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A novel CoCuP electrodeposited film with improved planar hard magnetic properties and film quality

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ABSTRACT

We designed to add Cu into Co-P hard magnetic films prepared via electroplating. The purpose was to make use of immiscibility between Co and Cu, hoping that Cu will segregate at Co-grain-boundaries to mediate magnetic decoupling. Copper is found very difficult to co-electrodeposit with Co due to the large difference in the reduction potentials. A slight variation of $CuSO_4$ concentration in the electrolyte from 1 mM to 2 mM results in a big difference of Cu content from 3.8 wt% to 13 wt% in CoCuP films. However, the CoCuP films are amazingly crack-free up to a thickness no less than 6 μm. The films electroplated with $CuSO_4$ concentration 1.3 mM at pH 4.7 and 25 °C have a Cu content 5.5 wt%, P content 3.1 wt% and exhibit the best magnetic properties. The in-plane magnetic properties are Hc 360 Oe, Br 7450 G, and (BH)m 1.21 MGOe. The perpendicular ones are Hc 800 Oe, Br 1600 G, and (BH)m 0.35 MGOe. The evolution in film composition, microstructure and crystal structure well explains the variation in resultant magnetic properties. These films are readily applicable in mini- and micro-devices which need in-plane magnetic performance.

1. Introduction

Hard magnetic films have been extensively studied in recent years. Those films with plausible magnetic properties have wide applications in mini-/micro-electro-mechanical systems (MEMS), micro actuators, magnetic encoders, and sensors due to the distinct magnetic force conferred at a distance [1–6]. Nowadays, researchers make efforts to produce films that possess high magnetic performance by different processes such as sputtering, pulsed-laser deposition (PLD), electroless plating, and electroplating. Grapes et al. [3] pointed out that the film structure was amorphous by PLD and sputtering processes. Therefore, annealing is required to crystallize the magnetic films. However, annealing at high temperatures is unsuitable for many materials used in the fabrication of MEMS and related components. Thus electroplating is considered favorable for the hard magnetic films for use in MEMS, micro devices and components because of its scalable and controllable process parameters.

Electroplated magnetic films are usually cobalt-rich alloys, including CoP, CoNiP, CoMnP, CoNiMnP, CoPt, CoPtP, and etc. [7–10]. Luborsky et al. found that the non-magnetic elements tend to segregate at grain boundaries to impede grain growth during electroplating, resulting in small grains, which, in turn, enhances the film coercivity by increasing the number of non-magnetic segregating sites [3,11]. However most electroplated magnetic films contain a large amount of micro-cracks which result in a lot of drawbacks. This is a long annoying problem specifically at films thicker than 1 μm. The purposes of current study were three folds. The first was to make use of immiscibility between Co and Cu, hoping that Cu will segregate at Co-grain-boundaries to mediate magnetic decoupling. The second was to study magnetic performance of the novel electroplated CoCuP films thereof. The third was to explore the possibility to affect film quality, such as finer grains or others, due to the new additive Cu.

To address the large number of synergistic electroplating parameters simultaneously is generally difficult. In this study, we aimed to explore the effect of specific parameters, including electrolyte concentration, pH value and bath temperature, on magnetic properties of the electrodeposited CoCuP films. Thickness, crystal structure, composition, magnetic properties, and surface morphology of the electroplated films were investigated in details.

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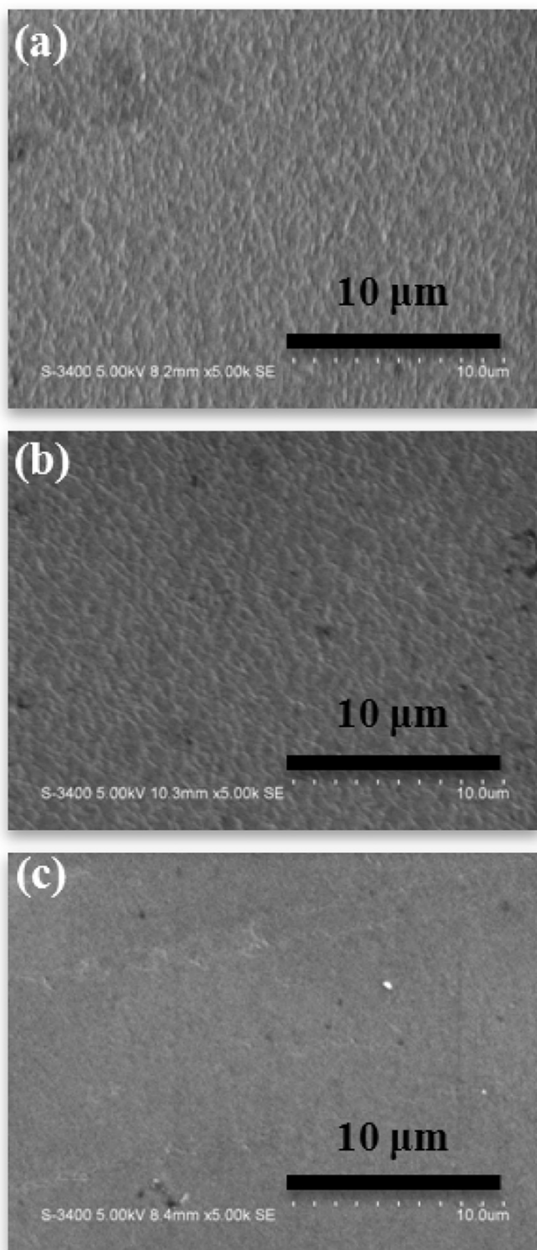

Fig. 1. Surface morphology of the CoCuP films electroplated in the bath with [$CuSO_4$] at (a) 1.0 mM, (b) 1.5 mM, and (c) 2.0 mM.

