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Preparation and Magnetic Properties of Ni-Co-Fe-P Coating on Silicon Substrate

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Abstract **– Ni-Co-Fe-P soft magnetic coating with amorphous structure was electroless plated onto silicon wafer substrate. The surface morphology, thickness, composition, structure and magnetic properties of coatings were observed and determined by scanning electron microscope (SEM), energy dispersive X-ray spectrometry (EDX), X-ray diffractometer (XRD) and vibrating sample magnetometer (VSM). Permeability spectra of the sample was obtained by a shorted micro strip transmission-line perturbation method. The plating with the saturation magnetization of 381 emu/cc, and the coercivity of 1.6 Oe. The film exhibits an in-plane uniaxial anisotropy of 18 Oe, and the ferromagnetic resonance frequency was as high as 760 MHz, implying that the film is promising for high frequency applications.**

Keywords **– Electroless Ni-Co-Fe-P plating, Magnetic Properties, High Frequency.**

I. INTRODUCTION

Electroless Ni-P coating possesses a characteristic in magnetism, such as low coercivity, so it is generally used as a soft magnetic material [1]. However, the saturation magnetization (M_s) of electroless Ni-P alloy is relatively low, which can't meet the requirements of actual soft magnetic materials [2]. In order to improve the saturation magnetization of Ni-P alloy, ternary and quaternary Ni-P based coatings with the addition of Co, Fe and rare earth elements were developed and reported [3-5].

As we all know, the saturation magnetization of bulk iron and cobalt are 1710 emu/cc and 1400 emu/cc, which are much higher than the saturation magnetization of bulk nickel (480 emu/cc) [6-8]. Therefore, the co-deposition of cobalt and iron in the process of electroless Ni-P plating can greatly improve the soft magnetic properties of the coating. For example Ni-Fe-P plating was developed on the surface of hollow glass microspheres, and the saturation magnetization of the composite microspheres increased from 8.55 emu/g (Ni-P shells) to 25.58 emu/g (Ni-Fe-P shells) [9]. Ni-Co-P ternary alloy deposits with soft magnetic characteristics were prepared by electroless plating, and the saturation magnetization, remanence and coercivity are found to increase with cobalt content of the deposit [10]. Ni-CO-Fe-P alloy was successfully deposited on surface of flake graphite by electroless plating, and the saturation magnetization (M_s), the remnant magnetization (M_r) and the coercivity (H_c) of the Ni-Co-Fe-P-coated flake graphite are 2.41 emu/g, 0.72 emu/g and 19.2 Oe [11]. The soft magnetic materials used in the high frequency field require a higher saturation magnetization, a lower coercivity and an in-plane uniaxial magnetic anisotropy [12]. But so far, there are few reports on the performance of electroless Ni-Co-Fe-P coating in high frequency.

In this paper, Ni-Co-Fe-P alloy coating was successfully deposited on surface of silicon wafer by electroless plating technology. The surface morphology, thickness, composition, structure, static and dynamic magnetic properties were investigated and characterized.

II. Experimental

A. *Preparation*

Ni-Co-Fe-P coating was prepared on silicon wafer by electroless plating method. Before plating, silicon substrate was treated by cleaning, dipping, sensitizing and activation processes which described in detail in reference [3]. The silicon substrate was immediately taken into the electroless plating bath for the preparation of Ni-Co-Fe-P coating after activation as soon as possible. The bath composition and other parameters were given in Table 1. The specimen were coated for 10min, removed from the bath, washed with water and dired with electric drier.

Table 1. Composition of the electroless plating bath and operating conditions.

