Role of a Pb²⁺ Stabilizer in the Electroless Nickel Plating System: A Theoretical Exploration

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The electroless nickel plating process involves multiple chemical reactions that interrelate mutually in intricate ways and take place almost simultaneously. This work attempts to provide a theoretical template for understanding this complicated system from the role of heavy metal stabilizers. Pb²⁺ ion was selected for the study because it is the most effective species in this category. A theoretical expression of the nickel deposition rate is created by envisioning the Stern-Grahame electrical double layer presumably attached to the plating frontier (the inner Helmholtz plane) as a one-dimensional potential well and the electron transfer from the Fermi level of plating frontier to Ni^{2+} ions at the outer Helmholtz plane as the quantum tunneling effect. The deposition of P atoms is assumed to go through the oxidative-addition of hypophosphite (H₂PO₂⁻) ions at Ni atoms on the plating frontier and on this basis its theoretical deposition rate is developed. Another adsorption state of $H_2PO_2^-$ on the surface Ni atoms is proposed to form by its two oxygen atoms, and the P(I) center supplies electrons to the plating frontier through these two oxygen bridges. Establishing the relationship between Pb²⁺-ion concentration and the Fermi level of the plating frontier (i.e., inside the solid Ni-P alloy deposition layer on the plating substrate) is an important step for deriving the nickel and element phosphorus deposition rates. The stabilizing effect of the lead ion is attributed to its participation as the neutral atom in the lattice of the Ni-P film at the plating frontier, which results in the ascension of Fermi energy. Thus, the oxidation of hypophosphite at the plating frontier is retarded, which in turn slows down the deposition of both Ni and P that needs electrons. The dependence of the deposition rates of Ni and P on concentrations of Pb²⁺ ion was experimentally examined. It is found that the theoretical models predict well the experimental trends. The parameters designated in the theoretical model are determined through a self-consistent computation procedure.

1. Introduction

Since the pioneering work by Brenner and Riddell in 1946,¹ the electroless nickel (EN) plating technique, a solution reaction of metal deposition, in which a chemical reducing agent is used in place of external electric current, has achieved a broad spectrum of industrial applications ranging from protective and decorative coatings^{2,3} to its use as a diffusion barrier between base metal and final gold overplate^{4,5} in the microelectronic packaging industry. The acid EN plating bath is the most frequently used system, in which the overall reaction is typically expressed by two equations

$$2H_2PO_2^- + 2H_2O + Ni^{2+} \xrightarrow{cat.}$$

Ni + 2H⁺ + 2H₂PO₃⁻ + H₂ (1a)
 $2H_2PO_2^- + 6H^- + 4H_2O \rightarrow 2P + 5H_2 + 8OH^-$ (1b)

However, the complicated nature of the reaction has yet to date been fully understood,^{6–11} in particular the stabilization mechanism, which is an essential element in ensuring that the plating system is free of propagation of colloidal Ni particles.¹¹ In an

EN-plating system, heavy metal ion stabilizers play a mysterious role since only a trace amount of them is sufficient to fulfill the function. More importantly it affects P% in the Ni-P deposition film. Hence, how these types of stabilizers act to intervene in the deposition rates of nickel and phosphorus represents the core knowledge of the EN process.

The electroless plating surface of an object is often regarded as self-catalytic because the Ni–P alloy film grows only at the surface once the deposition is initiated. This process differs from normal chemical reduction of metal ions in a water solution where metal blacks are produced everywhere. In an EN bath, although hypophosphite (H₂PO₂⁻) is known as a reducing agent, it seldom reduces the coexisting Ni²⁺ ion in a pure single phase solution at plating temperature. However, the plating would take place forthwith when a palladium metal grain is introduced into the solution. This simple fact indicates that hypophosphite itself is not the reductive species from which Ni²⁺ can gain electrons directly. Instead, the reductive species is generated through chemical adsorption of $H_2PO_2^-$ on the reactive surface metal (first Pd and then Ni) atoms.^{12,13} These surface atoms possess unsaturated-coordination environment compared to those located in the bulk phase. It is supposed, therefore, that the EN plating mechanism involves the following four key reaction steps:

(1) How does $H_2PO_2^-$ undergo cleavage on the plating frontier?

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| TA | BLE | 1: | Substrates | Used f | for | EN | Plating |
|----|-----|----|------------|--------|-----|----|---------|
|----|-----|----|------------|--------|-----|----|---------|

| substrates | equipment | thickness | size |
|----------------------|---|--------------------------|-----------------------------|
| brass | | 0.2 mm | $2.5 \times 2 \text{ cm}^2$ |
| | Anelva, Japan model 43 N | $\sim 1 \mu \mathrm{m}$ | $1 \times 1 \text{ cm}^2$ |
| E-beam evaporated Al | base P \leq 5 \times 10 ⁻⁷ Torr; V = 3.7 to 4.1 kV | | |

deposition temp. = $25 \text{ °C} \sim 50 \text{ °C}$

(2) How are elemental P and orthophosphate ion $H_2PO_3^-$ produced?

(3) How do Ni²⁺ ions gain electrons from the plating surface?

(4) How does the Pb²⁺ ion affect the above reaction steps? Theoretically, we propose that these questions be accessed from the perspectives of coordination activation and interfacial electron transfer. The first two reactions are believed to be driven by coordination to surface Ni atoms for the formation of P(III) and P(0) species, which requires electron transfer between H₂PO₂⁻ and Ni atoms, whereas the coordination provides low activation energy pathways. Question 3 is essentially governed by the Fermi energy of the plating frontier as it represents the level with 0.5 probability of all electron states, and therefore, it affects electron-transfer efficiency in the Stern–Grahame (S–G) EDL. Question 4 is related to the re-location of the Fermi level due to the presence of Pb in the lattice of the plating frontier.

The S-G EDL attached to the plating frontier consists of the inner Helmholtz plane (IHP) and the outer Helmholtz (OHP). The space embraced between is also known as the Stern layer. In this work, reduction of nickel ions within the EDL is deemed as the electron tunneling effect to penetrate the energy barrier including the effect of (i) the Fermi level of the Ni-P layer, over which there are statistically 50% of electronic states available for accommodation of electrons, and (ii) the potential in the Stern layer. The basic concepts of interfacial tunneling have been described in the book of Bockris and Khan.¹⁴ Besides deposition of Ni atoms at the plating surface, it is inevitable that a small portion of Ni atoms formed in the EDL is going to migrate reversely, as the agglomeration form (tiny Ni particles), into the plating solution through OHP. These tiny seeds possess highly reactive surfaces and thus have capability of causing decomposition of the plating solution through a quick proliferation process.¹¹ Heavy metal cations, especially Pb²⁺, are known as effective reagents^{15,16} to inhibit the propagation of Ni colloidal particles. The heavy metal ions are generally thought to furnish a geometric block via adsorption on the plating frontier¹⁷ of Ni seeds. However, this explanation is unsatisfactory due to two experimental facts: (1) there is a rather large gap in Pb^{2+} concentration between the minimum and the critical levels, in which the plating rate of Ni slows down, and (2) the content of phosphorus in the Ni-P deposition film decreases with increasing concentration of Pb2+. In this work, an alternative interpretation is proposed: Pb^{2+} ions act by lowering the reductive potential of the plating frontier after they are co-deposited into the Ni lattice.

