Journal of Alloys and Compounds 729 (2017) 730–734

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

Microstructure refinement and magnetization improvement in CoFe thin films by high magnetic field annealing

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ARTICLE INFO

Article history:
Received 27 March 2017
Received in revised form
20 September 2017
Accepted 21 September 2017
Available online 22 September 2017

Keywords:
Magnetic field annealing
CoFe
Thin films
Ferromagnetism
Chemical solution deposition

ABSTRACT

Co-Fe alloy thin films with high magnetization are desirable in numerous applications. Co-Fe thin films prepared by solution methods with refined microstructures have not been achieved up to now. Here, high magnetic field annealing (HMFA) is introduced for the preparation of $Co_{70}Fe_{30}$ alloy thin films. The effects of HMFA on their microstructures and room temperature magnetic properties are investigated. The thickness of the derived $Co_{70}Fe_{30}$ thin films is dramatically decreased from a value of 590 nm without HMFA to 320 nm with 7 T magnetic field annealing, and the refinement of microstructures is also observed with HMFA. The derived $Co_{70}Fe_{30}$ film annealed under 7 T magnetic field exhibits a saturation magnetization of ~2.43 T, close to the theoretical value of 2.45 T. Overall, HMFA provides a feasible way to fabricate larger-area and denser Co-Fe thin films with excellent magnetic properties.

1. Introduction

As an important type of transition metal alloy, CoFe binary alloys show excellent soft magnetic properties, including high saturation magnetization, low coercivity, high permeability, good thermal stability, and giant magnetostriction [1–6]. Hence, CoFe-based nanoparticles and thin films are considered as promising candidates for a number of applications in the fields of magnetic data storage, nanocomposite permanent magnets, high frequency apparatus, catalysts, etc [7,8]. Additionally, as one type of electromagnetic wave absorption material, the main absorption band and intensity can be obviously controlled by varying the Co/Fe molecular ratio and the microstructures [9,10]. Currently, various methods, including both physical and chemical routes, have been used to prepare CoFe alloy thin films [1,11–16]. Compared with the physical methods, the chemical solution methods have several advantages, such as low-cost, large-scale fabrication, and easy control from the view-point of applications [17]. Nevertheless, CoFe alloy thin films derived by chemical solution methods such as electrodeposition usually show loose and/or porous microstructures, resulting in low magnetization [18–20]. To improve the performances of CoFe alloy thin films, it is crucial to improve the thin film density. The common route to enhancing density is to increase the grain size by prolonging the dwell time during annealing or increasing the annealing temperature, although the applications of CoFe alloys with large grain size are limited. Thus, it is very vital to prepare CoFe alloy thin films with refined microstructures by solution methods to make them suitable for a wide range of applications.

Previous theoretical calculations have suggested that high magnetic field annealing (HMFA) can strongly affect the microstructure as well as the magnetic properties of Co-Fe alloys [21]. Experimentally, low magnetic field (no more than 1 T) annealing has been used to improve the microstructures and properties of electrodeposited CoFe alloys thin films in recent years. In CoFe thin films, a changed structure and an enhanced deposition mass are observed when they are fabricated by an electrochemical method in an applied field of 500 mT [22]. An increased compressive stress was induced in $Co_{0.3}Fe_{0.7}$ thin films by post-deposition field-annealing in 100 Oe from 100 to 400 °C [23]. With 10 kOe magnetic field annealing, FeCo films achieved desirable, thermally stable

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https://doi.org/10.1016/j.jallcom.2017.09.227
0925-8388/

properties for high frequency functions [17]. Due to the low applied magnetic fields, however, investigations of the magnetic annealing effects have been limited. Thus, a further investigation of HMFA effects on the grain growth, the microstructures, and the magnetic properties of CoFe alloys thin films is desirable.

In this work, polycrystalline $Co_{70}Fe_{30}$ (CF) thin films have been prepared by chemical solution deposition on yttrium stabilized zirconia (YSZ) substrates. The HMFA effects on the grain growth, the microstructures, and the magnetic properties of the thin films are investigated. Due to the enhancement of nucleation and the extra grain growth force induced by the magnetic field, the grain growth rate is enhanced, resulting in variation of the microstructures for the derived thin films. CoFe thin films with refined microstructures, enhanced thin film density, and high saturation magnetization close to the theoretical value can be prepared by HMFA processing.

