annealing process were completed. We observed that the film prepared with

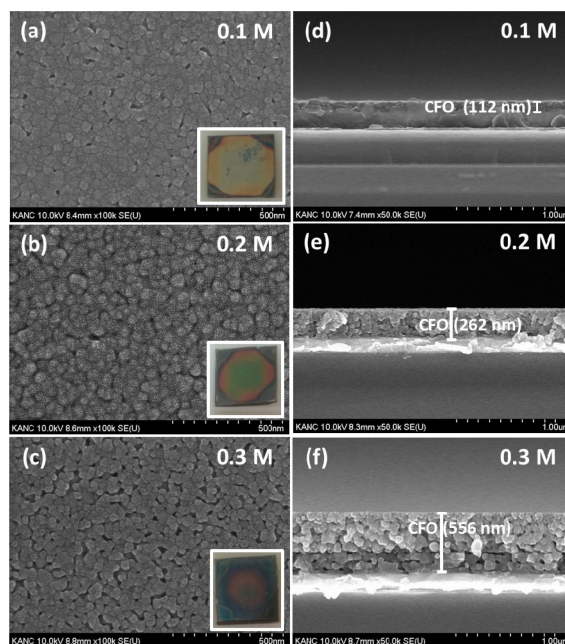


Fig. 1. (Color online) SEM images of the surface and cross-section of CoFe_2O_4 thin films prepared with different concentrations, and 5 time coatings. The photographic insets in (a)-(c) show the corresponding film surface.

0.2 M solution had the smoothest surface.

Figures 1(d)-(f) show that the thickness of the films was 112, 262, and 556 nm for films prepared with 0.1, 0.2, and 0.3 M solutions, respectively. Apparently, higher concentration of the precursor solution renders a thicker film for each coating. The average film thickness per coating was 22.4, 52.4, and 111.2 nm for 0.1, 0.2, and 0.3 M solutions, respectively. The inset photographs in Figs. 1 (a)-(c) also show the difference in thickness. The darker color indicates a thicker film. Several pinholes appear on the surface of the film shown in Fig. 1(a). These may be due to the low viscosity of the solution causing a poor coverage on the substrate surface. The film prepared with the 0.3 M precursor solution shows a few cracks in the center, which may be caused by the accumulated stress as the thickness increases. Note that the surface SEM image in Fig. 1(c) also appears more porous, as compared to the other two films in Figs. 1(a) and (b). Our results imply that 0.2 M is an optimized concentration for the preparation of CoFe_2O_4 thin films, when using 2-methoxyethanol as a solvent. This concentration may provide an appropriate reaction rate that allows enough time for grain growth to form larger-sized particles. For concentration of 0.3 M, the reaction rates may be too high to allow complete reaction and optimum bonding of atoms, resulting in particles of smaller size [27].

We then used the precursor solution with 0.2 M con-

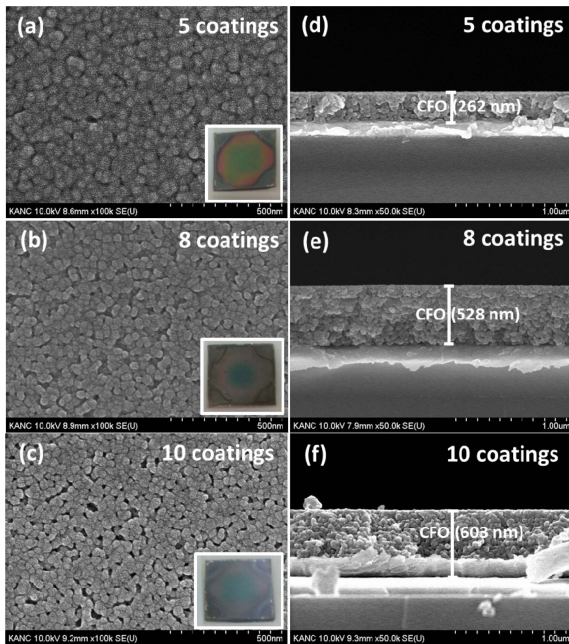


Fig. 2. (Color online) SEM images of the surface and cross-section of CoFe_2O_4 thin films prepared with 0.2 M precursor solution, and 5, 8, and 10 coating layers. The photographic insets in (a)-(c) show the corresponding film surface.

centration to investigate the effect of coating layers. The repeated coating was performed for 5, 8, or 10 times. Figures 2(a)-(c) clearly show that the surface uniformity worsens as the coating layers increase. Cracks can be observed from the SEM surface images and the inset photographs of the films prepared with 8 and 10 time coatings. The naked eye could clearly observe that the film surface becomes quite rough after coating with 10 layers. Moreover, the particle size decreases from 65 nm in Fig. 2(a) to about 45 nm for the films shown in Figs. 2 (b) and (c). Obviously, the films get thicker with more coating layers, as shown in Figs. 2(d)-(f), and the average thickness of each coating is about 50-60 nm, as estimated from the cross sectional SEM images, which is consistent with Fig. 1(e). The above discussion implies that CoFe_2O_4 thin films prepared with 0.2 M solution and 5 coating layers show the best surface morphology, as compared to the other conditions.