In addition to preventing the EN bath from running away, Pb²⁺ ions also function to restrict the deposition of phosphorus on the plating frontier regardless of the desired plating item or colloidal Ni particles. As mentioned just now, the co-deposition of Pb on the plating surface would raise its Fermi level, which we found from the experiment to affect less the Ni deposition rate than the phosphorus deposition rate. It is also interesting to note that an EN plating process comprises virtually numerous oscillation cycles in the deposition rates of both Ni and P despite the fact that detection of the phenomenon experimentally is relatively difficult, though not impossible. Two theoretical rate expressions describing the dependence of deposition rates of

TABLE 2: Pretreatment Procedures for the Al Substrates

| step | immersion | temperature/time |
|------|-----------------------|------------------|
| 1 | soak clean | 60 °C/5 min |
| 2 | 50 g/L NaOH etching | room temp./15 s |
| 3 | 50 vol % HNO3 etching | room temp./10 s |
| 4 | 1st zincation | room temp./30 s |
| 5 | 50 vol % HNO3 etching | room temp./10 s |
| 6 | 2nd zincation | room temp./30 s |
| 7 | drying by air jets | until dry |

phosphorus and nickel upon the Pb²⁺ concentration in a plating solution are proposed on the deduction basis. The experimental deposition rates were employed to determine those parameters that derived from fundamental assumptions in the models via a self-consistent computation procedure.

2. Experimental Section

2.1. Substrates and Their Activation. Two kinds of substrates, a brass sheet $(2 \times 2.5 \text{ cm}^2, 0.2 \text{ mm}$ thickness) and an Al deposited silicon wafer $(1 \times 1 \text{ cm}^2 \text{ Al layer and thickness} = 1\mu\text{m})$, were used in this work as the substrates for the EN plating. The brass substrate was employed to investigate the dual effects of a Pb²⁺ stabilizer on the Ni plating rate and P content in the deposited films since a larger size of it than that of the Al/Si substrate can offer more reliable results by measuring the mass gained with time. The Al-deposited silicon wafer with smaller dimensions was used to examine the composition of the deposited Ni–P films.

The EN plating cannot take place directly on an aluminum substrate as there is an overlaying thin layer of oxides.¹⁸ A double zincation process was used to remove the oxides and to form a thin protective zinc layer (Table 1). Commercial soak cleaner (PSC1139, Plaschem Singapore) and zincation solution (PZB 1800, Plaschem Singapore) were used. The substrate was thoroughly rinsed with DI water after every step of processing.

The brass substrate was first cleaned with the soak cleaner in an ultrasonic bath (Elma, T1040H) for 10 min under room temperature to remove contamination and followed by removing surface oxides in a H₂SO₄ solution (10 vol %) for 2 min at ambient temperature. Pure brass cannot be electrolessly plated by nickel; thus, tiny Pd particles were introduced to the brass surface as the seeds for initiating the catalytic reduction of Ni. After being rinsed with DI water, the cleaned brass is activated with an activation solution having ingredients as PdCl₂ 0.18 g/L, FeCl₃ 0.8 g/L, NiSO₄ 5 g/L, HAc 25 mL/L, D,L-malic acid 20 g/L, 69% HNO₃ 10 mL/L, and NaF 10 g/L, for 20s at room temperature.

2.2. Electroless Nickel Plating. The EN solution used in this work was formulated in-house (Table 2). The initial pH value of the plating bath was adjusted by a dilute NaOH solution (5 wt %) to 5.0 ± 0.1 . The pH value of the plating process was monitored by a CyberScan pH 500 m (Eutech). The bath temperature was controlled within 90 \pm 1 °C through a TE–10D thermoregulator (TECHNE) at atmospheric environment. The plating was conducted by immersing one piece of the substrate into a magnetically stirred EN solution (80 mL) in a 100 mL beaker for 20 min. The plating rate (*R*) (mg/cm² h or can be converted to mA/cm² by the Faraday relationship) on

 TABLE 3: Composition of Electroless Plating Bath

| NiSO ₄ •6H ₂ O | 26 g/L |
|--|--------------------|
| NaH ₂ PO ₂ •H ₂ O | 28 g/L |
| NaAc | 10 g/L |
| DL-malic acid | 15 g/L |
| lactic acid (90%) | 15 mL/l |
| borax | 6 g/L |
| $Pb(Ac)_2$ | variable |
| pH adjuster | NaOH (0.2M) (pH 5) |
| | |

the brass substrate was determined with the gravimetrical method and then calculated according to the following formula:

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

where t is the plating duration (min), M_t (mg) is the mass of the object plated for a length of time t, M_0 (mg) is the the initial weight of substrate, and A_s is the surface area of specimen (cm²).

The phosphorus deposition rate (R_P) and the nickel deposition rate (R_{Ni}) were calculated as follows:

$$R_{\rm P} = R \times \rm P\% \tag{3}$$

$$R_{\rm Ni} = R \times (1 - P\%) \tag{4}$$

where P% is the phosphorus content by mass in the Ni-P film.

2.3. Composition of the Deposited Films. The phosphorus mass content (P%) of the deposited films on the brass was determined using an energy dispersive X-ray (EDX) micro-area analyzer (JEOL JSM-5600LV). The surface composition of deposited EN films was examined using the X-ray photon spectroscopy (XPS). The XPS was carried out on an instrument (Kratos Axis His, Manchester, U.K.) equipped with the Al K α X-ray source (at 1486.6 eV) by using the takeoff angle at 90°. The pass energy is 40 eV for high-resolution scans.

3. Structural Relevancy for Electron Transfer in the Stern-Grahame Layer

3.1. Electron Transfer through Ni(0)-H₂PO₂⁻ Coordination Complexes Formed at the IHP. As proposed in the Introduction, the Pb^{2+} stabilizer affects the plating rate (*R*) and phosphorus content (P%) in the deposition layer (Ni-P alloy) via the electronic effect. The electron effect means the fluctuation of electron flow density occurring in the S–G EDL^{19-21} (Figure 1), wherein the IHP is attached by anions (e.g., $H_2PO_2^{-}$, H₂PO₃⁻, and SO₄²⁻) except water molecules and the OHP mainly by solvated cations (e.g., Ni²⁺, Na⁺, etc.). On the basis of this model, Ni²⁺ ions pick up electrons and are converted to metal atoms within the EDL. To describe the electron flow density occurring in the S-G layer, a suitable theoretical method is to treat the flow of electrons as the quantum mechanical tunneling. Namely, the S-G layer can be presumed to be the one-dimensional potential well. On the other hand, the phosphorus content is affected by the adsorption state of hypophosphite ions on the IHP of the S-G layer. With reference to the adsorption model proposed by Smith and Sadakow, $^{12-13}\ a$ clearer picture to describe it should be based on the concept of the transition metal complex, i.e., hypophosphite ion as the ligand and Ni atom as the central metal.²² The redox reaction of hypophosphite can thus take place within the coordination sphere rather than within the S-G layer. This is important to differentiate the deposition of Ni atoms from the deposition of P atoms as well as the generation of the orthophosphite ion. The key assumptions of the hydrogen landing model proposed by Smith & Sadakkow^{12,13} are as follows:



Figure 1. Schematic illustration of the electric double layer likely to be formed along the plating frontier in an EN plating system.

(1) $H_2PO_2^-$ anions are more strongly adsorbed on the catalytic nickel surface via the H corner of the tetrahedron than other phosphoroxy anions ($H_2PO_3^-$, $H_2PO_4^-$, etc.).

