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Effect of Cd^{2+} as a stabilizer in the electroless nickel plating system

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ABSTRACT

Bath decomposition is a major problem in the electroless nickel (EN) plating system. Although the stabilization mechanism is far from being fully understood, bath stabilizers are normally added to extend the bath life in a viable EN plating solution. In this study, the effects of Cd^{2+} as a stabilizer on the plating rate, bath stability, and phosphorus content, corrosion resistance and microstructure of the deposits were investigated. The deposited films were examined using a scanning electron microscope (SEM) equipped with energy dispersive X-ray (EDX) spectroscopy and the X-ray photo spectroscopy (XPS). The electronic tunneling mechanism was used to elucidate the effect of the Cd^{2+} stabilizer on the plating system theoretically. The results calculated from theoretical method agreed well with the experimental data.

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1. Introduction

Electroless nickel (EN) plating is a chemical reduction process, in which the nickel ions are catalytically reduced without the use of electrical energy. A chemical reducing agent in an aqueous solution is the driving force for the reduction of nickel ions. Due to its excellent corrosion resistance, good electrical conductivity and high hardness, EN plating has been widely employed in industries for corrosion protection [1–3], electromagnetic interference (EMI) shielding [4–6], and other surface finishes [7–10]. The acidic EN plating bath containing hypophosphite ion ($H_2PO_2^-$) as the reducing agent is the most frequently used system, and the overall reaction could be described as follows:

$$2H_2PO_2^- + Ni^{2+} + 2H_2O \xrightarrow{\text{cat.}} 2H_2PO_3^- + 2H^+ + H_2 + Ni^0. \quad (1)$$

Since the discovery of the EN plating stabilizer by Brenner and Riddell in 1946 [11], many studies have been performed to elucidate the acidic EN plating process [12–16]. However, the EN plating process is so complicated that the exact mechanism is still far from being fully understood till now. Many parameters, which include bath composition, stabilizer, bath pH value, and plating temperature, affect the EN plating process. It is well known that the type of stabilizer and its concentration will affect not only the plating rate but also the quality of the plated deposits. Many investigations about heavy metal ions used as stabilizers in EN plating have been reported (e.g., Sn^{2+}, Pb^{2+}, Cu^{2+}) [17–20]. Yin et al. [21] proposed a novel electronic tunneling mechanism to explain the effect of the Pb^{2+} stabilizer on the EN plating system successfully in 2004. Chen et al. [22] modified the electronic tunneling model and successfully applied it to the Cu^{2+} stabilizer.

Cadmium is a commonly used stabilizer in EN plating although it is of great of concern in environment. Many studies have been carried out to investigate the various amendments added to soil to prevent or enhance Cd uptake [23–28]. It is well known that soil factors (such as pH, phosphate, zinc, and organic matter), Cd hyperaccumulation, and soil amendments affect Cd availability [24], which makes it viable for the use of Cadmium as a stabilizer in EN plating. In the present study, the effects of Cd^{2+} as a stabilizer in acidic EN plating process were investigated experimentally, and the electronic tunneling mechanism was used to elucidate the effect of the Cd^{2+} stabilizer on the EN plating system theoretically.

2. Experimental details

2.1. Materials and their activation

Brass sheets (2 cm×2.5 cm, 0.2 mm thick) were used as the substrates for the EN plating. The brass sheets were first cleaned with soak cleaner in an ultrasonic bath for 10 min under room temperature to remove contamination, and then immersed in H_2SO_4 solutions (10 vol.%) for 2 min at ambient temperature to remove surface oxides. After being rinsed with DI water, the cleaned brass was activated with an activation solution having ingredients as $PdCl_2$ (0.5 g/L) and HCl (50 ml/L), for 20 s at room temperature. Therefore, Pd particles were introduced to the brass surface as the seeds for initiating the catalytic reduction of Ni.

2.2. Electroless nickel plating

The EN plating solution used in this work was formulated as Table 1. The initial pH value of the plating bath was adjusted by dilute NaOH

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Table 1
Bath composition and deposition conditions

Composition		Condition	
$NiSO_4 \cdot 6H_2O$	30 g/L	pH	5.0±0.1
$NaH_2PO_2 \cdot H_2O$	25 g/L	Temperature	90±1 °C
CH_3COONa	18 g/L		
H_2NCH_2COOH	15 g/L		
$Cd(Ac)_2$	Variable		
NaOH	For adjusting pH		

solutions to 5.0±0.1. The pH value during plating process was monitored by a pH meter. The bath temperature was controlled within 90±1 °C through a digitally thermostat under atmospheric environment. The plating process was conducted by immersing one piece of the substrate into magnetically stirred EN plating solution (80 ml) in a 100 ml beaker for 20 min.

2.3. Measurement of plating rate

The plating rate, R (mg/cm^2 s), is determined by the gravimetrical method and calculated as follows:

$$R = \frac{(M_t - M_0) \times 60}{A_s \times t} \tag{2}$$

where M_t (g), M_0 (g), A_s (cm^2), t (min), are the mass of the substrate plated for a length of time t, the initial mass of the substrate, the surface area of the substrate, and the plating duration, respectively.