Figure 3(a) presents XRD spectra of films prepared with different solution concentrations. Although no peak is observed from the thin film prepared with 0.1 M solution, clear diffraction peaks that match with spinel CoFe_2O_4 (ICDD card No. 22-1088) appear in the XRD spectra for the films obtained from the 0.2 and 0.3 M solutions. Furthermore, diffraction peaks of the (111), (222), and (333) planes are all observed in addition to (311) and (440) peaks. For comparison, Fig. 3(a) also

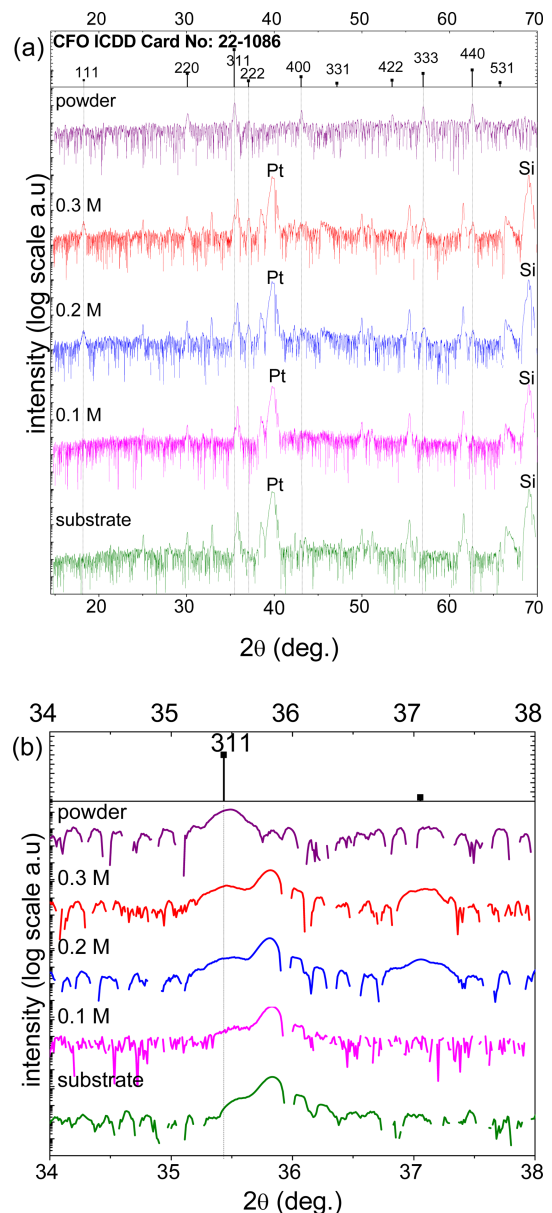


Fig. 3. (Color online) XRD spectra of CoFe_2O_4 nanoparticles prepared with 0.2 M solution, and CoFe_2O_4 thin films prepared with different precursor concentrations. (a) XRD spectra with 2θ range from 14 to 70° , and (b) Magnified view of the (311) peaks.

presents the XRD pattern of CoFe_2O_4 nanoparticles prepared with the same 0.2 M solution via a sol-gel method. We note that (311) and (440) peaks are the two strongest diffractions for the polycrystalline CoFe_2O_4 nanoparticles, whereas the (111) and (222) peaks are invisible. The difference between the XRD spectra of the CoFe_2O_4 nanoparticles and thin films implies that the CoFe_2O_4 thin films prepared by spin-coating are textured with preferential growth in the $\langle 111 \rangle$ direction. Our result is similar to

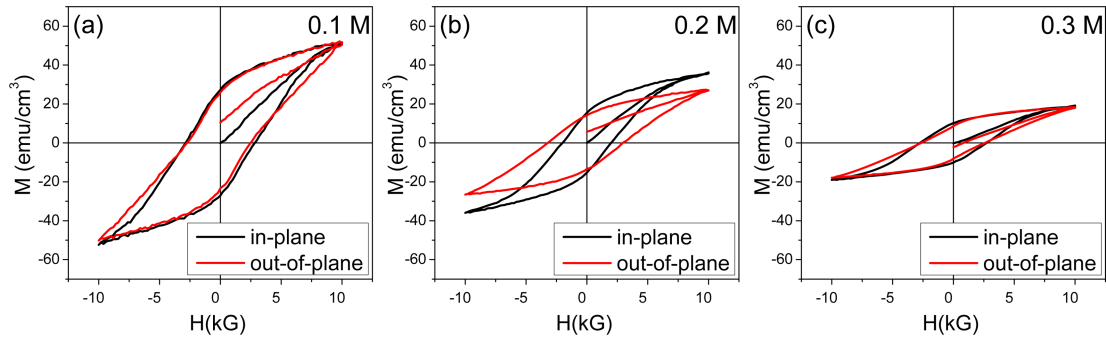


Fig. 4. (Color online) In-plane and out-of-plane M - H curves of CoFe_2O_4 thin films prepared with 5 time coating, and solutions of (a) 0.1 M, (b) 0.2 M, and (c) 0.3 M.