(2) Electrons can transfer from the hypophosphite to the corner of the tetrahedron via hydrogen atoms and be surrendered to the nickel substrate.

(3) Electrons can also transfer from the substrate to adsorbed hypophosphite.

The above assumptions could be modified by the following two different pathways of chemisorption: (1) the oxidative addition,²² by which the P-H bond of $H_2PO_2^-$ undergoes hemolytic cleavage on a Ni atom, and (2) the Ni-O bonding model, in which hypophosphite anion lands at the IHP via its oxygen ends (Figure 2). The oxidative addition produces P and the surface hydrogen atoms, which needs to abstract three electrons from the surface Ni atoms (eq 5). With respect to the oxygen-landing model in association with the oxidation of hypophosphite, oxygen has a stronger affinity and greater spatial accessibility than hydrogen to the surface Ni atoms. Moreover, according to Taube's theory, 2^{23-25} the oxygen atom is more proper than the hydrogen atom in functioning as the bridge for electron transfer from phosphorus (I) to Ni. The products of this pathway are orthorphosphite, electrons to the IHP and protons discharged to the plating solution (eq 6)

$$H_2PO_2^{-}_{(ads)} + 3e^{-}(Ni_m) + 4H^+ \rightarrow Ni_m - 2H_{(suf)} + Ni_m - P_{(suf)} + 2H_2O$$
 (5)

$$H_2PO_2^{-}_{(ads)} + H_2O \rightarrow 2e^{-}(Ni_m) + H_2PO_3^{-}_{(aq)} + 2H^{+}$$
 (6)

$$Ni^{2+} + 2e^{-}(Ni_m) \rightarrow (Ni_m)$$
(7)

where (Ni_m) represents the Ni atoms on the surface plating frontier or at the IHP. It may note that these three equations are proposed to describe the reactions happening on the surface of "electrode", and they do not represent elementary steps.



I: $H_2PO_{2(ads)}^- + H_2O \rightarrow 2e^-(Ni_m) + H_2PO_{3(aq)}^- + 2H^+$

II: $H_2 PO_{2(ads)}^- + 3e^- (Ni_m) + 4H^+ \rightarrow (Ni_m) 2H_{(suf)} + (Ni_m)P + 2H_2O$

Figure 2. Sketch to show the two different reaction pathways through which hypophosphite ions are converted to orthophosphate and phosphorus, respectively.

Various types of atomic clusters containing the Ni(0)-P(0)bond have been known.²⁶ From the viewpoint of coordination chemistry, a phosphorus atom is a σ ligand that could cause an increase in electron density at the nickel atoms coordinated.^{22,26} It has been known that the negative charge density at the central transition metal atom (or ion) of a complex is a favorable factor to the oxidative addition of reactant molecules. Once a phosphorus atom is deposited on the IHP, its adjacent nickel atoms would show a higher preferentiality to the oxidative addition of hypophosphite. This action will be therefore followed by deposition of phosphorus (eq 5) at the neighborhood of this site. However, this trend can be constrained by the oxidation step that supplies electrons to the oxidative addition (eq 6). The coordination chemistry points out that oxidative addition requires the Ni atoms which have low coordination numbers (CN), which happen at edges or corners, whereas the oxidation step does not have such spatial preferentiality. The surface complexes are formed upon adsorption of hypophosphite to the Ni atoms. Hence, it is rational to propose that the oxidative addition and the oxidation of hypophosphite take place at the IHP simultaneously but at different locations. This mutually promoting deposition mechanism could well account for the laminated Ni/P structure and nonhomogeneous P distribution in the Ni-P deposition layer (Figure 3), which have been found experimentally.27,28 The content and distribution of P(0) in the Ni/P deposition layer are known to affect the corrosion resistance of the layer.

3.2. Relation of Adsorption at EDL and the Work Function of Ni Deposition Film. According to Grahame's theory,^{29,30} the potential decreases linearly from the IHP to the OHP, whereas it decreases almost exponentially in the diffuse layer. We can assume that k_1 is the ratio of charge of the hypophosphite anion to the total negative charge (from other types of coexisting anions) at the IHP, and k_2 is the ratio of

charge carried by nickel ions to the total cationic charge at the OHP. At an equilibrium of plating, k_1 and k_2 should vary negligibly. Thus, the plane density of nickel ions at the OHP, $n_{\text{OHP}}^{\text{Ni}}$ (m⁻²), has a linear relationship with the plane density of hypophosphite anions at the IHP, $n_{\text{IHP}}^{\text{P}}$:

$$n_{\rm OHP}^{\rm Ni} = k_{\rm r} n_{\rm IHP}^{\rm P} \tag{8}$$

where k_r is a constant $(k_r = k_2/k_1)$.

Furthermore, $n_{\rm IHP}^{\rm P}$, can be described as

$$n_{\rm IHP}^{\rm P} = C_{\rm B}^{\rm P} \tilde{V} N_{\rm ads} \exp(-G_{\rm ads}/kT)$$
(9)

where $C_{\rm B}^{\rm P}$ is the bulk concentration of hypophosphite anions in the EN bath, \tilde{V} is the molar volume of the solution, $N_{\rm ads}$ denotes the number of available adsorption sites for hypophosphite anion per unit surface area on the IHP, k is the Boltzmann's constant, T stands for the absolute temperature, and $G_{\rm ads}$ means the Gibbs adsorption energy per adsorbate species (e.g., a H₂PO₂⁻ anion).

It has been aware that the rate of adsorption of hypophosphite is affected to a large extent by the thermodynamic work function (Φ) that includes the vacuum work function of the solid adsorbent in question and the effect due to the presence of adsorbates on surface ($\Phi = \Phi_{vacuo} + b$). The change in the work function represents the collective effect of the individual coordination adsorption sites as aforementioned, and therefore, the free energy of adsorption has a linear relationship with the work function.³¹ Applying this concept, we could presume that the adsorption of H₂PO₂⁻ at the IHP obeys the relationship as follows when a change in the work function is incurred due to the adsorption of stabilizer species at the IHP

$$G_{\rm ads} + k_{\rm G} \Phi = G_{\rm ads}^0 + k_{\rm G} \Phi_0 \tag{10}$$

In eq 10, G_{ads}^0 is defined as the average Gibbs free energy of adsorption for the landing of a hypophosphite anion onto the IHP in the absence of stabilizers, Φ_0 is the corresponding work function of the Ni deposition film, and k_G is a proportional constant describing the influence of work function on the adsorption tendency of H₂PO₂⁻. Combining eqs 9 and 10, the adsorption plane density of hypophosphite anion at the IHP can be related to the work function of the plating frontier

$$n_{\rm IHP}^{\rm P} = n_{\rm IHP}^{\rm P0} \exp[k_{\rm G}(\Phi - \Phi_0)/kT]$$
 (11a)

in which

$$n_{\rm IHP}^{\rm P0} = C_{\rm B}^{\rm P} \tilde{V} N_{\rm ads} \exp[-G_{\rm ads}^0 / kT]$$
(11b)

 $n_{\rm IHP}^{\rm P0}$ is the plane density arrived at equilibrium in a system where nil stabilizer is present. Similarly, $n_{\rm OHP}^{\rm Ni}$ can be also linked with eq 11a by applying eq 8

$$n_{\text{OHP}}^{\text{Ni}} = k_{\text{r}} n_{\text{IHP}}^{\text{P0}} \exp[k_{\text{G}}(\Phi - \Phi_0)/kT]$$

= $n_{\text{OHP}}^{\text{Ni0}} \exp[k_{\text{G}}(\Phi - \Phi_0)/kT]$ (12)

where n_{OHP}^{Ni} is the number of hydrated Ni²⁺ ions per unit area at the OHP.

