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Tuning microstructure and magnetic properties of electrodeposited CoNiP films by high magnetic field annealing

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ABSTRACT

A high magnetic field (up to 12 T) has been used to anneal 2.6-μm-thick $Co_{50}Ni_{40}P_{10}$ films formed by pulse electrodeposition. The effects of high magnetic field annealing on the microstructure and magnetic properties of CoNiP thin films have been investigated. It was found that a high magnetic field accelerated a phase transformation from fcc to hcp and enhanced the preferred hcp-(002) orientation during annealing. Compared with the films annealed without a magnetic field, annealing at 12 T decreased the surface particle size, roughness, and coercivity, but increased the saturation magnetization and remanent magnetization of CoNiP films. The out-of-plane coercivity was higher than that the in-plane for the as-deposited films. After annealing without a magnetic field, the out-of-plane coercivity was equal to that of the in-plane. However, the out-of-plane coercivity was higher than that of the in-plane when annealing at 12 T. These results indicate that high magnetic field annealing is an effective method for tuning the microstructure and magnetic properties of thin films.

1. Introduction

CoNiP thin films have been widely used as micro-electro-mechanical system devices, magnetic recording media, corrosion resistance media, wear resistance media, and diffusion barriers because of their excellent properties [1–4]. Because the properties of CoNiP thin films are closely related to their microstructure (such as crystallographic structure and surface morphology), many experimental techniques have been performed to produce these films with the desired properties. Electrodeposition has attracted much attention because it is mature and low-cost and offers the ability to tailor the microstructure of CoNiP films [2,5]. Tuning the microstructure of CoNiP films by varying electrochemical parameters (e.g., pH, current density, organic additives, and temperature) has been widely studied [5–7]. Additionally, post-annealing for the as-deposited CoNiP films has also proven to be a promising method for tuning the microstructure and properties [8–11].

Recently, a high magnetic field, based on the roles of magnetic force, Lorentz force, magnetic torque, and magnetization energy, has been applied to the fabrication of thin films [12–14]. High magnetic field annealing has a significant effect on crystallographic structure [15,16] and surface morphology [16,17] of thin films. For P-rich $Co_{45}Ni_{37}P_{18}$ films [18], high-magnetic field annealing was shown to be an effective method to tune their microstructures. However, the phases of these annealed films were so complex that they were not suitable for studying the influence of the high magnetic field on the magnetic properties of CoNiP films. Thus, CoNiP thin films with lower P content have been annealed under a high magnetic field in this paper. The effects of the high magnetic field on the evolution of the microstructural and magnetic properties have been studied.

2. Experimental procedure

The 2.6-μm-thick $Co_{50}Ni_{40}P_{10}$ films were obtained by electrodeposition from an aqueous solution containing 30 g/L $CoSO_4\cdot 7H_2O$, 240 g/L $NiSO_4\cdot 6H_2O$, 40 g/L $NiCl_2\cdot 6H_2O$, 30 g/L H_3BO_3, 30 g/L NaH_2PO_2, and 0.1 g/L $C_{12}H_{25}NaO_4S$. All experiments were performed at room temperature and pH 3.7 for 30 min. Pulse current with a 1:5 duty ratio was used, and the maximum current density was 5 mA/cm^2. A 1×2 cm^2 nickel electrode was used as an anode. The cathode was a Cu plate (1×1 cm^2) with Ni (60 nm) as a seed layer [13]. The as-deposited samples were annealed at 673 K for 4 h under a protective atmosphere of high-purity argon in a

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vertical furnace, which was placed inside a super-conducting 12 T magnet; the magnetic field direction was perpendicular to the films.

Film thickness and composition were measured using a SUPRA 35 field-emission scanning electronic microscope equipped with an energy-dispersive spectroscopy device. The crystallographic structure was detected by grazing incidence X-ray diffraction (XRD) using an Ultima IV with Cu Kα1 radiation, and a standard Rietveld method was applied to fit the patterns of the annealed films. Surface morphologies and section profiles were obtained using a Multimode IV atomic force microscope (AFM). Magnetic hysteresis loops of the samples were measured using a Lakeshore 7407 vibrating sample magnetometer; the demagnetization correction was applied, and at least three samples obtained under the same conditions were measured.

3. Results and discussion

3.1. Phase composition

The XRD patterns of CoNiP films are presented in Fig. 1. According to the standard Powder Diffraction File (PDF#74-5694 and PDF#71-7353), the as-deposited CoNiP films were indexed as fcc crystallographic structures with peaks of (111) and (200), the so-called high temperature γ-phase of Co-based alloys. After annealing at 673 K, the low-temperature ε-phase with hcp crystallographic structure was detected. The phases of CoNiP thin films were dependent on the composition and preparation process; the composition of the as-deposited and annealed thin films was $Co_{50}Ni_{40}P_{10}$ (atom percentage with 1.5% error), which can exhibit both ε- and γ-phases [6]. In this paper, the electrodeposited CoNiP film was known to produce the γ-phase [19]. During annealing, the γ-phase would transform to the ε-phase during the cooling process, and the phase content of the ε-phase was dependent on the cooling conditions [20,21].