Bath Constituents and Parameters		**Operating Conditions**
$Ni_2SO_4 \cdot 6H_2O$	0.03 mol/L	Temperature = 85 °C pH = 9.0 Mild-mechanical agitation
$CoSO_4 \cdot 6H_2O$	0.03 mol/L	
$FeSO_4 \cdot 7H_2O$	0.01 mol/L	
$NaH_2PO_2 \cdot H_2O$	0.1 mol/L	
$Na_3C_6H_5O_7 \cdot 2H_2O$	40g/L	
$(NH_4)_2SO_4$	40g/L	
$C_6H_8O_6$	Trace amount	

B. *Characterization*

The surface and cross section morphology of Ni-Co-Fe-P coating were observed by electron microscopy (FESEM, Hitachi S-4800, Japan) operated at 5.0 kV, and the composition of plating was determined by the energy-dispersive X-ray spectrometry (EDS). And the thickness of plating was directly measured from the cross-section images. Atom force microscope (AFM, MFP-3DTM, America) was also used for observing the surface topography of the electroless Ni-Co-Fe-P coating using a tapping mode on an area of 10 um×10 um.

The structure of Ni-Co-Fe-P coating after heat treatment was measured by X-ray diffraction analyzer (XRD, Cu K_α-1.54056Å, PAN alytical X'Pert, Philips X' pert, Holland).

The magnetic properties of Ni-Co-P-Ce coating was determined by using vibrating sample magnetometer (VSM, Lakeshore 7304, America) at room temperature. By analyzing the magnetic hysteresis (*M*-*H*) curves, the saturation magnetization (M_s) and coercive force (H_c) of Ni-Co-Fe-P coating were obtained. In the end, the permeability spectra of the samples were obtained from 100 MHz to 5 GHz by a shorted micro strip transmission-line perturbation method. The measurement was performed along the hard axis in-plane of the film.

III. Results and Discussions

A. *The Morphology and Composition of the Ni-Co-Fe-P Plating*

Fig. 1 presents the surface morphology (Fig. 1a) , the cross-section morphology (Fig. 1b) and the composition (Fig. 1c) of the Ni-Co-Fe-P coating. After plating, nodular particles are evenly distributed on the surface of the silicon substrate, and the particle size is between a few microns and a dozen microns. The thickness of plating is measured using the Nano Measure software to measure the cross-section view. The specific method is to select ten locations for thickness measurement, and take the average value to obtain the average thickness of the coating. The calculated coating thickness of Ni-Co-Fe-P plating is about 830 nm. The plating is mainly composed of Ni, Co, Fe and P, and the contents of these four elements is shown in Table 2. The concentration ratio of Ni^{2+}, Co^{2+} and Fe^{2+} in the plating solution is 3:3:1, but the content ratio of these three elements in the coating is about 54.7:34.8:2.5. This result shows that the deposition rates of these three elements are significantly different. Ni is the easiest to deposit, followed by Co, and Fe is the most difficult to deposit. Because the reduction potential of Ni^{2+}, Co^{2+} and Fe^{2+} are −0.22 eV, −0.28 eV and −0.44 eV, respectively, the rate (v) of reduction and deposition is $v_{Ni^{2+}} > v_{Co^{2+}} > v_{Fe^{2+}}$ [13]. The deposition mechanism of nickel, cobalt and iron are shown below [14]:

$$Ni^{2+}+H_2PO_2^-+H_2O \rightarrow HPO_3^{2-}+2H^++Ni \quad (1)$$

$$Co^{2+}+H_2PO_2^-+3OH^- \rightarrow Co+HPO_3^{2-}+2H_2O \quad (2)$$

$$Fe^{2+}+H_2PO_2^-+3OH^- \rightarrow Fe+HPO_3^{2-}+2H_2O \quad (3)$$

$$H_2PO_2^-+OH^- \rightarrow 2[H]+HPO_3^{2-}+2H_2O \quad (4)$$

$$2[H] \rightarrow H_2 \quad (5)$$

$$H_2PO_2^-+[H] \rightarrow H_2O+OH^-+P \quad (6)$$

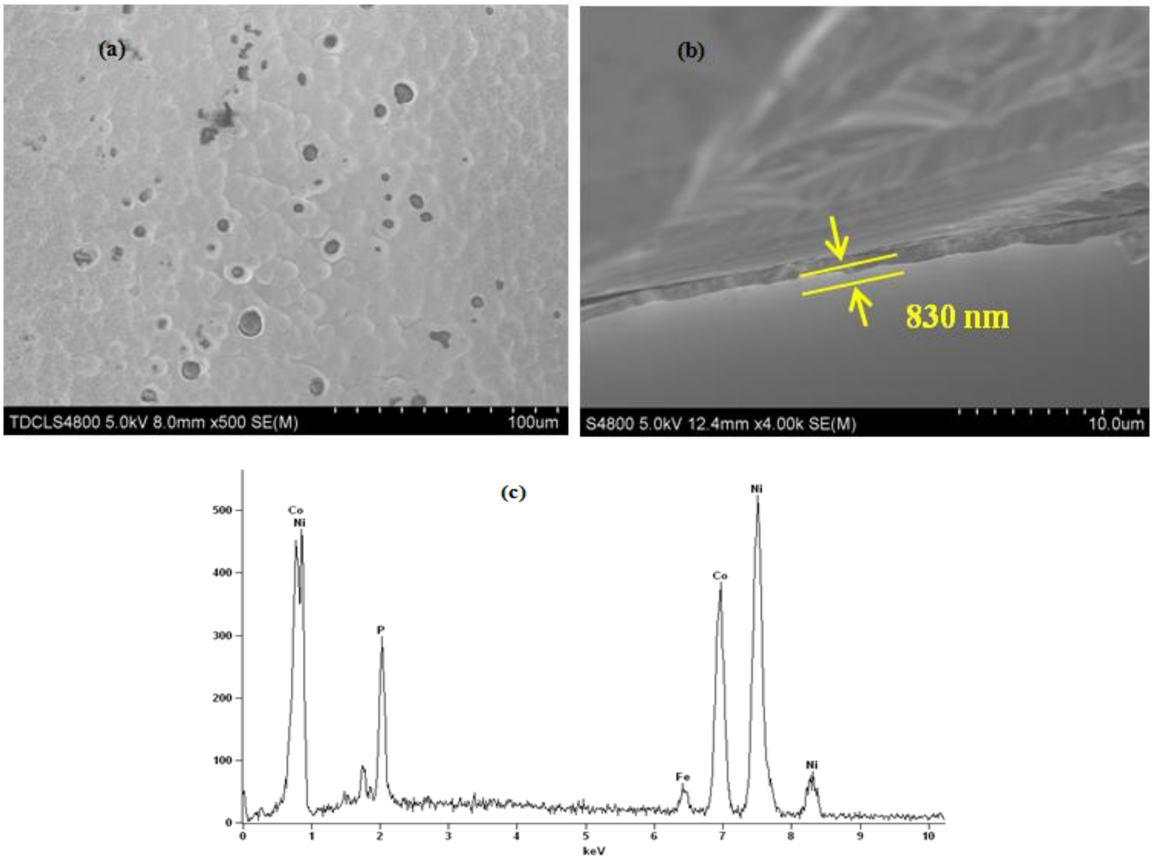

Fig. 1. The morphologies and composition of Ni-Co-Fe-P plating, (a) the surface morphology, (b) the cross-section view and (c) the composition.

Table 2. Elementary composition of Ni-Co-Fe-P plating.

Elements	**Ni (wt %)**	**Co (wt %)**	**Fe (wt %)**	**P (wt %)**
Contents	54.7	34.8	2.5	8.0

Fig. 2 shows the AFM topographic of the Ni-Co-Fe-P plating. It can be clearly seen that the plating exhibits a spherical nodular feature.