3.3. Diffusion of Free Pb²⁺ Ions toward the OHP. As aforementioned, Ni^{2+} ions are reduced at the OHP, and the required electrons come from the plating frontier through the S–G layer (tunneling effect). Most of the nickel atoms (or colloids) formed at the OHP deposit on the substrate. However, a handful of them are to diffuse outward into the bulk solution



Figure 3. Schematic illustration of the periodical change of the phosphorus rich region.



Figure 4. (a) Schematic illustration of the diffusion directions of Ni–P colloids and Pb^{2+} ; (b) The concentration profiles for the diffusion of colloidal nickel particles diffusion from the OHP to the bulk of solution and the diffusion Pb^{2+} from bulk phase to the OHP.

through the diffuse layer.¹¹ The Pb²⁺ ions in the bulk of the solution will set down quickly on these Ni colloidal particles as they have a much larger and hence reactive specific surface area than the plating object. It may be note that, besides the desired plating surface, the individual Ni colloidal particle also has an EDL. Hence, there is a flux of Pb²⁺ from the bulk of the solution toward the OHP in response to the decrease of Pb²⁺ concentration hereabout (Figure 4). Assume this process will quickly reach the steady state, which means that the flux of the plating surface) has a linear relationship with the inward Pb²⁺ diffusion flux from the solution body. In the case that the Pb⁺² concentration in the bulk (C_B^{Pb-C}), Pb⁺² can diffuse to the OHP of the desired plating surface, and the concentration in (very close proximity to) the

OHP can be written as

$$C_{OHP}^{Pb} = C_{B}^{Pb} - k_{Pb/Ni} \frac{D_{Ni}^{app}}{D_{Pb}^{app}} C_{OHP}^{Ni} \approx C_{B}^{Pb} - C_{B}^{Pb-C} \quad (C_{B}^{Pb} > C_{B}^{Pb-C}) \quad (13a)$$
$$C_{OHP}^{Pb} = 0 \ (C_{B}^{Pb} \le C_{B}^{Pb-C}) \quad (13b)$$

where $D_{\text{Ni}}^{\text{app}}$ and $D_{\text{Pb}}^{\text{app}}$ are the apparent diffusivities of nickel particles and lead ions, respectively, resulting from the approximation of the mass conservation law

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} + r \approx D^{\mathrm{app}} \frac{\partial^2 c}{\partial x^2}$$

where r is the term denoting generation or consumption by the reaction. Furthermore, the steady-state assumption leads to

$$D_{\text{Ni}}^{\text{app}} \frac{\partial^2 C^{\text{Ni}}}{\partial x^2} = D_{\text{Pb}}^{\text{app}} \frac{\partial^2 C^{\text{Pb}}}{\partial x^2} = 0 \quad \text{or} \quad k_{\text{Pb/Ni}} D_{\text{Ni}}^{\text{app}} \frac{\partial C^{\text{Ni}}}{\partial x} = D_{\text{Pb}}^{\text{app}} \frac{\partial C^{\text{Pb}}}{\partial x}$$
(13c)

where $k_{Pb/Ni}$ is the corresponding flux ratio of lead ions to tiny nickel particles, C_B^{Pb} and C_{OHP}^{Pb} are the concentrations of the lead ions in the bulk of solution and at the OHP, respectively, C_{OHP}^{Ni} is the concentration of Ni colloidal particles at the OHP, and C_B^{Pb-C} is the critical bulk concentration of lead ion, over which the lead ion concentration influences both the plating rate and phosphorus content at the desired plating surface. In the integration of eq 13c to obtain eq 13a, $C_B^{Ni} = 0$ means no unstabilized (by the adsorption of Pb²⁺) nickel colloidal particles are present in the bulk of plating solution.

3.4. Effect of a Stabilizer on the Work Function of Ni Colloidal Particles. In EN plating baths, substantially low concentrations of the heavy metal ion stabilizer, such as Pb²⁺ (in ppm level), are normally used. It is unlikely that Pb²⁺ ions inhibit the propagation of Ni colloidal particles through the action of spatial blocking, namely, by forming an obstructing layer on Ni particles. Being identified as an effective stabilizer, the lead ion must play a catalytic role in the deactivation of Ni particles. From the viewpoint of physics, the work function of Ni colloidal particles (substrate) would be very sensitive to adsorption of Pb²⁺ on them. The change in the thermodynamic work function of the substrate, $\Delta \Phi = \Phi - \Phi_0$, is found to be proportional to the number N and the dipole moment p of adsorbed species^{32,33} 10924 J. Phys. Chem. B, Vol. 108, No. 30, 2004

$$\Delta \Phi = -4\pi pN \tag{14a}$$

The negative sign in eq 14a means that the work function of pure nickel ($\sim 4.9 \text{ eV}$) is decreased by the adsorbed Pb, whose work function is about 4.25 eV. Heavy metal cations have larger ionic radii and can be more easily adsorbed on the surface of Ni particles through electrochemical displacement

$$(Ni_n) + nPb^{2+} \rightarrow (Pb_n) + nNi^{2+}, \quad E^\circ = 0.1319 V^{34}$$
(14b)

As the concentration of lead ions is substantially low, it can be assumed that there is a simple and approximate relationship between N and C_{OHP}^{Pb}

$$N = a(C_{\rm OHP}^{\rm Pb}) \tag{15}$$

where *a* is the constant signifying the fraction of those Ni surface sites on an individual Ni particle at which the displacement of Ni with Pb²⁺ ions can carry out. These Ni sites must have low coordination numbers. The work function (Φ) of the substrate can now be linked with the concentration of Pb²⁺ ion in an EN plating solution ($C_{\rm B}^{\rm Pb}$) by combining eqs 14a and 15

$$\Phi = \Phi_0 - 4\pi p a (C_{\text{OHP}}^{\text{Pb}}) \tag{16a}$$

Here Φ_0 is the work function of clean Ni–P layer (without carrying Pb). On the other hand, to figure out the change of work function in the desired plating surface when $C_{\rm B}^{\rm Pb}$ > $C_{\rm B}^{\rm Pb-C}$, we just need to plug eq 13a into 16a. Therefore, the work function of the desired plating surface can be linked with the concentration of Pb^{2+} (C_B^{Pb}) in plating solution

$$\Phi = \Phi_0 - 4\pi p a (C_{\rm B}^{\rm Pb} - C_{\rm B}^{\rm Pb-C})$$
(16b)

At this point, the relationship of the work function and the Fermi energy $(E_{\rm f})$ becomes essential. According to the theoretical model described by Eisberg and Resnick³⁵, there is an abrupt leap of the potential energy of an electron (V_0) in a metal at the boundary from bulk to environment, representing the depth of the potential well from the lowest energy state to the state of electron being far outside the metal. It is also understandable that most energetic electrons in the metal are in the state having an energy interval Φ_0 below the top of the potential well ($V_0 >$ Φ_0). Thus, the relationship between the work function Φ_0 (or Φ) and Fermi energy $E_{\rm f}^0$ (or $E_{\rm f}$) can be expressed as

$$V_0 = \Phi_0 + E_f^0 \approx \Phi + E_f \tag{16c}$$

in which Φ and $E_{\rm f}$ are the thermodynamic work function and Fermi energy, respectively, and the subscript or superscript "0" represent under the condition without the co-deposited stabilizer Pb.