the textured NiFe_2O_4 polycrystalline thin film prepared by Seifikar *et al.* [24]. Figure 3(b) shows the magnified XRD spectra around the (311) peaks. As the solution concentration increases from 0.1 to 0.3 M, increase of the intensity of (311) is clearly seen.

The magnetic properties were measured at room temperature using VSM in the field range of 0-1 Tesla. The magnetic field was applied in the in-plane (IP) and out-of-plane (OOP) directions, and Figs. 4(a)-(c) show the obtained magnetization hysteresis loops, with the background data from the substrate and sample holder subtracted. The hysteresis loops show that the magnetization is not saturated at 1 Tesla. Here we take the magnetization at 1 Tesla as the saturation magnetization (M_s). Table 1 lists the values of M_s and coercivity (H_c) for IP and OOP hysteresis loops, and these values show that M_s decreases as the film thickness increases. Textured NiFe_2O_4 polycrystalline film has been reported to have similar magnetic properties, in which the magnetization decreases from about 225 to 210 emu/cm^3 , with the film thickness increasing from 50 to 150 nm [24]. Table 2 summarizes our results and other reported works on epitaxial, polycrystalline, and textured CoFe_2O_4 thin films. As evidenced from the SEM images in Figs. 1 and 2, the porosity of the thin films increases with film thickness. The much lower magnetization in our CoFe_2O_4 thin films could originate from the larger porosity and degraded crystallinity, due to

Table 1. Measured and calculated parameters for CoFe_2O_4 thin films.

Concentration	Thickness (nm)	Particle size (nm)	H_c (Gauss)		M_s (emu/cm^3)	
			IP	OOP	IP	OOP
0.1 M	112	50	2932	2549	51	51
0.2 M	262	65	2000	3046	35	27
0.3 M	556	44	2800	2600	14.3	14.3

Table 2. Comparison of magnetization at 1 Tesla with previous works.

CoFe_2O_4 Thin Film	Deposition technique	Thickness (nm)	M at 1 Tesla (emu/cm^3)		References
			IP	OOP	
Epitaxial	PLD	260	200	175	[20]
Polycrystalline	sol-gel	70	200	283	[16]
Textured	PLD	33	225	260	[29]
Textured	Sol-gel	262	35	27	This work

the much larger thickness than other reported samples.

The coercivity measures the resistance of a material to a reversed magnetic field, and usually decreases with improved crystallinity due to lesser grain boundaries [28]. It is interesting to note that the change of the coercivity with the size of the particles showed different trends for the IP and OOP directions. The IP hysteresis showed that larger particle size had larger coercivity, whereas the opposite dependence was observed from the OOP hysteresis. This can be mainly attributed to the magnetic anisotropy in the CoFe_2O_4 thin films prepared with the 0.2 M solution, because the IP and OOP hysteresis are almost the same for the films obtained with other solutions. In Fig. 4 (b), the in-plane magnetization is higher, and the coercivity is much lower than those of the out-of-plane ones, implying that the easy axis of magnetization of the corresponding CoFe_2O_4 thin films lies parallel to the in-plane direction. It is well-known that in contrast with other cubic ferrites that normally have the $\langle 111 \rangle$ direction as an easy axis, cobalt ferrite or mixed ferrite containing a large amount of cobalt usually has the easy axis in the $\langle 100 \rangle$ direction, and hard axis in the $\langle 111 \rangle$ direction [28]. The change in the magnetic anisotropy observed among the CoFe_2O_4 thin films discussed in this work also indicates that the preparation conditions and film thickness can have direct effects on the magnetic properties of

spin-coated CoFe_2O_4 thin films [16, 20].

4. Conclusion

Textured CoFe_2O_4 thin films with (111)-preferred orientation were prepared on Pt(111)/ TiO_2 / SiO_2 /Si substrates, using a sol-gel method. Spin-coating the precursor solution with a concentration of 0.2 M for 5 times resulted in a CoFe_2O_4 thin film of about 262-nm thickness. The film has a smooth surface, as evidenced from direct observation and SEM images; and the magnetic characterization revealed anisotropy, with an in-plane easy axis. CoFe_2O_4 thin films prepared using 0.1 or 0.3 M precursor solutions showed rough surface, together with the disappearance of magnetic anisotropy.

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