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Magnetic CoFe_2O_4 films with controllable dendritic arrays by a combined method of electrodeposition and anode activation

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Cobalt ferrite (CoFe_2O_4 , CFO) films with dendritic arrays were prepared on Pt/ TiO_2 / SiO_2 /Si substrates using a combined electrochemical method of electrodeposition and anode activation. First, the CoFe_2 (CF) alloy films were electrodeposited from a solution of Fe_2SO_4 and Co_2SO_4 at room temperature. Then, CFO films were prepared by anode-activating and annealing the alloy films. Effects of preparation conditions on the crystalline structure, microtopography and magnetic properties of CFO films were investigated. Interestingly, different from the reported results, smooth CFO films were obtained after annealing CF films in air, even without anodization, while controllable dendritic arrays of CFO were observed after anode-activating and annealing processes. Anodization was not necessary to form the CFO films, but had an important effect on the morphology of the CFO films, and CFO films with desirable dendritic morphology could be formed by controlling anode activation process parameters.

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Introduction

Ferrite thin films have been increasingly attracting scientific interest because of their low cost, easy manufacturing and remarkable electric and magnetic properties. Among the various ferrite materials, the spinel cobalt ferrite, CoFe_2O_4 (CFO), is a well-known hard magnetic material with wide applications due to its high coercivity, moderate magnetization saturation, remarkable chemical stability and mechanical hardness.^{1,2} It was also used in combination with ferroelectrics to produce a magnetoelectric effect due its large magnetostriction.^{3,4} In addition, CoFe_2O_4 was also studied as a potential material for gas sensors⁵ and photocatalysts,⁶ in recent years.

To meet more and more application requirements, considerable attention has been paid to understand how to control the microstructure and morphology of CFO films. CFO films could be prepared by quite a few techniques, such as sol-gel,³ hydrothermal,⁵ pulse laser deposition,⁴ sputtering⁷ and electrodeposition methods.^{8–10} Among these techniques, electrodeposition is reported to be a promising and effective method for controlling the microstructure and morphology of films by tuning many parameters, such as deposition time, temperature, pH, current and potentials. However, it is known that electrochemical deposition is often used for preparing metal^{11,12} or semiconductor films¹³ but seldom used for the preparation of insulators like complex oxides.

S. D. Sartale *et al.*^{8,9} reported the deposition of CFO thin films by an electrochemical deposition process, using electrodeposition of a CoFe_2 alloy followed by its anodization. The anodization process at ambient temperature ($\sim 27^\circ\text{C}$) was performed to form the CoFe_2O_4 films. However, some results differing from previously reported results were observed in our experiments.

In this work, using a combined electrochemical deposition process and anode activation method, CFO films with an oriented columnar morphology were prepared on Pt/ TiO_2 / SiO_2 /Si substrates. Contrary to S. D. Sartale's conclusion,^{8,9} the anodization process was not necessary to form the CFO films, but had an important effect on the morphology of the CFO films. The smooth CFO films could be obtained after annealing CoFe_2 (CF) alloy films in an air atmosphere, even without an anode activation process, while dendritic arrays of CFO were observed after anode-activating and annealing processes. X-ray diffractometry (XRD) and scanning electron microscopy (SEM) were used to characterize the crystalline structure and morphology of the films, and a vibrating sample magnetometer (VSM) was used to measure the magnetic properties of the films. The effects of electrochemical deposition conditions on the morphology and magnetic properties of CFO films were investigated.

Experimental section

Electrochemical deposition^{9,14} was carried out in a three-electrode cell linked to an electrochemical workstation (CHI660C, CH Instrument Co., Ltd., China). The Pt/ TiO_2 / SiO_2 /Si