To quantitatively analyze the weight percentage of the γ- and ε-phases in annealed films, a standard Rietveld method was applied to fit the patterns. In Fig. 1, the red lines are the fitted patterns and the blue lines are the difference patterns between measured and fitted patterns. Clearly, the fitted patterns agreed well with the measured patterns (black line), weight percentage of films annealed at 12 T (50.0%) was higher than that at 0 T (22.6%). This result indicated that the phase transformation from γ to ε was accelerated by the magnetic field, which was caused by the magnetic field-induced magnetocrystalline anisotropy energy during the cooling process, similar to anisotropic field-induced martensitic transformation in Co and Co alloys [20,21]. The phases of the annealed $Co_{50}Ni_{40}P_{10}$ films were not the same as those in Ref. [18] because the phosphide (fcc-Ni) did not precipitate after annealing. This occurred because the P content in this study (10 at%) was lower than that of Ref. [18] (18 at%), and similar to NiP alloys [22,23], the nickel precipitated would not precipitate at 673 K when the P content was approximately 9.1 at%.

3.2. Grain size and orientation index

The textures of the films were calculated by the orientation index M, $M_{hkl}=[I_{hkl}/\sum I_{h'k'l'}/[I_{hkl}^{0}/\sum I_{h'k'l'}^{0}]]$, where I^0 is the standard X-ray diffraction intensity (γ-phase, PDF#74-5694. ε-phase, PDF#71-7353) and I is the experimental data; the results are shown in Fig. 2(a). The M value of fcc-(111) from the as-deposited CoNiP film was greater than 1, which means the as-deposited film has a (111) texture. However, the (111) preferred orientation of the γ-phase disappeared after annealing. The M value of hcp-(002) increased from 2.1 without a magnetic field to 3.2 with a 12-T

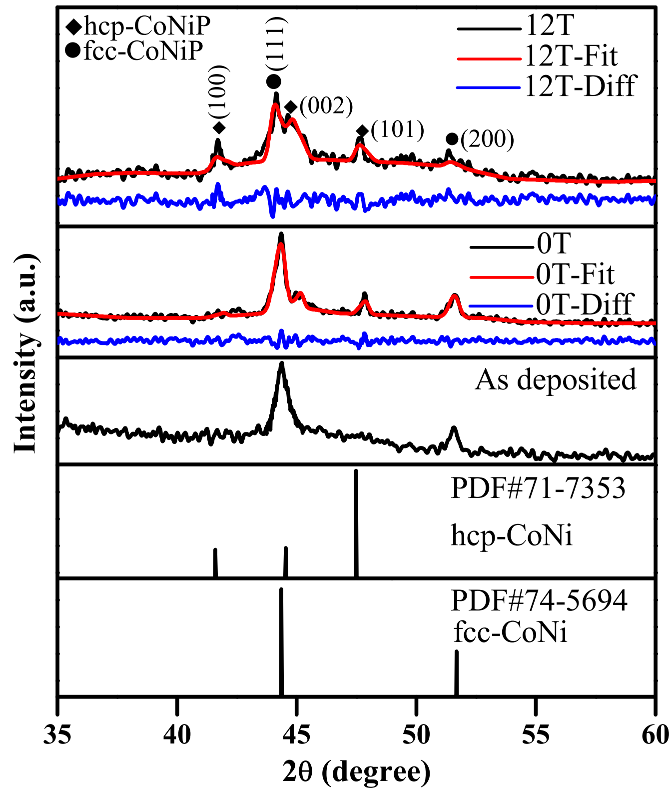

Fig. 1. XRD patterns of as deposited and post-annealed CoNiP films. (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)

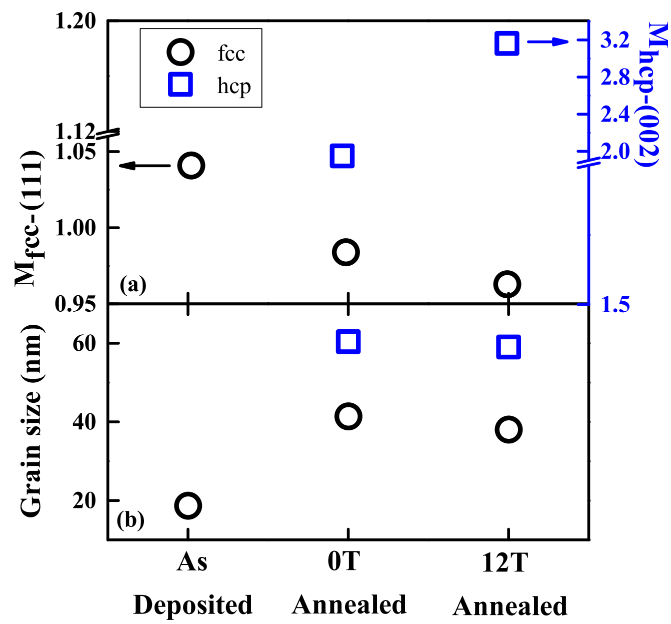

Fig. 2. (a) Orientation index M and (b) grain size of as-deposited and post-annealed CoNiP films.

magnetic field, which means the ε-phase showed a (002) preferred orientation in annealed CoNiP films [6]. More noteworthy, the 12-T magnetic field, which enhanced the (002) preferred orientation during annealing, was the reason that ⟨001⟩ was the easy magnetization axis of the ε-phase. The grain size D of films can be calculated using the Scherrer formula, $D=K\lambda/\beta\cos\theta$, where λ is the X-ray wavelength ($\lambda=0.154056$ nm), θ is the diffraction angle, and β is the full width at half-maximum. The grain size values are