The above approximation equal sign implies that, if the concentration of co-deposited Pb atoms in the Ni-P lattice of the plating surface is considerably low, the influence incurred on V_0 can be ignored. Hence, the following expression can be obtained from eqs 16b and 16c

$$E_{\rm f} = E_{\rm f}^0 + 4\pi pa(C_{\rm B}^{\rm Pb} - C_{\rm B}^{\rm Pb-C})$$
(16d)

where $E_{\rm f} = E_{\rm f}^0$ if $C_{\rm B}^{\rm Pb} < C_{\rm B}^{\rm Pb-C}$. On the basis of eqs 16a and 16d, it can be concluded that participation of Pb(0) into the Ni-P lattice of both Ni colloidal particles and the desired plating surface causes a decrease in the work function and an increase in the Fermi energy. The



Figure 5. Schematic illustration of the electron tunneling process from nickel surface to the dehydrated Ni²⁺ ions at the OHP.

effect is that electrons over the plating frontier are easier to give up relative to the pristine Ni-P lattice. As discussed above, the resulting IHP can promote the oxidative addition of hypophosite (the cathodic process) from the viewpoint of electronic factor. However, it inhibits the oxidation of hypophosphite (the anodic process). Therefore, the deposition rates of both Ni and P are to be pulled down with tightening up of the electron supply channel.

3.5. Nickel Deposition. The electroless plating system is often explained as being driven by an auto-catalytic surface because the reduction of Ni²⁺ at OHP has the certain relationship with the adsorption of hydrogen atoms at the plating frontier.¹¹ The surface Ni-H species will have two destinies, being released either as protons or as hydrogen molecules. An EN plating process is always accompanied by the release of hydrogen bubbles and a decrease in the pH value. A tenable explanation for this is that the adsorbed hydrogen atoms can undergo coupling to form hydrogen gas or depart as protons after transferring electrons to Ni²⁺ ions through the IHP.

With respect to the transfer of electrons from the plating frontier to the Ni²⁺ ion within the S-G layer, it is assumed to be an electron tunneling process (Figure 5), which can be described using a rectangular potential energy barrier expressed as³⁶

> U(x) = 0, x < 0 in region I $U(x) = U_0, \quad 0 < x < L$ in region II U(x) = 0, x > L in region III

where L and U_0 represent the width and the height of the potential barrier, respectively. U_0 as illustrated in Figure 5 includes the contribution of all electronic states (or energy levels) to the tunneling process, despite the fact that electrons from the states of $E > E_{\rm f}$ (labeled by the solid rectangle) have a much higher probability to penetrate through the barrier. The height of potential barrier U_0 was estimated to be ~14.8 eV,¹⁴ in which the Fermi level of Ni-P (~10 eV) can be obtained from the universal equation given in the book of Eisverg and Resnick,35 and the relationship between U_0 and the thermodynamic work function Φ is $V_0 = \Phi + E_f = U_0 + b$, where b reflects the influence of adsorption on the work function. The adsorption of negative charges on the plating surface, e.g., hypophosphite, creates a repulsive action to the entrance of electrons into the

solution. For this, the work function is related to the interfacial potential, in which the adsorption free energy takes the main part.

Using the WKB (after Wentzel, Kramers, and Brillouin) approximation,^{37–39} the tunneling probability of the state with a energy level *E*, W(E), can be expressed by

$$W(E) = \exp\left\{-\frac{4\pi L}{h}\sqrt{2m(U_0 - E)}\right\}$$
(17)

where *m* is the static mass of electron, $U_0 = 14.8 \text{ eV}$, *h* is the Planck's constant, and the barrier width *L* is chosen as 5×10^{-10} m. For the cathodic reaction, if the interfacial electron transfer is the rate determining step, the most generic expression of the current density is given by the form³⁹

$$i_{\rm c} \propto e_0 \int \int C(x) G(x, E) W(x, E) f(E) \rho(E) \, \mathrm{d}E \, \mathrm{d}x$$
 (18a)

where e_0 is the charge of an electron, C(x) is a one-dimensional concentration of the acceptor (Ni²⁺) within the Stern layer at distance *x* from the plating frontier, G(x,E) is the probability of finding the acceptor possessing potential energy *E* at distance *x* from the plating frontier, W(x,E) is the probability of electrons migrating from an energy level *E* in the plating frontier to Ni²⁺ ion within the S–G layer, f(E) is the Fermi–Dirac distribution of occupied electron states with an energy level *E* in the metal electrode, and $\rho(E)$ is the density of electronic state with an energy level *E* in the cathode (the Ni plating frontier). Since it is rational to assume, according to the tunneling effect, that most of the dehydrated nickel ions gain electrons at the OHP of the desired plating surface, the G(x,E) and W(x, E) functions in the integral can thus be reduced to be ones with a single variable *E*. Consequently, the above double integral becomes

$$i_{c} \propto e_{0}(\int C(x)|_{x=L} dx)(\int G(E)W(E)f(E)\rho(E) dE)$$
(18b)

The integration of the C(x) term yields the plane density of Ni²⁺ at the OHP that is expressed by δ_{OHP}^{Ni}

$$i_{\rm c} = \lambda e_0 \delta_{\rm OHP}^{\rm Ni} \int G(E) W(E) f(E) \rho(E) \, \mathrm{d}E \qquad (18c)$$

 λ is introduced here as a proportional constant. According to the Boltzmann's distribution, the energy-level distribution of the acceptor, G(E), in solution is given as¹⁴

$$G(E) = G(E_g) \exp[\beta(E - E_g)/kT]$$
(19)

where $E_{\rm g}$ is the ground-state energy of the acceptor (Ni²⁺ ion). The second ionization energy of Ni can be used to approximate the ground state of Ni²⁺ ion. The factor β is the symmetry factor (0 < β < 1) describing the geometry of the lowest unoccupied orbitals of Ni²⁺, which are the d orbitals having symmetry with respect to the center, so the β value is chosen as 0.5. At a temperature *T* above absolute zero, the Fermi–Dirac distribution^{40–43} for the expectation of occupancy of a state with energy *E* in the metal electrode is

$$f(E) = \frac{1}{1 + \exp\left(\frac{E - E_{\rm f}}{kT}\right)}$$
(20)

where E_f is known as the Fermi energy (of the Ni–P deposition layer in this particular case) and k is the Boltzmann constant. The density of states $\rho(E)$ at the energy level E, whether it is



Figure 6. Independent of $K_{\rm F}$ value on the Fermi energy ($E_{\rm f}$).

filled or not, is given by per unit volume,⁴² where *m* is the static mass of electron and $\hbar = h/2\pi$

$$\rho(E) = \frac{8m\pi}{h^3} \sqrt{2mE} = \frac{1}{2\pi^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} E^{1/2}$$
(21)