2. Experiment

The amorphous CF thin films were deposited on the YSZ single crystal substrates by chemical solution deposition (CSD). The CF precursor solution with a concentration of 0.01 M was prepared from cobalt (II) acetate anhydrous and iron (III) nitrate nonahydrate as precursor salts, and 2-methoxyethanol as a solvent. The precursor was spin-coated onto the YSZ substrates with a rotation rate of 5000 rpm for 10 s, and then baked at 150 °C for 2 min. A further pyrolysis treatment at 400 °C for 10 min in air was carried out to remove the organic residues. To enhance the film thickness, the above processing was repeated eight times. Finally, each thin film was annealed at 700 °C in a forming gas (ratio of N_2:H_2 4:1 v/v) for 60 min under magnetic fields of 0, 1, 3, 5, or 7 T, where the magnetic field was parallel to the thin film surface. In the annealing processing, the precursor network collapses, and the final CoFe phase will nucleate and grow, resulting in different thin film thickness. Due to the high magnetic field effects on the increased nucleation and grain growth, the collapse of the precursor network is more severe, and the thin films become denser, which leads to the decrease in thin film thickness under the HMFA processing. The derived thin films at each corresponding magnetic field (in Tesla) are respectively labeled as CF0, CF1, CF3, CF5, and CF7. Glancing angle X-ray diffraction (XRD) was performed with monochromatic Cu K_α radiation on an X'pert Pro machine (PANalytical B. V., Almelo, Netherlands) to investigate the phase and quality of the derived thin films. The surface morphology and thickness were determined using a field-emission scanning electron microscope (FE-SEM, SU8020, Hitachi, Japan). The in-plane microstructure was characterized by a transmission electron microscope (TEM, JEM-2010, JEOL, Japan). Magnetic properties at room temperature were measured with a superconducting quantum interference device (SQUID) (MPMS XL5, Quantum Designed, USA).

3. Results and discussion

The glancing angle XRD patterns of the derived CoFe (CF) thin films annealed under different high magnetic fields are shown in Fig. 1. All the diffraction peaks match well with the pattern of bulk body-centered cubic $Co_{70}Fe_{30}$ (JCPDS 048-1818), which well agree with the reference data [24]. Notably, all thin films exhibit a strong (110) diffraction peak and two weak diffraction peaks, suggesting the polycrystalline nature of the as-prepared CF thin films. The lattice constant of all the derived CF alloy films is approximately 0.284 nm, which is similar to that of the electrodeposited CF [25] and shows no changes with increasing the magnetic field. The average crystallite size was estimated by the Scherrer Equation, and the results are shown in the inset table of Fig. 1. As shown in the table, the average crystallite size decreases initially and then increases with increasing magnetic field. The initial decrease in the crystallite size with increasing magnetic field indicates that high magnetic fields can affect the CF thin film nucleation. The following increased crystallite size with further increase in the magnetic field suggests that the grain growth is obviously affected by the applied magnetic field.

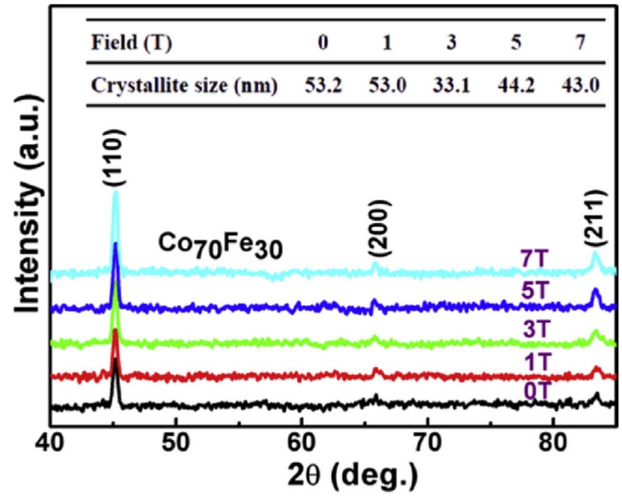

Fig. 1. Glancing XRD patterns for the CF thin films annealed under different high magnetic fields. The average crystallite size is listed in the inset table.

Surface and cross-sectional FE-SEM images of the as-prepared CF thin films annealed under different high magnetic fields are shown in Fig. 2(a–e) and (f–k), respectively. Usually, the thin film particle size, with each particle containing several crystallites, as shown in Fig. 2(a–e), decreases initially and then increases with increasing magnetic field. The variation in the particle size corroborates the results shown in the inset table of Fig. 1. Additionally, some pores exist in the thin film CF0 without HMFA, as shown in Fig. 2(a), which may be caused by the removal of the organic residues at high annealing temperature. Interestingly, the pores are notably reduced under low magnetic field annealing (LMFA) and even eliminated under HMFA. Additionally, in the case of the CF thin films annealed under higher magnetic fields, some much larger particles are observed, as shown in Fig. 2(d) and (e), indicating the existence of abnormal grain growth [26]. The occurrence of abnormal grain growth suggests that a compressive strain is always induced during the CF thin film grain growth. In contrast, as shown in Fig. 2(f–k), the thickness of the prepared CF alloy thin films decreases from 590 nm for the CF0 film to 320 nm for the thin CF7 film. The obvious reduction in thickness indicates that thin film density increases with HMFA. During the processing, the magnetic field can enhance the nucleation rate and the grain growth rate, which leads to the changes in the grain size and particle size. Due to the enhancement of nucleation and grain growth, the pores in the thin films will be reduced, resulting in denser and thinner thin films. Thus, the loose CF alloy thin films can be drastically densified by HMFA processing.

To further investigate the HMFA effects on the microstructure and the surface morphology of the thin films, TEM observations of the derived CF0 and CF5 thin films were carried out, and the results are shown in Fig. 3. The selected area electron diffraction (SAED) pattern of the CF0 film and the high-resolution TEM (HRTEM) image of the CF5 thin film are displayed in the corresponding insets of Fig. 3. The clearer and sharper inner reflections, as shown in the SAED pattern, imply better crystallization and a body-centered cubic structure for the derived CF thin films. Clear lattice strips with lattice fringe spacing values close to the bulk lattice constant