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substrate, a platinum sheet and a saturated calomel electrode were used as the working electrode, the auxiliary electrode and the reference electrode, respectively. CoFe₂ (CF) alloy films were first deposited by the electrochemical deposition method on clean Pt/TiO₂/SiO₂/Si substrates, referring to F. Lallemand and Y. Ye's work.^{15,16} The cobalt-iron electrolyte source is an aqueous solution containing 25 mM CoSO₄ and 50 mM FeSO₄. The pH value of the solution was adjusted to 4 using 5 mM H₃BO₃. Some organic additives, including 4.4 mM saccharin, 0.28 mM sodium dodecyl benzene sulfonate (SOBS) and 10 mM sodium citrate, were added to make the films smoother and better. Saccharin was used as a brightening agent, while sodium dodecyl benzene sulfonate was used as a surfactant, and both could make the electrodeposited films brighter, smoother, more compact and more leveled. Even the presence of saccharin was helpful to achieving the preferred orientations of the CoFe₂ alloy deposition.¹⁵ Sodium citrate could chelate metal ions in the solution as a stabilizer to prevent the metal ions from oxidizing.¹⁶ The solution was stirred in a water bath at 28 °C for 3 h. Electrochemical deposition was carried out by applying constant potentials of -1.5 V to -2.1 V with a deposition time of 180 s. The distance between the substrate and the auxiliary electrode was fixed at 1.8 cm. After electrodeposition, the CF alloy films were treated with three methods, as follows: (1) anode activation, (2) annealing and (3) anode activation, and then annealing. For anode activation, the CF film with the Pt/TiO₂/SiO₂/Si substrate acted as an anode while a platinum sheet was used as a cathode. An aqueous solution of 1.5 M KOH was used as the electrolyte source. The alloy films were anode-activated using a steady current of 0.1–0.2 A for 30 min. The annealing process was implemented in air at 550 °C or 600 °C for 3 h.

X-ray diffraction (XRD; Rigaku D/MAX-RB, Japan) with Cu K α radiation was used for the phase analysis of the films at 40 kV and 30 mA. Scanning electron microscopy (SEM; INSPECTF FEI, Netherlands) was used to observe the microstructures. X-ray photoelectron spectroscopy (XPS, Kratos XSAM800, UK) was used to analyse the chemical state of the elements in the films. The magnetization of the films was characterized by a vibrating sample magnetometer (VSM, LakeShore 7410, USA).

Results and discussion

Before obtaining the CFO thin films, CF alloy films were first prepared by a usual electrodeposition method.¹⁷ Fig. 1 shows the cross-section of the CF alloy film deposited with a potential of -2.1 V for 180 s at ambient temperature (27 °C). The alloy film shows a columnar-like topography with a rough surface. The XRD pattern of the CF alloy film, in Fig. 2a, indicates that a (110) preferential orientation of the CF alloy film was easily produced with the simple electrodeposition method. By changing the deposition potential and deposition time, CF alloy films with different thicknesses can be easily obtained.

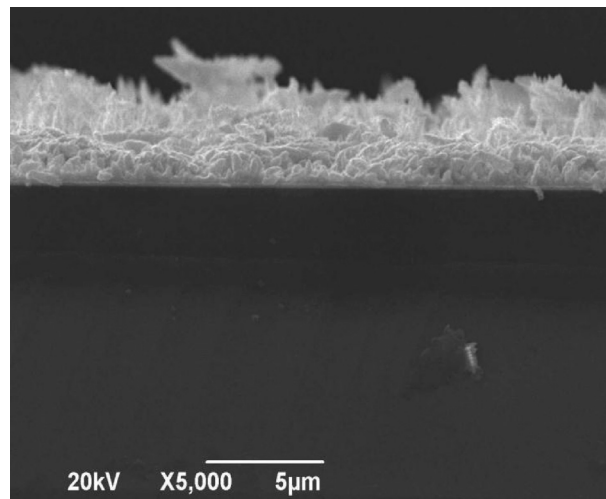


Fig. 1 SEM image of the CF alloy film prepared on the Pt/TiO₂/SiO₂/Si substrate with a deposition potential of 2.1 V and a deposition time of 180 s.

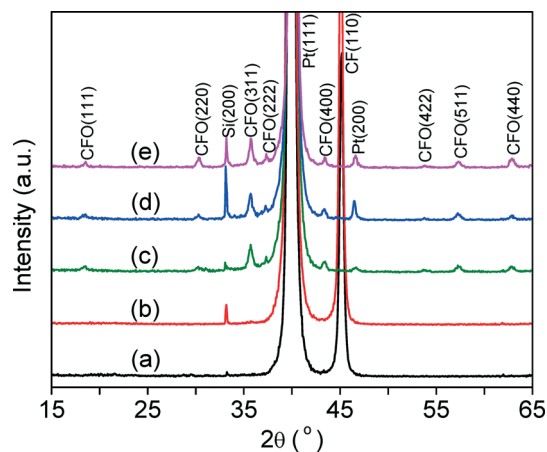


Fig. 2 XRD patterns of the films by different processes: (a) the CF alloy film by electrodeposition; (b) the anode-activating CF alloy film; (c) the film from annealing an alloy film at 550 °C without anode activation; (d) the film from annealing an alloy film at 600 °C without anode activation; (e) the film from anode-activating, and then annealing an alloy film at 550 °C.