Submitting eq 17 and 19–21 into eq 18c, the current density, $i_{\rm C}$, can be expressed as

$$i_{\rm C} = K_0 \delta_{\rm OHP}^{\rm Ni} F(E, E_{\rm f})$$
(22a)

in which $F(E,E_f)$ is a function of the Fermi energy (E_f) and the energy level (E) of interest

$$F(E,E_{\rm f}) = \int \frac{\exp\left[\left(\frac{\beta E}{kT} - \frac{4\pi L}{h}\sqrt{2m(U_0 - E)}\right)\right]\sqrt{E}}{1 + \exp\left(\frac{E - E_{\rm f}}{kT}\right)} \, \mathrm{d}E$$
(22b)

whereas K_0 can be expressed as

$$K_0 = \lambda \frac{e_0}{2\pi^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} G(E_g) \exp\left(-\frac{\beta E_g}{kT}\right)$$
(22c)

From eqs 12 and 16b, we obtain

$$\frac{n_{\text{OHP}}^{\text{Ni}}}{n_{\text{OHP}}^{\text{Ni0}}} = \exp[k_{\text{G}}(\Phi - \Phi_0)/kT] = \exp\left[-\frac{4\pi \, pak_{\text{G}}}{kT}(C_{\text{B}}^{\text{Pb}} - C_{\text{B}}^{\text{Pb}-\text{C}})\right]$$
(23)

Substituting the value of barrier height ($U_0 = 14.8 \text{ eV}$), barrier width ($L = 5 \times 10^{-10}$ m), the symmetry factor ($\beta = 0.5$), and the EN plating temperature (T = 363 K) into eq 22b and integrating the equation over the range $0 \le E \le U_0$, it becomes

$$F(E_{\rm f}) = K_{\rm F}\sqrt{E_{\rm f}} \exp[(16E_{\rm f} - 5.1\sqrt{14.8 - E_{\rm f}})] \quad (24a)$$

$$K_{\rm F} = \int_{0}^{14.8} \frac{\sqrt{E} \exp[(16E - 5.1\sqrt{14.8 - E_{\rm f}})]}{1 + \exp[32(E - E_{\rm f})]} \, \mathrm{d}E \quad (24b)$$

The exponential term in eq 24a is purposely inserted in order to obtain a constant value when $E = E_{\rm f}$. The value $K_{\rm F}$ calculated is equal to 0.0987 (eV^{1.5}) and independent of the Fermi energy ($E_{\rm f}$; Figure 6). Furthermore, it is appropriate to presume that electrons taking part in the tunneling process should have energy states above the Fermi level of substrate⁴³ being considered. Thus, eq 24a expressed by $E_{\rm f}$ can be taken as the energy threshold to calculate electron current density within the Stern layer 10926 J. Phys. Chem. B, Vol. 108, No. 30, 2004

$$F(E_{\rm f}) = 0.0987 \sqrt{E_{\rm f}} \exp[(16E_{\rm f} - 5.1\sqrt{14.8 - E_{\rm f}})] \qquad (25)$$

Therefore, the electric current density $i_{\rm C}$ within the Stern layer would be

$$i_{\rm C} = K_0 n_{\rm OHP}^{\rm Ni0} \sqrt{E_{\rm f}} \exp \left[(16E_{\rm f} - 5.1\sqrt{14.8 - E_{\rm f}}) - \frac{4\pi k_{\rm G} p a}{kT} (C_{\rm B}^{\rm Pb} - C_{\rm B}^{\rm Pb-C}) \right]$$
(26)

As far as the electron transfer between the two Helmholtz planes is concerned, nickel deposition rate $R_{\rm Ni}$ (mg h⁻¹ cm⁻²) depends on $i_{\rm C}$. Theoretically, this process could be also described by Faraday's law of electrolysis

$$R_{\rm Ni} = \alpha k_{\rm e} i_{\rm C} \tag{27a}$$

where $k_{\rm e}$ is the electrochemical equivalent for the reduction Ni²⁺ + 2e = Ni; and α is proportional constant and its value depends on plating loading as well as the percentage of nickel colloidal particles in the total Ni–P deposits at the moment t.

The nickel plating rate $R_{\rm Ni}$ (eq 27a) becomes

$$R_{\rm Ni} = k_{\rm Ni} \sqrt{E_{\rm f}} \exp \left[(16E_{\rm f} - 5.1\sqrt{14.8 - E_{\rm f}}) - \frac{4\pi k_{\rm G} pa}{kT} (C_{\rm B}^{\rm Pb} - C_{\rm B}^{\rm Pb-C}) \right]$$
(27b)

where $k_{\rm Ni} = \alpha k_e K n_{\rm OHP}^{\rm Ni0}$. For $C_{\rm B}^{\rm Pb} \leq C_{\rm B}^{\rm Pb-C}$, as aforementioned, no Pb²⁺ ions enter the OHP of the desired plating surface under this condition. Equation 27b is thus shortened as

$$R_{\rm Ni}^0 = k_{\rm Ni} \sqrt{E_{\rm f}^0} \exp(16E_{\rm f}^0 - 5.1\sqrt{14.8 - E_{\rm f}^0})$$
 (27c)

The term R_{Ni}^0 is the nickel deposition rate without interference of Pb²⁺ stabilizer. This concept will be elaborated in section 4.

The electron flow rate within the Stern layer is mainly affected by both the Fermi level of the Ni-P deposition layer and the concentration of nickel ion at the OHP. Equations 27b,c offer an interpretation for the catalytic deactivation effect of the Pb2+ ion. If we take the ratio $R_{\rm Ni}/R_{\rm Ni}^0$

$$\frac{R_{\rm Ni}}{R_{\rm Ni}^0} = \sqrt{\frac{E_{\rm f}}{E_{\rm f}^0}} \exp\left(\frac{\beta}{kT}(E_{\rm f} - E_{\rm f}^0)\right) \exp\left(\frac{4\pi L\sqrt{2m}}{h}(\sqrt{U_0 - E_{\rm f}^0} - \sqrt{U_0 - E_{\rm f}})\right) \exp\left(-\frac{4\pi k_{\rm G} P a}{kT}(C_{\rm B}^{\rm Pb} - C_{\rm B}^{\rm Pb-C})\right)$$
(27d)

where $\beta/kT = 16 \text{ eV}^{-1}$, $U_0 = 14.8 \text{ eV}$, $[4\pi L\sqrt{(2m)}]/h = 5.1$ eV^{-0.5}.

The equation can be approximated as

$$\frac{R_{\rm Ni}}{R_{\rm Ni}^0} \approx \sqrt{\frac{E_{\rm f}}{E_{\rm f}^0}} \exp\left(\frac{\beta}{kT} (E_{\rm f} - E_{\rm f}^0)\right) \exp\left(-\frac{4\pi k_{\rm G} P a}{kT} (C_{\rm B}^{\rm Pb} - C_{\rm B}^{\rm Pb-C})\right)$$
(27e)

Combining it with eq 16d, i.e., $E_f = E_f^0 + 4\pi Pa(C_B^{Pb} - C_B^{Pb-C})$, one obtains

$$\frac{R_{\rm Ni}}{R_{\rm Ni}^0} \approx \sqrt{\frac{E_{\rm f}}{E_{\rm f}^0}} \exp\left(\frac{4\pi Pa}{kT}(\beta - k_{\rm G})(C_{\rm B}^{\rm Pb} - C_{\rm B}^{\rm Pb-C})\right) \quad (27f)$$

In eq 27f, the maximum value of β is one. As for $k_{\rm G}$, we have the relation from eq 10

$$k_{\rm G} = \frac{G_{\rm ads} - G_{\rm ads}^{\rm o}}{\Phi_0 - \Phi}$$

From the normal adsorption heat, the numerator term can be estimated to have a magnitude of about 0.1 eV/molecule; and from the difference of vacuum work functions of Ni metal (4.9 eV) and Pb metal (4.25 eV), the denominator term falls in the range of about 0.1-0.01 eV as the Pb content in Ni is very low. Therefore, $k_{\rm G} > \beta$. On the basis of this estimation, it is clear that $R_{\rm Ni} < R_{\rm Ni}^0$.

