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Preparation and magnetic properties of Ni–P–La coating by electroless plating on silicon substrate

Yun Gao [a], Jihui Wang [a,*], Jing Yuan [a,b], Haiqin Li [b]

[a] Tianjin Key Laboratory of Composite and Functional Materials, School of Materials Science and Engineering, Tianjin University, Tianjin 300072, PR China
[b] College of Physics and Electronic Information Engineering, Qinghai University for Nationalities, Xining, Qinghai 810007, PR China

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ABSTRACT

Ni–P–La coatings were prepared on Si substrate by electroless plating method under different La content, pH value, plating temperature and plating time. The surface morphology, chemical composition, structure and magnetic properties of coatings were observed and determined by scanning electron microscope (SEM), energy dispersive X-ray spectrometry (EDS), X-ray diffractometer (XRD) and vibrating sample magnetometer (VSM). The results showed that Ni–P–La coating is smooth and uniform with a cellular morphology grown in columnar manner. With the increase of La content, pH value and plating time, the thickness and saturation magnetization of coating are increased continuously, but the stability of plating bath is decreased greatly with La content and pH value. Under higher plating temperature, the thickness and saturation magnetization of coatings are obviously enhanced. But too high plating temperature is harmful to the plating bath and coating. The optimum plating conditions for Ni–P–La coating is La_2O_3 addition of 10 mg L^{-1}, pH value of 5.0, plating temperature of 75 °C and plating time of 45 min. The role of La element is to benefit the deposition of Ni element, promote the formation of Ni phase during the annealing process, and thus improve the magnetic properties of Ni–P–La coating.

1. Introduction

Electroless plated Ni–P coating has a wide application in the mechanical, petrochemical, aerospace, automobile, microelectronics and semiconductor industries due to its excellent mechanical, corrosion resistant, tribological, magnetic and electrical properties [1–7]. For example, the coating thickness, composition, structure, hardness and corrosion behavior of electroless Ni–P coating were investigated [8,9], and the plating time and heat treatment condition were optimized [5]. In addition, the ternary and quaternary Ni–P based coatings such as Ni–Cu–P, Ni–W–P and Ni–W–Cu–P coatings were prepared to improve the mechanical and corrosion resistant properties of electroless plated Ni–P coating [10,11].

With the growing need of electronic devices and integrated circuits in the communication and computer industries, the magnetic behavior of Ni–P coating is recently getting more attention. Huang et al. [12] analyzed the structure and magnetic properties of deposited Ni–P film on Si substrate, and demonstrated that the columnar structure of Ni–P film was responsible for the film's unusual magnetic anisotropy. Bozzini et al. [13] investigated the magnetic susceptibility of Ni–P coating in the different temperatures with magnetic field, and determined the field-independent susceptibility and ferromagnetic behavior of Ni–P coating.

In order to improve the magnetic properties of Ni–P coating, ternary Ni–P based coating such as Ni–Co–P coating was prepared, and the effect of preparation conditions on the magnetic property of Ni–Co–P coating was determined [14]. On the other hand, the rare earth elements (REEs) such as La, Ce, Yb elements could also be incorporated in Ni–P coating due to REE's unpaired electrons in 4f state and larger nucleus charge number. And the effect of rare earth (Ce, La) on the microstructure, hardness, plating rate and bath stability of Ni–P deposits was investigated and discussed, but the substrate used for Ni–P–(Ce, La) coating was mainly on carbon steel substrate [15] and polymer materials [16]. However, the preparation and magnetic properties of rare earth element incorporated Ni–P coating on Si substrate were hardly reported.

In this text, Ni–P–La coatings were prepared on Si substrate by electroless plating method under different La content, pH value, plating temperature and plating time. The surface morphology, composition, structure and magnetic properties of Ni–P–La coating were observed and determined. Based on these results, the role of La element in the coating was discussed and revealed, and the optimum plating conditions for Ni–P–La coating could be obtained.

* Corresponding author.
E-mail address: jhwang@tju.edu.cn (J. Wang).

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2. Experimental

2.1. Preparation

Ni–P–La coating was prepared on silicon substrate by electroless plating method. Before plating, silicon wafer with (100) crystal plane parallel to the surface was cleaned in acetone solution with ultrasonic oscillation for 15 min, then dipped in H_2SO_4/H_2O_2 (1:1, vol.) solution for 15 min, and finally etched by HF/H_2O solution (1:1, vol.) for 10 min. After rinsed with deionized water, the cleaned silicon substrate was sensitized by immersion in $SnCl_2$/HCl solution (40 g L^{-1} $SnCl_2$ + 40 mL/L HCl) for 5 min and then activated by $PdCl_2$/HCl solution (0.2 g L^{-1} $PdCl_2$ + 4 mL/L HCl) for 5 min. After activation, the silicon substrate was immediately taken into the electroless plating bath for the preparation of Ni–P–La coating [17].

The electroless plating solution had the following composition: 20 g L^{-1} $NiSO_4{\cdot}6H_2O$, 27 g L^{-1} $NaH_2PO_2{\cdot}H_2O$, 16 g L^{-1} $Na_2C_4H_4O_4{\cdot}6H_2O$, 1 mg L^{-1} $Pb(NO_3)_2$ and different La content (La ions were added in the solution by the dissolution of La_2O_3 in dilute sulphuric acid, the additive amount of La_2O_3 was 0, 8, 10, 15, 20, 25, 30 mg L^{-1}, respectively) under pH value of 4.4, 4.7, 5.0, 5.3 and 5.6, adjusted with NaOH aqueous solution. During the plating process, different plating temperature (70, 75, 80, 85, 90 °C) and different plating time (1, 3, 5, 10, 15, 30, 45, 60 min) were chosen to optimize the plating condition. After plating, the sample was taken from the bath, and then cleaned with deionized water and dried with electric drier. Finally the prepared Ni–P–La coating was annealed at 400 °C for 2 min in the electric furnace with argon atmosphere [18].