The electrodeposited CF alloy films were treated by the following three methods: (1) anode activation, (2) annealing at 550 °C or 600 °C and (3) anode activation, followed by annealing at 550 °C, and then four different samples, as well as the untreated film, were obtained. The XRD patterns of the four samples are shown in Fig. 2b–e, respectively. It is observed from Fig. 2b that the anode-activated CoFe₂ alloy film shows the (110) peak of the CoFe₂ alloy without any obvious difference from the XRD pattern of the unactivated CoFe₂ alloy film in Fig. 2a. The result implies that the anode activation process without annealing was not able to oxidize the CoFe₂ alloy to cobalt ferrite. The films obtained by annealing with or without anode activation show good XRD peaks of cobalt ferrites, as shown in Fig. 2c–e. The peaks

correspond to the (111), (220), (311), (400), (422) and (511) planes of spinel cobalt ferrite polycrystals, in accordance with the standard PDF card (PDF# 22-1086), which indicates that the CFO films were prepared by annealing the CoFe₂ alloy films, even without anode activation. As a result, it is the annealing process, not the anode activation process that oxidizes alloy films to ferrite films. When the annealing temperature is increased from 550 °C to 600 °C, the intensity of the XRD peaks noticeably increase, which suggests that the annealing process causes better crystallization. However, comparing the two CFO films obtained from the annealing processes at the same temperature of 550 °C with or without anode activation, indicates that the CFO film obtained by anodizing, and then annealing a CF alloy film shows slightly sharper and stronger XRD peaks than the CFO film obtained by only annealing a CF film without anode activation process. This indicates that the anode activation process has an effect on the formation and crystallization of the CFO films.

In order to confirm the above results, X-ray photoelectron spectroscopy (XPS) was used to analyse the chemical state of cobalt in the CF alloy film, the anodized CF alloy film and the CFO film, as shown in Fig. 3. The same atoms had different binding energies in different chemical environments. The binding energy of Co atoms in CF alloy, Co oxides and Co ferrite should be of a certain difference. However, XPS is a surface characteristic method and only detects a rather thin layer at the surface, in which Co metal exposed to the air would be oxidized and form a surface oxide thin layer. As a result, the XPS pattern of Co metal commonly shows the binding energy peaks of Co oxides but not Co metal. As shown in Fig. 3a, the Co 2p_{3/2} peak of the CF alloy film at 780.2 eV could be divided into two peaks at 781.3 eV and 780.0 eV, which correspond to CoO¹⁸ and Co₂O₃,¹⁹ respectively. Fig. 3b shows that the Co 2p_{3/2} main peak of the anode-activated CF alloy film at 780.0 eV corresponds only to Co₂O₃.¹⁹ In addition, the spectral feature is similar to those reported by Tan¹⁹ and Kim²⁰ for cobalt oxides, which shows a shoulder peak between 784.0 eV and 788.0 eV, corresponding to the Co 2p_{3/2} satellite peak of Co₂O₃ (ref. 19) or CoO.²⁰ The above XPS peaks corresponding to Co oxides should be caused by the thin oxide layer at the surface of the alloy films exposed to air. Fig. 3c shows the Co 2p_{3/2} main peak of the film from anode-activating and annealing CF alloy film at 779.9 eV corresponding to Co atoms in the CFO film,¹⁸ as well as a shoulder peak between 784.0 eV and 788.0 eV corresponding to the Co 2p_{3/2} satellite peak of Co₂O₃ (ref. 19) or CoO.²⁰ The abovementioned XPS results indicate that the CF alloy was not converted into CFO by anode activation, which is in agreement with the XRD results in Fig. 2. According to the abovementioned XRD and XPS analysis, the anode activation process did not oxidize the CF alloy films to cobalt ferrite films, but the annealing process under air conditions did. In other words, the annealing process is necessary to prepare cobalt ferrite films, whereas the anode activation process is not.