3.6. Phosphorus Deposition. According to eq 5 proposed, the deposition of phosphorus process is believed to experience the three elementary steps (Figure 2): (1) landing of hypophosphite anion through its hydrogen corners, (2) oxidative addition of it to surface nickel atoms, and (3) abstraction of the two oxygen poles from the adsorbed P atom. The oxidative-addition step could be considered as the rate determining step as it involves the transfer of three electrons and breaking up of the two P-H bonds. Thus, the P deposition rate can be written as

$$R_{\rm P} = k_{\rm p}^{\prime} \tau n_{\rm IHP}^{\rm P} = k_{\rm P} n_{\rm IHP}^{\rm P} \tag{28a}$$

where k'_{p} is the rate constant of oxidative-addition step; and τ is the percentage of those surface Ni sites that are unsaturated with coordination and allow the oxidative-addition to take place. With substitution of the eq 11a, eq 28a becomes

$$R_{\rm P} = k_{\rm P} n_{\rm IHP}^{\rm P0} \exp[k_{\rm G}(\Phi - \Phi_0)/kT]$$
 (28b)

With further including eq 16b, the eq 28b can be expressed as

$$R_{\rm P} = k_{\rm P} n_{\rm IHP}^{\rm P0} \exp[-k_{\rm G} 4\pi p a (C_{\rm B}^{\rm Pb} - C_{\rm B}^{\rm Pb-C})/kT] \quad (28c)$$

For $C_{\rm B}^{\rm Pb} \leq C_{\rm B}^{\rm Pb-C}$

$$R_{\rm P}^0 = k_{\rm P} n_{\rm IHP}^0 \tag{28d}$$

Here the term $R_{\rm P}^0$ is the phosphorus deposition rate in the absence of Pb²⁺ at the OHP of the desired plating surface. Equation 28c shows that the phosphorus deposition rate is to decrease with an increase in the concentration of lead ion.

4. Experimental Results and Discussion

4.1. Critical Stabilizer Concentration. In an EN plating system, there is usually a critical Pb(Ac)₂ concentration ($C_{\rm B}^{\rm Pb-C}$), below which the deposition rate and the composition of Ni-P film on the desired plating surface are not affected. Pb²⁺ ions can only diffuse to the OHP of Ni colloidal particles and accept electrons from the Ni particles because they possess much more reactive surface than the plating surface. For a given plating-bath, decreasing of Pb²⁺ concentration depends on two variables: (1) the plating loading (PL), which is defined as a ratio of the plating surface area to the volume of plating solution, and (2) the plating time. Figure 7 shows a negligible effect of Pb²⁺ on both Ni plating rate and phosphorus content of the deposit on the plating surface (the brass substrate with PL =1.67 dm²/L). Hence the concentration points $C_{\rm B}^{\rm Pb}$ tested are considered below the critical level. In this respect, the basic relationship is that $C_{\rm B}^{\rm Pb-C}$ increases with increasing PL because the Ni colloids concentration $C_{\rm OHP}^{\rm Ni}$ will rise with increasing PL (stated by eq 13a) and a higher level of Pb²⁺ concentration is



Figure 7. Effects of $Pb(Ac)_2$ concentration (below the critical concentration) on (a) the Ni plating rate and (b) the phosphorus content.

hence requested to prevent fast reproduction of Ni colloidal particles. In other words, for a given EN bath, the plating will cease shortly if the desired plating surface area is substantially smaller than the designed size.

To elaborate the Pb²⁺ concentration effect on the composition of the plating surface, XPS characterization was employed to examine the Ni-P films developed on the Al-coated silicon wafer. In this experiment, the PL value of $1.25 \times 10^{-2} \text{ dm}^2$ L^{-1} and 20 min of plating time were employed. The samples were thoroughly washed. The phosphorus content on the examined surface underwent a dramatic change in the concentration range of $C_{\rm B}^{\rm Pb}$ from 10 to 15 ppm. The P_{2p} peaks of elemental P⁰ at 129–130 eV appear on the plated surface only when $C_{\rm B}^{\rm Pb}$ is below 10 ppm (Figure 8a). Correspondingly, Pb species is found to emerge on the XPS spectrum when $C_{\rm B}^{\rm Pb}$ is greater than 10 ppm (Figure 8b). It may note hereby that the critical value $C_{\rm B}^{\rm Pb-C}$ differs from the $C_{\rm B}^{\rm Pb}$ at which Pb could be observed by XPS. The critical value must be far below the concentration that gives rise to XPS Pb peaks. The appearance of Pb(II) species on the XPS spectrum is due to oxidation of surface lead atoms since the samples were not stored in inert atmosphere after purification.

On the other hand, with using $C_{\rm B}^{\rm Pb} = 15$ ppm, the two Ni_{2p} peaks at 852 and 869 eV representing Ni⁰ species disappeared from its XPS spectrum (Figure 8c) despite the fact that an initial plating rate of about 12 mg cm⁻² h⁻¹ (or equivalent to11 mA/cm²) was still obtained. Instead, lead species was identified on the same surface (Figure 8a). This phenomenon shows the Pb-induced deactivation process, which is virtually self-promoted. It means that in the case of a larger $[C_{\rm B}^{\rm Pb} - C_{\rm B}^{\rm Pb-C}]$ value the electrochemical displacement reaction (eq 14b) will gradually overtake the deposition of Ni and consume the surface Ni atoms and eventually form a Pb deposition layer as long as the different in concentration $[C_{\rm B}^{\rm Pb} - C_{\rm B}^{\rm Pb-C}]$ exists. As aforementioned, a





Figure 8. XPS of the three elements in the deposition films (on Al/Si substrate) prepared by using different $Pb(Ac)_2$ concentrations.

large $[C_B^{Pb} - C_B^{Pb-C}]$ value can be caused by two ways: (1) for a given PL but using a higher concentration of Pb²⁺ or (2) for a given concentration of Pb²⁺ but reducing PL dramatically.

4.2. Dependence of Deposition Rates R_{Ni} and R_{P} on the **Stabilizer Concentration** C_{B}^{Pb} . The reliance of the phosphorus deposition rate on the Pb(Ac)₂ concentration has been investigated by using the brass substrate (PL = 1.67 dm²/L, Figure 9), on which two concentration ranges symbolized by the different rates can be identified. The P deposition rate slips very slightly in the low concentration range (0~10 ppm) but perceptibly in the higher concentration range. In the low stabilizer concentration range, both the nickel deposition rate ($R_{\text{Ni}}^0 = 12.23 \text{ mg cm}^{-2} \text{ h}^{-1}$ or equivalent to 11.22 mA/cm²) and phosphorus deposition rate ($R_{\text{P}}^0 = 1.24 \text{ mg cm}^{-2} \text{ h}^{-1}$ or equivalent to 0.478 mA/cm²) are nearly constant (Figure 7).