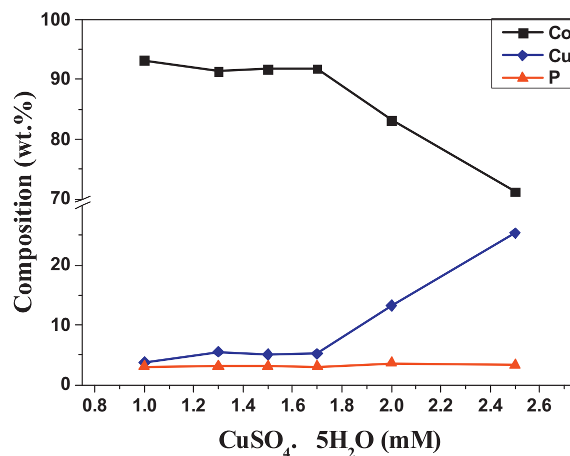

Fig. 2. The dependence of film composition of the CoCuP films on [$CuSO_4$] concentrations.

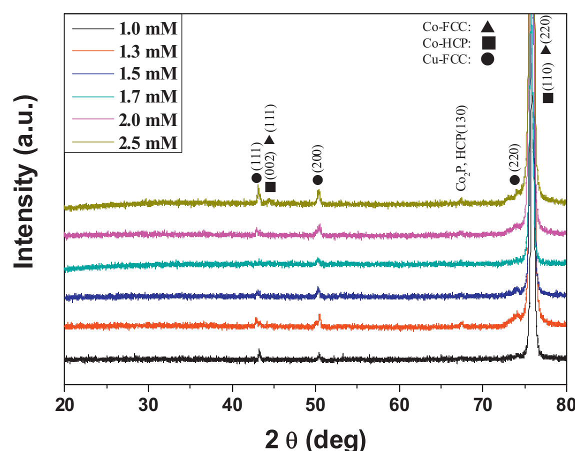

Fig. 3. XRD patterns of the CoCuP films electroplated at different [$CuSO_4$] concentrations.

2. Experimental

Electroplating was carried out by a three-electrode setup. A copper plate with thickness of 0.5 mm was used as the cathode, i.e., the substrate, because of its non-magnetic nature and high conductivity. A 3 cm × 3 cm cobalt sheet and a saturated calomel electrode (SCE) were used as the counter electrode and reference electrode, respectively.

The electrolytes are reagent grade chemicals, including $CoSO_4.7H_2O$ (0.2 M), $CuSO_4.5H_2O$ (1–2.5 mM), and $NaH_2PO_2{\cdot}H_2O$ (0.3 M) as the sources of Co, Cu, and P in the film, respectively. Boric acid (0.4 M) was used as the buffering agent. The pH of the electrolytic baths was adjusted by the addition of HCl or NH_4OH in the range of 2.0 to 5.0. The studied bath temperatures were 15, 25, 35, 40 and 45 °C, respectively. In the studies of bath temperature and bath pH effects, the optimal $CuSO_4$ concentration of 1.3 mM was adopted.

Prior to electroplating, the copper substrate was mechanically ground to 4000 grit sand paper and polish with alumina powder, followed by degreasing using acetone, acid activation with HCl (35 wt%), removal of residual acid using dilute NH_4OH, and final rinsing using deionized water. The exposed area for electroplating was fixed at 1 cm × 1 cm, as defined using the polyimide tape.

During electroplating, the current density (CD) was kept constant at 5 mA/cm^2 and the electrolytic bath was agitated with a magnet stirrer at 300 rpm throughout the process. Electroplating time was fixed at 1 h.

The surface morphology and composition of the electroplated CoCuP film were characterized using a Hitachi S3400N scanning electron microscope (SEM) equipped with an energy dispersive spectrometer (EDS). The thickness of the film was measured via an alpha-stepper (α-step, Surfcorder ET3000). The magnetic properties were characterized using a vibrating sample magnetometer (VSM, Lake Shore 7407) with an applied magnetic field from 0 to 1.2 Tesla. Finally, the crystal structure of the film was identified using a high resolution X-ray diffractometer (XRD, Bruker D8) with Cu Kα (λ = 0.15406 nm) over a scanning range from 20° to 80° at a scanning rate 4°/min.

3. Results and discussion

3.1. Effects of the bath concentration

By keeping constant concentrations of $CoSO_4{\cdot}7H_2O$ (0.2 M), $NaH_2PO_2{\cdot}H_2O$ (0.3 M) and boric acid (0.4 M), the effect of varying [$CuSO_4{\cdot}5H_2O$] concentrations in the range 1 mM ~ 2.5 mM on

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