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The effect on the microstructures of electroless nickel coatings initiated by pulsating electric current

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Abstract

In this study, pulsating electric current was applied during the electroless Ni plating process. The applied current is controlled to avoid the formation of an immersion (displacement) deposit. The effects of the current density (0.5 and 1.0 A/dm^2), duty cycle (0 to 100%, in a step of 10%), and bath pH value (4.4 and 4.8) were investigated systematically. The as-plated coatings were examined by atomic force microscopy, transmission electron microscopy, X-ray diffraction, synchrotron X-ray absorption spectroscopy, etc. Amorphous or amorphous-like microstructure was obtained for all as-plated coatings and the phosphorus content was higher than 8.9 wt.%. Experimental results showed that pulsating electric current can initiate Ni nanocrystallization (~ 5 nm), improve crystal growth, and accelerate electroless Ni deposition. An obvious increase in deposition rate was also observed with pulsating electric current.

Keywords: Pulsating electric current; Electroless Ni plating; Nanocrystalline coatings

1. Introduction

Electroless plating has been used to prepare nanocrystalline powders [1,2] or coatings [3] and has attracted much R&D interests. Electroless nickel plating can be commonly used to prepare coatings with excellent corrosion and wear resistance, and possesses much potential for use in the microelectronic industry. The microstructures of the as-plated coatings will be influenced by its composition. An amorphous coating is obtained with high phosphorus content, but a nanocrystalline deposit forms when there is less phosphorus present [4]. Modifications of the electroless plating process, such as the use of ultrasonically assisted plating [5,6] have also been attempted to further extend its applications.

Conventional electroless Ni coating is done without an applied external electrical current. When electric current is introduced into an electrochemical system, electrodeposition may occur and nanocrystalline coatings can be prepared by controlling processing parameters [7,8]. In the electrodeposition process, an electric double layer exists which hinders adion diffusion. Pulse plating can eliminate the existing electric double layer and accelerate diffusion of adions toward the electrode surface. Nanocrystalline materials can also be prepared by pulse electrodeposition [9,10].

Only limited work concerning electroless nickel plating with superimposed pulsed current has been reported [11]. In this study, we investigated the electroless nickel plating process with pulsating electric current using an acidic bath of pH 4.4 or 4.8. The effects of the peak current density and duty cycle on the deposition rate and microstructure of the as-plated coatings were systematically investigated.

2. Experimental procedures

Low carbon steel substrates, 50 × 20 × 1 mm^3, were used for the electroless nickel plating. The substrates were ground, degreased, immersed in 1 M hydrochloric acid for ~ 5 min to remove any possible rust, and rinsed with deionized water. The substrates were activated by dipping in 1 M HCl and rinsed before deposition. Nickel sulfate, sodium hypophosphite, and lead

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nitrate were used as the nickel ion source, reducing agent, and stabilizer, respectively. All of the chemicals (extra pure grade or better, Nihon Shiyaku Industries, Ltd., Japan) were used without any further purification. In addition to the traditional electroless plating, a pulsating electric current of 0.5 or 1.0 A/dm^2 was applied during the process. Each rectangular pulse cycle (pulse on time plus pulse off time) was 100 ms. The duty cycle is defined as the percentage of pulse on time divided by the pulse on time plus pulse off time. The pulsating electric current parameters include the duty cycle (0 to 100%, in steps of 10%) and peak electric current (0.5 and 1.0 A/dm^2). In order to control the coating thickness to ~10 μm, the overall deposition time for electroless nickel plating with pulsating electric current was varied depending on the duty cycle. The plating bath composition and processing parameters were summarized in Table 1.

The as-plated samples were examined by X-ray diffraction (XRD, MAC Science MXP18, Japan), inductively couple plasma atomic emission spectroscopy (ICP-AES, Jarrell-Ash, ICAP 9000, USA), scanning electron microscopy (SEM, TOPCON, ABT-150S Thermionic Emission SEM, Japan), atomic force microscopy (AFM, Digital Instrument, NS4/D3100CL/Multi-mode, Germany), and transmission electron microscopy (TEM, ZEISS EM902A, Germany). The phase was determined by XRD using Cu Kα radiation and the composition of the as-plated coatings were examined by ICP-AES. While the surface morphology and the grain size were revealed by SEM, AFM, and TEM observations.

