Development of Iron-Phosphorus Electrodeposition Bath for Soft Magnetic Films with High Saturation Magnetization

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高飽和磁化軟磁性用 FeP 電析浴の開発

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Introduction

Recently, demands have been made to develop soft magnetic materials with high saturation magnetization, due to the necessity to use the higher saturation magnetic induction film for the core of thin film head or inductive thin film head in order to use higher density magnetic recording.

For such a purpose, the films formed by the electroplating or electroless plating is superior to those formed by sputtering, because platings are able to form thicker film more than several μm . High saturation magnetization materials by means of electroplating are reported by some papers^{1)~3)}. On the basis of such circumstances, we focus on the electrodeposited Fe-based films due to its high saturation magnetization of iron element. Recently we succeeded to get the soft magnetic FeP film with high saturation magnetization by means of an electroplating method, and its film magnetic properties and microstructure were reported⁴⁾.

In this letter, we report the development of its Fe-based electrodeposition bath with indicating several important factors of its bath and operating conditions.

Experimental

Test samples with $1.5\ \mu\text{m}$ thick were deposited on sputtered Cu/Cr(150/30nm thick) on polished NiP/Al substrate of a rigid magnetic disk substrate. This substrate was selected after comparing with three substrates, i. e., Cu/Cr/NiP/Al,

$8\ \mu\text{m}$ thick and 0.1mm thick copper foils. The basic bath compositions and its operating conditions for electrodeposited FeP film were shown in **Table 1**. The substrate for electrodeposition was set in a RDE (rotating disk electrode) as the working electrode. A Pt mesh was used as a counter electrode. A Ag/AgCl was used as a reference electrode. The film composition was analyzed with an inductively coupled argon plasma atomic emission spectroscopy (ICP) and an electron micro-probe analysis (EPMA). MH loops were measured with a vibrating magnetometer equipped with an earth magnetic field compensation circuit (VSM). Structural properties were examined with X-ray diffractometer (XRD, Fe-K α).

Results and Discussion

The bath composition for electrodeposited FeP film was optimized as shown in **Table 1**. Since iron (II) sulfate is used for the iron element source, ascorbic acid is added to prevent oxidation of ferrous ion. The concentration of ascorbic acid is higher than an usual case, thus it might work not only as preventing oxidation of ferrous ion, but also as the other factor. Sodium

Table 1 Basic bath compositions and operating conditions for electrodeposited FeP films.

Chemicals	Concentration [mol dm ⁻³]
FeSO ₄ · 7 H ₂ O	1.0
(NH ₄) ₂ SO ₄	0.1
C ₆ H ₇ O ₆	0.1
NaH ₂ PO ₄ · H ₂ O	0.01
Current density	10mA cm ⁻²
Rotation per minute	1000rpm
Bath temperature	room temp.
Bath pH	2.5

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Fig. 1 The effect of rotation per minute of RDE (a) and current density (b) on H_c of electrodeposited FeP films with $1.5\mu\text{m}$ thick prepared by 10mA cm^{-2} and at 1000rpm .

phosphinate is used for the source of codepositing phosphorus into the film. Sodium phosphinate 0.005 and 0.1mol dm^{-3} makes the coercivity, H_c , of FeP film lower. Ammonium sulfate is used as buffer reagent.

The hydrodynamics of plating solution and the current density greatly affect the soft magnetic properties of FeP films as indicated in Fig. 1 (a, b). The H_c of electrodeposited FeP film without rotation of disk electrode becomes about 20Oe , however, the H_c decreases with increasing a rotation speed. The lowest H_c value of 0.2Oe was attained at more than 800rpm at as-deposited conditions. Since the unstable deposition potential became stable at more than 800rpm , the faster hydrodynamics conditions might stabilize the interface pH condition, and also extract hydrogen gas evolution.

The effect of current density on H_c is so clear as is seen in Fig. 1(b). So lower H_c value of 0.2Oe drastically increases at the region more than 30mA cm^{-2} , at 1000rpm . Fig. 2 demonstrates a representative MH loop for FeP soft magnetic film, where the saturation magnetization and film composition were 140emu g^{-1} (1.4T) and $80\text{at}\%\text{Fe-20at}\%$

$\%\text{P}$, respectively. The results of XRD analysis for the FeP films prepared with less than 25mA cm^{-2} displayed no peaks except for those of Cu substrate. The most suitable soft magnetic FeP film was suggested to be an amorphous state or hyper-fine crystalline structure indicated by TEM results ¹⁾.

The species of substrates also affects strongly the soft magnetic properties. The most suitable soft magnetic properties of FeP film are given by using Cu/Cr/NiP/Al substrate when comparing other two Cu foil substrates. However, the XRD and TEM results give no difference among three substrates. Thus, the most suitable soft magnetic properties might come from the other important factor on the basis of amorphous or hyper-fine crystalline structure.

Conclusion

By selecting some factors of plating bath, the soft magnetic FeP film with high saturation magnetization at as-deposited conditions without external magnetic field was developed. A faster hydrodynamics condition, a lower current density and a selection of substrate are the most important factors to obtain the soft magnetic properties for FeP films, even though the bath composition is determined.

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Fig. 2 Representative MH loop of electrodeposited FeP film with $1.5\mu\text{m}$ thick.