Fig. 4 shows SEM cross-sectional images of CFO films prepared in different anode activation conditions. The CFO film obtained by annealing the CF alloy film without anode

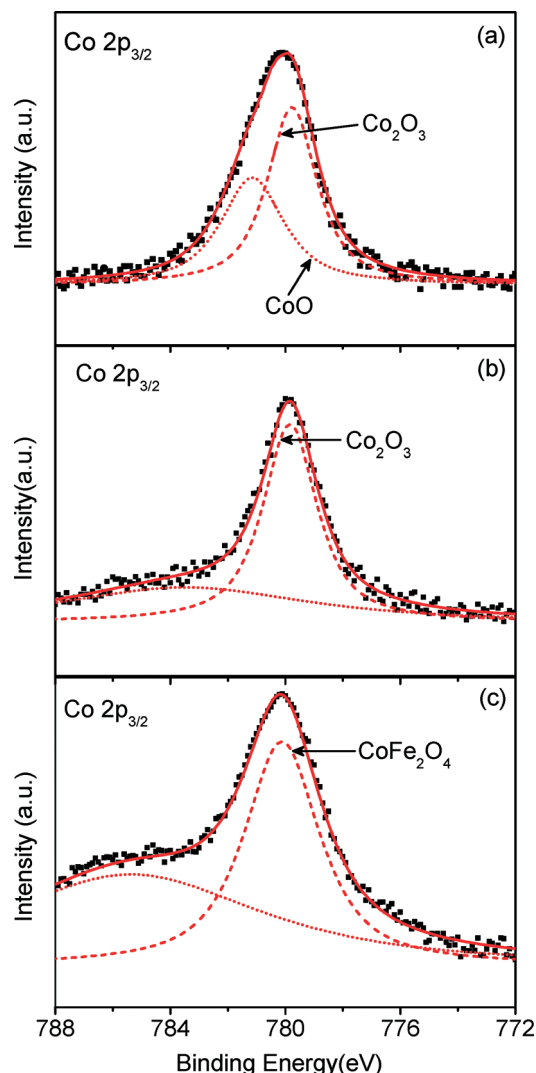


Fig. 3 XPS patterns of Co in the CF alloy film (a), the anode-activating CF alloy film (b) and the CFO films from anode-activating, and then annealing alloy films (c).

activation is a compact, smooth film with a thickness of about 3.5 μm, as shown in Fig. 4a. Fig. 4b and c are SEM cross-sectional images of CFO films prepared with the successive anode-activating and annealing of CF alloy films. The anode activation process was carried out for 30 min at a voltage of 1.0 V or 1.7 V, with an anode activation current of 0.098 A or 0.13 A, respectively. It is observed that the morphology of CFO films with anode activation is quite different from that of CFO films without anode activation, which indicates that the anode activation condition plays an important role in determining the morphology of the deposited CFO films. Obvious dendritic arrays are observed at the surface of the CFO films with anode activation, while there are still compact layers at the bottom of these films. Fig. 4b shows the cross-sectional topography of the CFO film with an anode activation voltage of 1.0 V. There is a compact layer at the bottom with a thickness of 600 nm and a non-uniform dendritic array with a maximum height of about 2.9 μm and