Figure 9. Influences of the $Pb(Ac)_2$ concentration on the deposition rate of (a) phosphorus and (b) of nickel on brass substrate.

Combing eq 28c with eq 28d, the dependence of phosphorus deposition rate on Pb^{2+} concentration can be expressed as

$$R_{\rm P} = R_{\rm P}^0 \exp\left[-\frac{4\pi k_{\rm G} pa}{kT} (C_{\rm B}^{\rm Pb} - C_{\rm B}^{\rm Pb-C})\right]$$
(29a)

Since the difference between U_0 and E_f is much larger than the difference between E_f and E_f^0 , the term $\exp[-5.1\sqrt{(14.8 - E_f)}]$ can be approximated with $\exp[-5.1\sqrt{(14.8 - E_f)}]$. Substituting eq 16d into eq 27e, the nickel deposition rate can be written as

$$R_{\rm Ni} = \frac{R_{\rm Ni}^{0}}{\sqrt{E_{\rm f}^{0}}} \sqrt{E_{\rm f}^{0} + 4\pi pa(C_{\rm B}^{\rm Pb} - C_{\rm B}^{\rm Pb-C})} \exp\left[\left(16 \times 4\pi pa - \frac{4\pi k_{\rm G} pa}{kT}\right)(C_{\rm B}^{\rm Pb} - C_{\rm B}^{\rm Pb-C})\right] (29b)$$

In Eqs 29a and 29b, there are four physical terms whose values need to be determined

$$\frac{4\pi k_{\rm G} pa}{kT}$$
, $4\pi pa$, $E_{\rm f}^0$, and $C_{\rm B}^{\rm Pb-C}$

Fitting these two theoretical models with the experimental data was employed to figure out the above parameters. A Z value is thus defined, as eq 30a, through minimizing the discrepancy between the rates from experiments defined as $R_{\rm Ni}^{\rm exp}$ and $R_{\rm P}^{\rm exp}$ and from the above two equations. The Z value is minimized by using the Nelder–Mead method,^{44–45} and the minimization was conducted by using MATLAB 5.3 with a tolerance value of 1×10^{-4}

$$Z = \sum_{i=1}^{N} (R - R^{\exp})^2$$
 (30a)

Fitting eq 29a with experimental data of phosphorus deposition rate at T = 363 K, the values of $[(4\pi k_G pa)/(kT)]$ (0.07 ppm⁻¹) and $C_{\rm Pb^{-C}}^{\rm Pb^{-C}}$ (12.73 ppm) were obtained (Figure 9a). Further





Figure 10. The relationship between $4\pi pa$ and E_f^0 .



Figure 11. Change of the total plating rate (*R*) with the lead ion concentration ($C_{\rm S}$)



Figure 12. Change of phosphorus content (P%) of the Ni–P films on the lead ion concentration ($C_{\rm S}$).

substituting the values of $[(4\pi k_G pa)/(kT)]$ and C_B^{Pb-C} into eq 29b and fitting it with experimental data of nickel deposition rate, the values of $4\pi pa$ and E_f^0 were determined (Figure 9b). Fixing the value of E_f^0 and fitting the model with experimental data, Figure 10 shows the relationship of the term $4\pi pa$ with E_f^0 . It is obvious that under a small energy level (less than 0.5 eV) the initial Fermi energy value affects the simulation value $4\pi pa$ significantly. In contrast, if the initial Fermi energy level larger than 1 eV, the value of $4\pi pa$ is nearly a constant (i.e., 0.0009 eV/ppm). Using the above simulation values, k_G can be worked out to have a value near 2.4. That is, $k_G > \beta$, which supports the estimation obtained using eq 27f.

It is not an easy task to obtain the true initial Fermi energy level due to several reasons: namely, (1) the compositional nonuniformity of the deposited Ni–P film, (2) the effect of codeposited phosphorus, and (3) the aqueous solution instead of vacuum as the reaction medium. Inspite of this, the initial Fermi energy value is not absolutely necessary in the simulation as long as the modeling value worked out is not very small. In vacuo, the Fermi energy level of pure nickel is over 10 eV.⁴⁶ Therefore, we let the value of $4\pi pa$ be 0.0009 eV/ppm (Figure 9b). It is also worth mentioning that both the phosphorus and nickel deposition could still occur until $C_{\rm B}^{\rm Pb} = 30 \sim 35$ ppm when the brass substrate was plated (PL = 1.67 dm² L⁻¹, Figure 11). On the contrary, the phosphorus and nickel deposition cease at $C_{\rm B}^{\rm Pb} = 10-15$ ppm when Al/Si substrate was plated (PL = 1.25×10^{-2} dm² L⁻¹, Figure 8). This difference is consistent with the previous conclusion that $C_{\rm B}^{\rm Pb-C}$ varies with PL levels.

Substituting the simulation parameters into eqs 29a and 29b, the total plating rate, R, and the phosphorus content of the deposited films, P%, can be expressed as follows:

$$R = 14.33\sqrt{3 + 0.0009C_{\rm B}^{\rm Pb}} \exp(-0.0556C_{\rm B}^{\rm Pb}) + 3.02 \exp(-0.07C_{\rm B}^{\rm Pb})$$
(30b)

$$P\% = \frac{100\%}{1 + 4.75\sqrt{3 + 0.0009C_{\rm B}^{\rm Pb}}\exp(0.0144C_{\rm B}^{\rm Pb})} \quad (30c)$$

Figures 11 and 12 show both the experimental data and simulation results. From the above theoretical model and corresponding simulation, the reason for how the lead ions can decrease both the plating rate of Ni and the phosphorus content is now better understood. In comparison with the decrease in phosphorus deposition rate, the deposition rate of nickel is less affected by the presence of lead in the IHP. This is because a relatively high Fermi level will promote the electron tunneling probability $W(E_f)$ and will be, therefore, facilitating reduction of Ni²⁺ ions at the OHP.

Conclusions

In this paper, the structure of the Stern-Grahame electrical double layer (EDL) and the electronic tunneling theory of the quantum mechanics were applied for explaining the electroless nickel (EN) plating mechanism. The EDL of the substrate consists of the inner Helmholtz plane (IHP) and the outer Helmholtz (OHP). On the IHP, the H₂PO₂⁻ anions adsorb onto the substrate surface and donate electrons to the substrate (oxidation of $H_2PO_2^{-}$) or accept electrons from the substrate (reduction of $H_2PO_2^{-}$) to form deposited elemental phosphorus. Electrons tunneled from the plating frontier to the OHP and combined with nickel ions to form nickel atoms. A handful of Ni atoms produced at the OHP may diffuse into the bulk solution in the form of colloidal particles, which is the source of instability of the EN bath. To inhibit the propagation of Ni particles that undertakes through the same mechanism, a critical concentration of Pb²⁺ must be maintained in the solution. The plating rate will be sacrificed should the concentration of Pb²⁺ be higher than this level. Lead ion plays its role through displacement reaction with Ni atoms. Two mathematical models have been developed to explain the dependence of Ni plating rate and phosphorus content of a Ni-P deposit layer on the Pb²⁺ concentration. According to the models, lead atoms embedded in the Ni-P lattice can reduce work function of the plating frontier, thus clogging up the oxidation of hypophosphite. Consequently, both Ni plating rate and phosphorus content of the deposited film are reduced. With fitting the mathematic models with experimental data, the numerical values obtained could also arrive at the same conclusion.

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