In order to characterize the stability of plating bath, the palladium stability test by palladium chloride solution was carried out [15,19]. During the test, 5 mL palladium chloride solution with the concentration of 1×10^{-4} mol L^{-1} was combined with 50 mL electroless plating solution at 60 °C. The time when the bath decomposed and black precipitates appeared represented the stability of the plating solution, which could be called the decomposition time. According to this method, the stability of electroless plating solution under different addition of La_2O_3 and pH value was determined.

2.2. Characterization

The surface and cross section morphology of Ni–P–La coating were observed by Hatchi S-4800 field emission scanning electron microscopy (FESEM) operated at 5.0 kV, and the composition of coating was determined by the attached energy-dispersive X-ray spectrometry (EDS). The thickness of Ni–P–La coating was directly measured from the cross section image of coatings.

The structure of Ni–P–La coatings after heat treatment was measured by D/MAX-2500 X-ray diffractometer (XRD), and the relative amount of phases composition was refined and calculated by Rietveld method [20,21].

The magnetic properties of Ni–P–La coatings under different plating conditions were determined at room temperature by using LDJ-9600 vibrating sample magnetometer (VSM). By analyzing the magnetic hysteresis (M–H) curves, the saturation magnetization (M_s) and coercive force (H_c) of Ni–P–La coating were obtained.

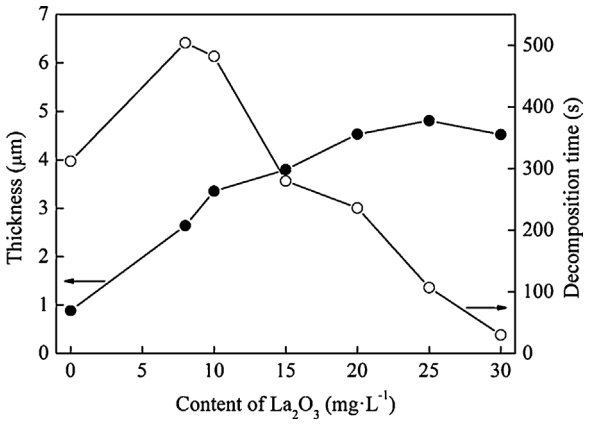

Fig. 2. Thickness of Ni–P–La coating and decomposition time of electrolyte under different content of La_2O_3 in electrolyte.

3. Results

3.1. La_2O_3 content

The surface and cross section morphology of Ni–P–La coating under La_2O_3 addition of 10 mg L^{-1} with pH value of 5.0, plating temperature of 75 °C and plating time of 45 min are shown in Fig. 1. It can be seen that the surface of Ni–P–La coating was smooth with a cellular structure (Fig. 1a), and Ni–P–La coating was grown by a columnar manner with a uniform thickness (Fig. 1b).

Fig. 2 is the coating thickness and decomposition time of Ni–P–La coating under different addition of La_2O_3 with pH value of 5.0, plating temperature of 75 °C and plating time of 45 min. In the addition range of 0–25 mg L^{-1} La_2O_3, the thickness of Ni–P–La coating was almost linearly increased with the increasing of La_2O_3 content in the plating bath. But the further addition of La_2O_3 to 30 mg L^{-1} was almost no contribution to the coating thickness. Although small amount of La_2O_3 content could promote the plating bath life, the decomposition time of plating solution was decreased obviously with the increase of La_2O_3 addition started from the content value of 15 mg L^{-1} (Fig. 2).

The magnetic hysteresis (M–H) curve of Ni–P–La coating under different addition of La_2O_3 is shown in Fig. 3, and the corresponding

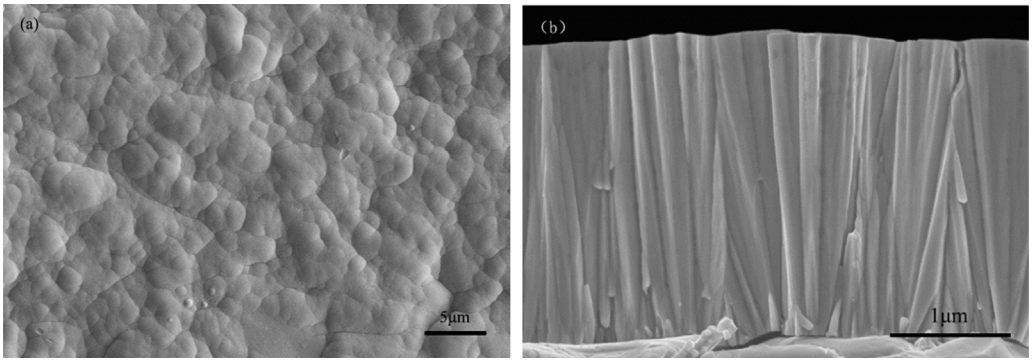

Fig. 1. (a) Surface morphology and (b) cross section of Ni–P–La coating (10 mg L^{-1} La_2O_3).