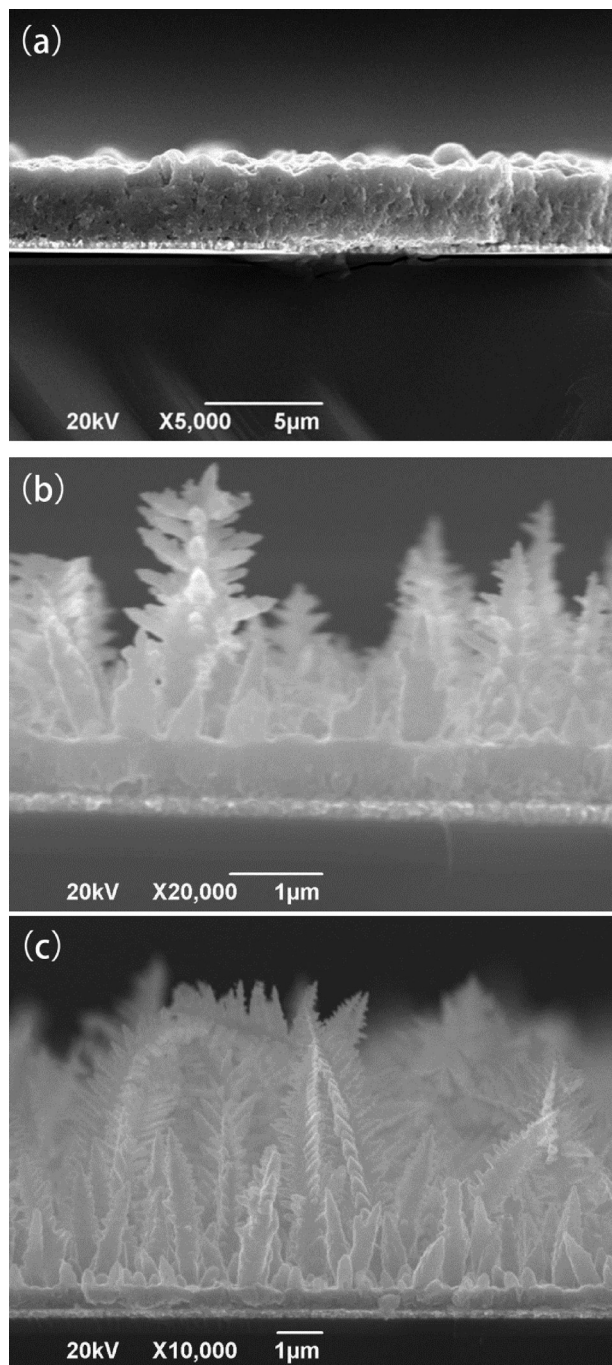


Fig. 4 SEM cross-sectional images of CFO films prepared by annealing CF alloy film without anode activation (a) and by annealing the CF alloy film anode-activated at a voltage of 1.0 V (b) and 1.7 V (c).

a maximum diameter of about 1.0 μm . When the anode activation voltage is increased to 1.7 V, the cross-sectional image of the obtained CFO film, shown in Fig. 4c, has a bottom compact layer thickness of 500 nm and a dendritic maximum diameter of about 1.0 μm , while the maximum height of the dendritic structure increases to about 6.4 μm . Among the non-uniform dendritic arrays, there coexist some salient points, columnar dendrites and even complex dendritic hierarchical structures. Concisely, when the anode activation

current increases, the height of the dendritic structure increases and the thickness of the bottom compact layer decreases. Thus, the anode activation process influences the morphology of CFO films and is demonstrated as an effective method to control the dendritic morphology of the deposited CFO films.

In order to illustrate the electrochemical growth process of CFO films, the evolution of the morphology of the films is shown in Fig. 5. Columnar CF alloy films were first obtained with a rough surface by the electrodeposition method as Fig. 5a. Actually, electrochemical deposition is a common method used to obtain metal or alloy films with a dendritic or columnar rough structure, according to the classic diffusion-limited aggregation (DLA) model.^{21,22} According to this model, the metal nanoparticles randomly deposit onto the surface from the electrolyte solution and diffuse onto the surface of the substrate. An attractive interaction between particles results in the adhesion of the particles to the growing structure, one by one, and then the formation of some type of dendrite and a rough topography. Then, when the CF alloy films are annealed in air for enough time, the CoFe_2 alloy films are fully oxidized by the following chemical equation: $\text{CoFe}_2 + 2\text{O}_2 = \text{CoFe}_2\text{O}_4$. Then, CFO films are prepared and crystallized. The films become compact and smooth to reduce the surface energy during the oxidation and crystallization process, as shown as Fig. 5b.

Electrochemical anodization is a practical oxidation method²³ and was reported by S. D. Sartale *et al.* to oxide NiFe_2 alloy to deposit spinel nanocrystalline NiFe_2O_4 thin films.¹⁰ However, when the CF alloy films were anodized in KOH solution according to the method reported by S. D. Sartale *et al.*,^{8,10} the CF alloy films were not oxidized to cobalt ferrite, as indicated in the XRD patterns (Fig. 2) and XPS results (Fig. 3), but the surface topography of the films was significantly changed into dendritic structures. Thus, here the phase of anode activation was used, as shown in Fig. 5c. The formation of dendritic structures can be explained as a consequence of a non-uniform electric field at the rough surface.

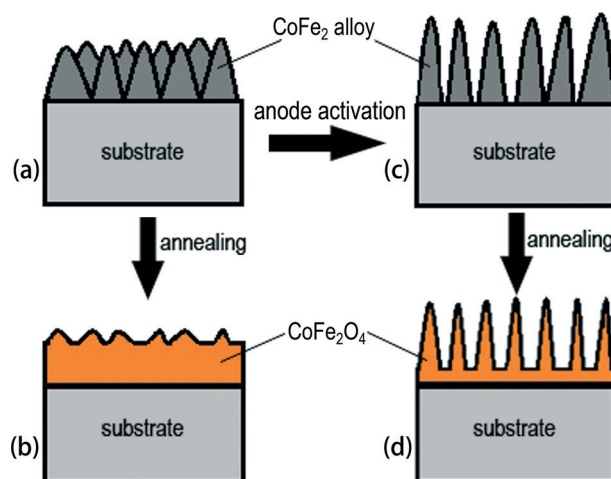


Fig. 5 The electrochemical growth process of CFO films.