2.4. Corrosion resistance of the deposits

The corrosion resistance of the deposits was investigated by immersing one piece of the deposit into 200 ml corrosion solution having ingredients as NaCl (20 g/L) and H_2SO_4 (10 vol.%) for a period under room temperature. The corrosion rate of the deposits is determined by the gravimetrical method and calculated as follows:

$$R_c = \frac{M_{c0} - M_{ct}}{A_{cs} + t_c} \tag{3}$$

where M_{c0} (g), M_{ct} (g), A_{cs} (cm^2), t_c (h), are the initial mass of the deposit, the mass of the deposit eroded for a length of time t_c, the surface area of the deposit, and the corrosion duration, respectively.

2.5. Bath stability test

The Palladium stability test method [18] was used to determine the effect of stabilizer concentration on the stability of the bath. This test was conducted at the lower temperature of 65±1 °C to amplify the difference in the stabilities of the plating solutions. When the solution temperature reached 65±1 °C, 1.00 ml of 40.0 mg/L $PdCl_2$ was added drop by drop for 25 s to the 80 ml EN plating solution. The time required for the solution to be decomposed was recorded. The end point, or the onset of bath decomposition, was defined as the decomposition time when the solution became dark green and opaque.

2.6. Surface analysis

The surface morphology of the Ni–P deposits was investigated using scanning electron microscope. Energy dispersive X-ray (EDX) micro-area analyzer (JEOL JSM-5600LV) was used to analyze the Ni and the P contents (wt.%) of the Ni–P deposits. Furthermore, the surface composition of the deposited films was examined using X-ray photon spectroscopy (XPS). The XPS was carried out on an instrument (Kratos Axis His, Manchester, U.K) equipped with an Al Kα X-ray source (at 1486.6 eV) by using the takeoff angle of 90°. The pass energy is 40 eV for high-resolution scans.

3. Results and discussion

3.1. Effect of stabilizer Cd^{2+} on plating rate and p content of the Ni–P deposits

The plating rate and P content of the Ni–P deposits are two most important factors that determine the possibility of the practical use. Fig. 1 (a) and (b) show the effect of the $Cd(Ac)_2$ concentration on the overall plating rate and P content of the deposits, respectively. It is found that there is a critical stabilizer concentration, beyond which the stabilizer has negative effect on the plating rate and P content. It is consistent with the investigations of Pb^{2+} and Cu^{2+} stabilizer effects on the plating rate and P content [21,22].

A mathematical model, which established the relationship between the stabilizer concentration and the Fermi level of the EN plating frontier, was proposed by Yin et al. [21] to explain the effect of the stabilizer concentration (C_s) on the deposition rates of nickel (R_{Ni}) and phosphorus (R_P) as follows:

$$R_{Ni} = R^0_{Ni}\sqrt{\frac{E^0_f + 4\pi pa(C_S - C^c_S)}{E^0_f}}\exp\left[\left(64\pi pa - \frac{4\pi pak_G}{kT}\right)(C_S - C^c_S)\right] \tag{4}$$

$$R_p = R^0_p \exp\left[-\frac{4\pi pak_G}{kT}(C_S - C^c_S)\right] \tag{5}$$

where p is the dipole moment, a is a constant, E^0_f is the Fermi energy level without stabilizer, k_G is the $H_2PO_2^-$ adsorption constant, k is the Boltzmann constant, R^0_{Ni} is the nickel deposition rate without stabilizer, R^0_P is the phosphorus deposition rate without stabilizer, and C^c_S is the critical stabilizer concentration.

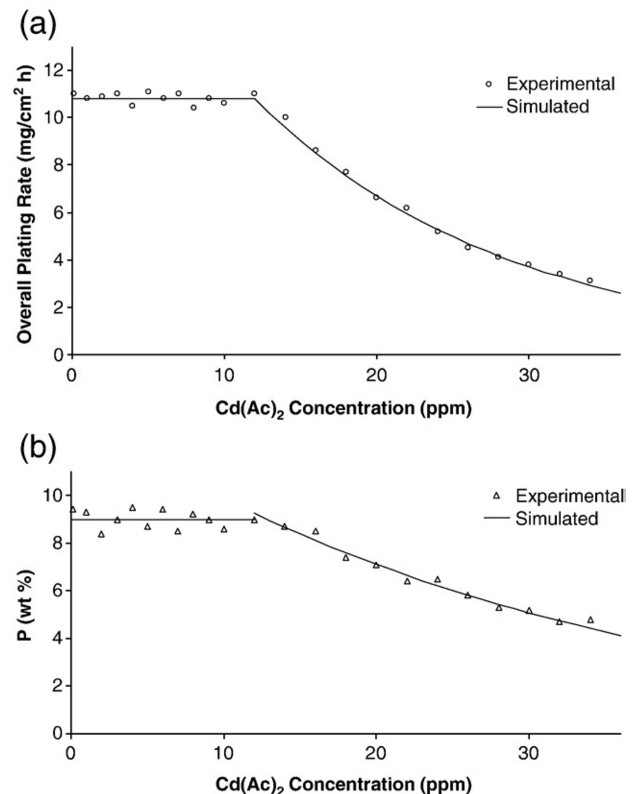

Fig. 1. Effect of $Cd(Ac)_2$ stabilizer concentration on (a) the overall plating rate; (b) the phosphorus content.

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