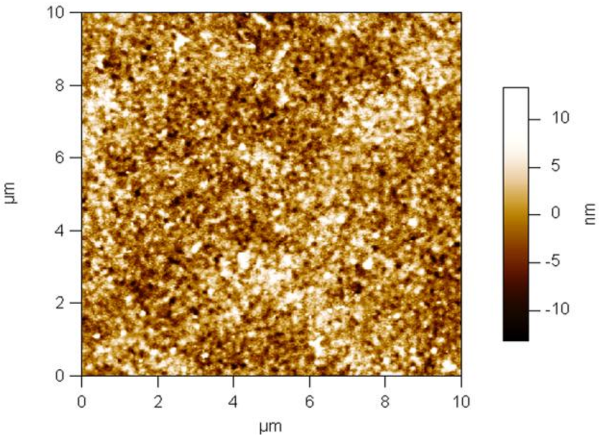

Fig. 2. AFM image for Ni-Co-Fe-P plating.

B. *The Structure of the Ni-Co-Fe-P Plating*

Fig. 3 is the XRD spectrum of Ni-Co-Fe-P plating. There in only a broadened diffraction peak at about 45^{o}, indicating that the coating is mainly composed of Ni(Co) amorphous phase [10].

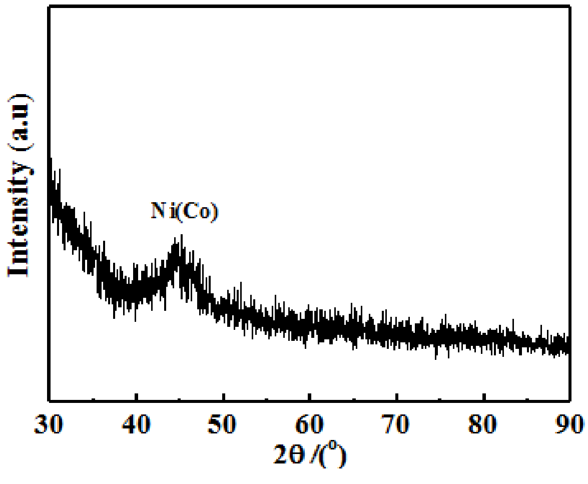

Fig. 3. The XRD spectrum of Ni-Co-Fe-P plating.

C. *The Magnetic Properties of the Ni-Co-Fe-P Plating*

The magnetic hysteresis curves (M-H), and the corresponding saturation magnetization *M*s and coercive force *H*c of Ni-Co-Fe-P coating is shown in Fig. 4. It is found that the Ni-Co-Fe-P film has good soft magnetic properties, the saturation magnetization is 381 emu/cc, and the coercivity is only 1.6 Oe. It is worth noting that even if no external force is applied, the Ni-Co-Fe-P film presents an in-plane anisotropy field. It has been reported that the addition of Fe^{2+} ions during the spin coating process makes Ni-Zn ferrite films spontaneously have in-plane anisotropy [15]. Therefore, the reason for the in-plane anisotropy field induced in this system should be the incorporation of Fe^{2+}. At the same time, we speculate that the direction of the anisotropic field may be affected by the crystal orientation of the single crystal Si substrate. In short, the film exhibits in-plane uniaxial anisotropy H_k of 18 Oe, which increases the FMR frequency resulting in good high-frequency performance.

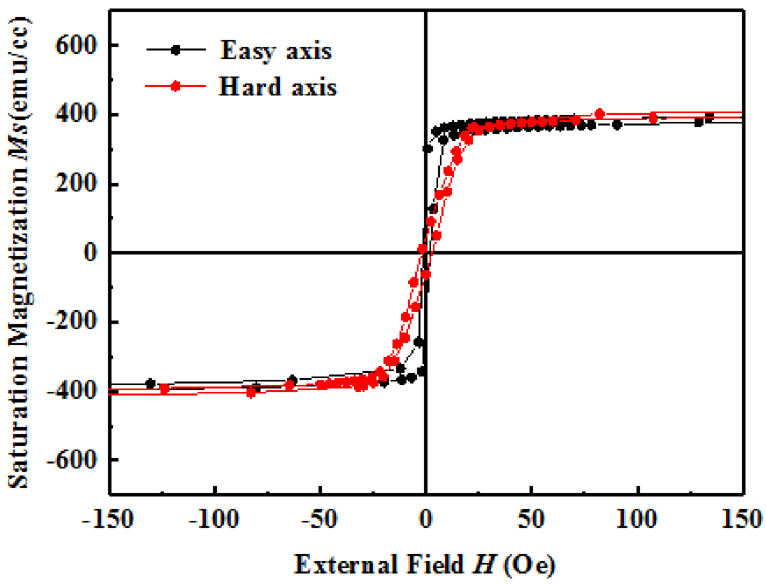

Fig. 4. Easy and hard axis loops for Ni-Co-Fe-P plating.