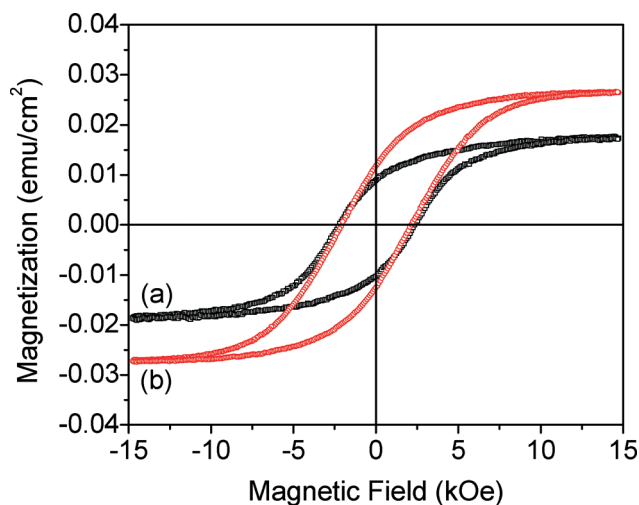


Fig. 6 Out-of-plane magnetic hysteresis loops of the CFO films by annealing the CF alloy film anode-activated at voltage of 1.0 V (a) and 1.7 V (b).

During the anode activation process, the rough CF film with the Pt/TiO₂/SiO₂/Si substrate acts as an anode electrode. There are some sharp points at the surface of the rough films. When applying an electric field, high electric fields will form at the sharp points. As a result, the electrolytes preferentially aggregate at the sharp points under the high electric field. The non-uniform growth on the anode electrode leads to the formation of dendritic structures. Finally, annealing in air is necessary to oxidize the anode-activated CF alloy films with dendritic structures and prepare dendritic CFO films. During the annealing process, the CFO films tend to become smooth and compact in order to reduce the surface energy. Consequently, a compact layer is formed at the bottom of the film, with a dendritic surface topography resulting from the anode activation process, as shown in Fig. 4.

Fig. 6 shows the typical magnetic hysteresis loops of the dendritic CFO films obtained with a magnetic field of up to 15 kOe by applying magnetic fields perpendicular to the film plane (out of plane). The high magnetic coercive fields (H_c) of 1880 Oe and 1950 Oe are observed from the loops of the CFO films formed by annealing the CF alloy film anode-activated at voltages of 1.0 V and 1.7 V, respectively, which agrees with the coercivity of the CFO films by a sol-gel processing in our previous work.³ The high H_c of the films further indirectly confirms that the prepared films are cobalt ferrite films and not CF alloy films, which are soft magnetic materials with low coercivity. Though the CFO films show different topographies and dendritic heights, they are prepared by anodizing CF alloy films of the same thickness. It is difficult to calculate the actual volume of the dendritic CFO films, and the magnetization of the CFO films is shown in emu cm^{-2} to define the magnetization of a film per unit area, as shown in Fig. 6. It can be observed that the magnetization of the dendritic CFO films increases with increasing height of the dendritic structure, which can be attributed to the differences in height of the dendritic array between the different CFO films.

Conclusion

In conclusion, high-quality cobalt ferrite films with differing topography can be prepared by a combined electrochemical method of electrodeposition and anode activation. First, the CoFe₂ alloy films with columnar rough structure can be electrodeposited according to the classic diffusion-limited aggregation model. Then, the smooth compact CFO films can be obtained by directly annealing CF alloy films in air without anode activation. Anode activation processing can change the morphology and form dendritic CFO films as a consequence of non-uniform electric field at the rough surface, but it cannot oxidize CF alloy films, which is interesting and different from the previous reports. The dendritic CFO films show high coercivity and good magnetization. This study demonstrates that the controllable dendritic topography of cobalt ferrite films can be obtained by a simple electrochemical method and gives some helpful enlightenment for developing new applications for cobalt ferrite films.

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