3. Results and discussion

It is generally known that the electroless nickel plating bath composition can influence the final microstructure of the coatings [12]. For instance, crystalline nickel coatings can be prepared from a basic solution [13,14]. While when an acidic bath is used for electroless plating, the lower the pH value the higher the phosphorus content in the as-plated coatings, and amorphous or amorphous-like microstructure can be observed [15,16]. Fig. 1a and b show the X-ray diffraction patterns of the as-plated Ni–P coatings as a function of duty cycle (peak current = 0.5 A/dm^2) prepared from an acidic bath of pH = 4.4 and 4.8, respectively. Though not shown here, similar results can be seen for those prepared with a higher peak current of 1.0 A/dm^2. Amorphous diffusion peaks were evident in all of the samples investigated in this study. This indicates that the as-plated nickel coatings exhibited an amorphous or amorphous-like microstructure and phosphorus content within the coatings was relatively high, in agreement with previously published research [15,16].

Table 1
Processing parameters for electroless nickel plating

Bath composition and plating parameters	Specifications
$NiSO_4 \cdot 6H_2O$	20 g/l
$Na_2C_2H_4O_4 \cdot 6H_2O$	16 g/l
$NaH_2PO_2 \cdot H_2O$	27 g/l
$Pb(NO_3)_2$	0.5 ppm
pH	4.4 or 4.8
Temperature	86±2 °C
Duty cycle [a]	0–100%
Peak electric current	0.5 or 1.0 A/dm^2

[a] Duty cycle = pulse on time/(pulse on time + pulse off time).

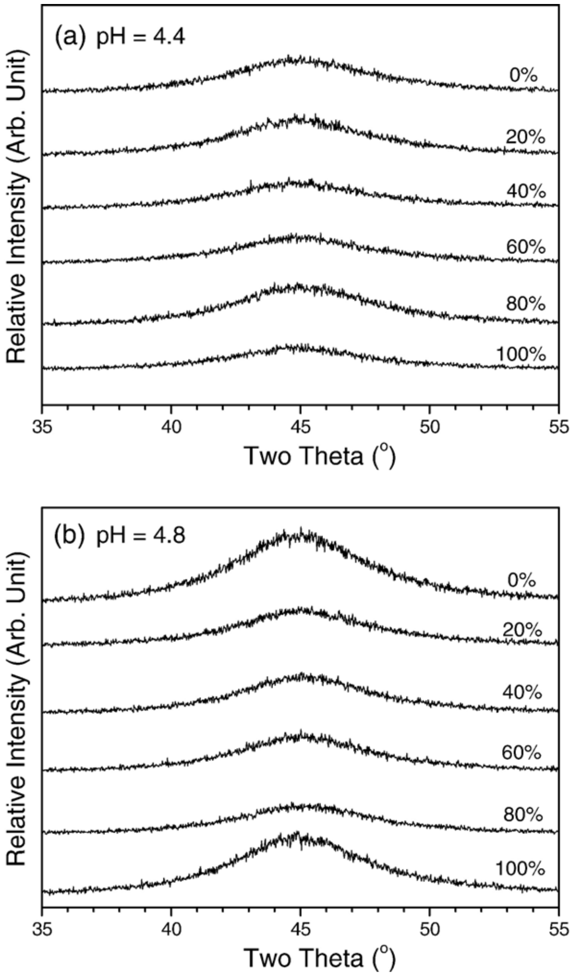

Fig. 1. XRD patterns of electroless nickel plating with pulsating electric current using an acidic bath of (a) pH = 4.4 and (b) pH = 4.8 as a function of duty cycle.

Though only one similar broadening peak can be noticed and the difference has been minimized due to normalization in Fig. 1a and b, it should also be noted that the peak intensities of the coatings prepared from the more acidic bath (i.e. pH 4.4) are usually two or three times smaller than those prepared by a pH 4.8 bath. This may suggest that the size of nickel nanocrystals in the former cases may be smaller than those in the latter ones. Fig. 2 shows the typical cross sectional and top view of as-plated nickel coatings. No significant differences in the cross sectional views (Fig. 2a to c) can be observed from the samples prepared by different processing parameters. All of the as-plated samples exhibited an island-like microstructure from the top view (Fig. 2d) which may be attributed to the nucleation and growth of nickel during electroless plating process.

Inductively coupled plasma atomic emission spectroscopy was used to reveal the phosphorus content within the as-plated nickel coatings and the results are summarized in Table 2. As-plated electroless nickel coatings prepared with an acidic bath of pH 4.4