Fig. 5 shows the dependence of complex permeability ($\mu = \mu' \text{-} j\mu''$) on frequency for Ni-Co-Fe-P plating, where μ' and μ'' represent the real and imaginary part of complex permeability, respectively. It is measured along the hard axis for Ni-Co-Fe-P plating. From the variation of μ'' with the frequency, there is a wider resonance peak around 760MHz, and the large resonance line width may be due to the large damping in the Ni-Co-Fe-P film or the thicker film. The μ' is decreasing with the increasing of frequency. When $\mu' = 0$, the frequency is about 1.14GHz.

In view of the in-plane uniaxial anisotropy of the film, its behavior of magnetization in high-frequency magnetic field can be described by the Landau-Lifshitz-Gillbert (LLG) equation [16]. And the final expression of the FMR frequency is obtained by solving the LLG equation [12]:

$$\mu' = 1 + 4\pi\gamma^2 M_s\{(4\pi M_s + H_k)\times(1+\alpha^2)[\omega_0^2(1+\alpha^2) - \omega^2] + (4\pi M_s + 2H_k)(\alpha\omega)^2\} \times\{[\omega_0^2(1+\alpha^2)-\omega^2]^2 + [\alpha\omega\gamma(4\pi M_s + 2H_k)]^2\}^{-1} \tag{1}$$

$$\mu'' = 4\pi\gamma M_s \times \{\frac{\omega\alpha\gamma[(4\pi M_s + H_k)^2(1+\alpha^2)+\omega^2]}{[\omega_0^2(1+\alpha^2)\omega^2]^2 + [\alpha\omega\gamma(4\pi M_s + 2H_k)]^2}\} \tag{2}$$

$$\omega_0 = \gamma\sqrt{H_k(4\pi M_s + H_k)} \tag{3}$$

$$f_r = \omega_0 / 2\pi \tag{4}$$

In the calculation process, we take $M_s = 381 emu/cc$, $H_k = 18 Oe$, $\gamma = 1.9\times10^7 Hz/Oe$, and the theoretical value obtained by this fitting is in good agreement with the experiment result (Fig. 5). We get that the damping factor of the film is indeed high, α = 0.1. This may be due to the fact that the film is an amorphous structure.

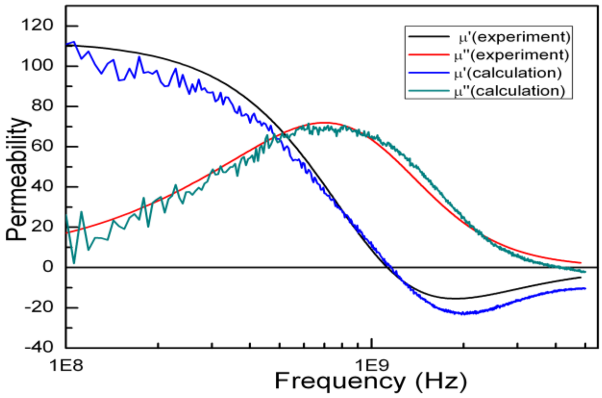

Fig. 5. Permeability characteristic for Ni-CO-Fe-P plating.

IV. Conclusions

Ni-Co-Fe-P plating was successfully deposited on surface of silicon wafer by electroless plating technique, and the film with amorphous structure which lead to film with low coercivity of 1.6Oe. The film exhibited in-plane uniaxial anisotropy H_k of 18 Oe, and the ferromagnetic resonance frequency was as high as 760 MHz, implying that the film is promising for high frequency applications.

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