

Electroless Deposition of Pure Nickel Films from a Simple Solution Consisting of Nickel Acetate and Hydrazine

by S. Yae*, K. Ito, T. Hamada, N. Fukumuro & H. Matsuda

We have developed an autocatalytic plating solution for pure nickel deposits using hydrazine as a reducing agent. The solution is characterized by its extended lifetime, high deposition rate and high deposit brightness. In this study, we have found that a simple solution consisting of nickel acetate and hydrazine can deposit black nickel films with stability. The deposition rate was 0.79 nm/sec. The addition of a small amount of formaldehyde to the plating solution gave bright nickel films. The purity of the deposited nickel was higher than 99.7%. Its electrical conductivity increased with purity.

The autocatalytic electroless plating of nickel is widely used in many industries. In general, autocatalytic electroless nickel films include phosphorus or boron from a reducing agent such as sodium hypophosphite or dimethylamine-borane. These impurities affect the properties of the deposited nickel films, including electrical conductivity and solderability. Thus, the electroless plating of pure nickel is attracting much attention in the electronics industry. Several solutions for the electroless plating of pure nickel using hydrazine¹⁻⁵ or Ti^{+3} ions⁶ as a reducing agent have been reported. None of these solutions produced all three of the desired properties, *i.e.*, solution stability, high deposition rate and high deposit luster. Recently,

we developed a solution for electroless pure nickel that has all three properties.⁷⁻⁹ The solution consists of nickel acetate, hydrazine, ethylenediaminetetraacetic acid (EDTA) and lactic acid. The hydrazine not only works as a reducing agent. It also is a complexing agent. Very recently, we found that a simple solution consisting only of nickel acetate and hydrazine can be used to produce pure nickel.¹⁰ This paper reports the effect of solution composition on the brightness, deposition rate, microstructure, impurity content and electrical conductivity of the pure electroless nickel deposits.

Experimental

Polished copper plates (20 × 25 × 0.3 mm; 0.79 × 0.98 × 0.012 in.) were used as substrates. Autocatalytic deposition was initiated galvanically. The volume of the plating solution was 0.20 L. Distilled water and reagent-grade chemicals were used in all the experiments. The initial solution pH was measured with a pH meter. The solution was heated with a water bath and was not stirred during deposition. The thickness of the deposited films was measured using the gravimetric procedure assuming a density of 8.9 g/cm³ (0.32 lb/in³) for pure bulk nickel. The reflectance of the 1- μ m (39.4- μ -in.) thick films was measured using a spectrophotometer in the specular reflection mode with an aluminum vacuum-coated mirror reference. The cross-sectional structure of the films was inspected with a transmission electron microscope. Cross sections of the films were prepared by an ultra-microtome. Surface inspection was performed with a tapping-mode atomic force microscope. The contents of carbon, sulfur and nitrogen in the films were measured with gas analyzers.

The electrical conductivity of the 5- μ m (197- μ -in.) thick films on aluminum oxide substrates was measured by the

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Electroless nickel processes commonly produce a nickel deposit containing significant quantities of phosphorus or boron. There is a growing interest in obtaining pure electroless nickel, for conductivity and solderability. This work investigates such deposits (above 99.7% pure) from a nickel acetate / hydrazine solution. Formaldehyde was needed to brighten the pure deposits. Although the use of formaldehyde is proscribed from industrial use today, this work is of interest in spurring further work with more chemically-benign electroless processes for pure nickel.

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four-point probe method. A sensitization-activation method was used to initiate the deposition onto aluminum oxide substrates.¹¹ The adhesion strength of the deposited films was measured by attaching adhesive tape to the surface of the sample and peeling it off vertically at a constant velocity. The tensile force of peeling was measured with a digital force gauge.

Results and discussion

Figure 1 shows the solution pH at room temperature and the deposition rate of the nickel films at the solution operating temperature of 72°C (161°F) as a function of nickel acetate concentration. The solution color was blue and deepened with increasing nickel acetate concentration. The pH increased with the hydrazine concentration and decreased with the nickel acetate concentration. All solutions were stable for more than three hr at 72°C (161°F). The deposition rate increased with nickel acetate except in the higher nickel acetate range with 0.1 to 0.2 mol/L hydrazine. The deposits were black or dark gray.

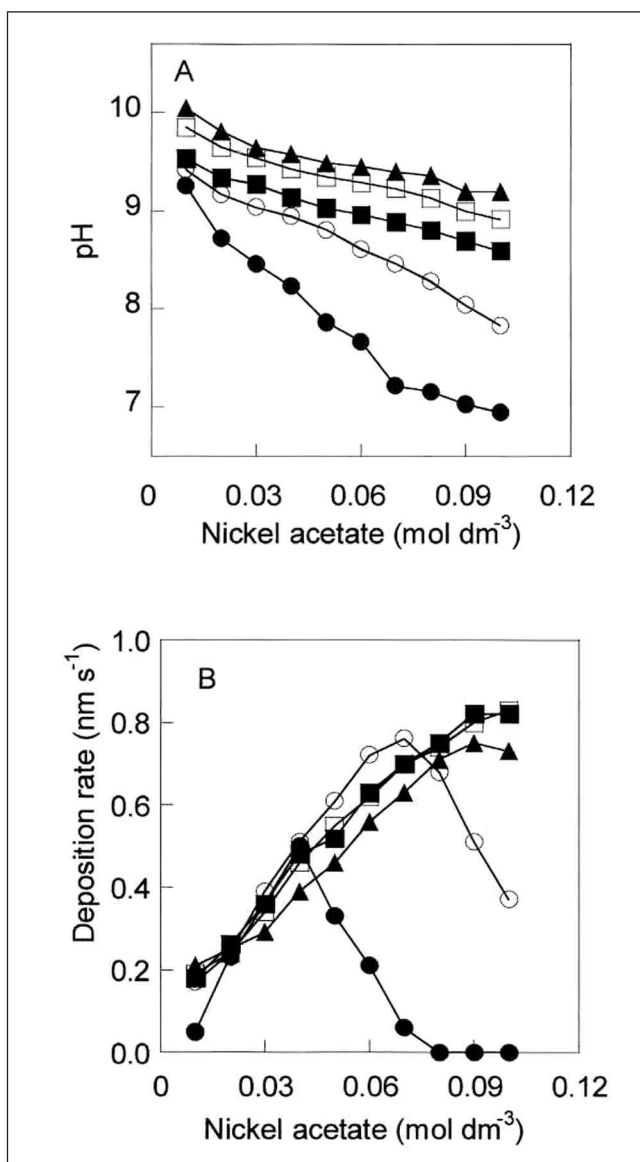
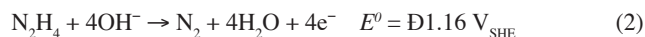


Figure 1—(a) Solution pH at room temperature and (b) nickel deposition rate at the solution operating temperature of 72°C (161°F), as a function of nickel acetate concentration. The hydrazine concentrations are: 0.1 (●), 0.2 (○), 0.3 (■), 0.4 (□) and 0.5 (▲) mol/L.

The deposition rate is plotted versus pH for each value of hydrazine concentration in Fig. 2. The figure shows peaks at pH values between 8.0 and 9.0. These changes are related to the action of hydrazine as a reducing agent, complexing agent and base. Nickel ions and hydrazine form the following complex:



The common logarithms of the equilibrium constants of each step are $K_1 = 2.76$, $K_2 = 2.44$, $K_3 = 2.15$, $K_4 = 1.85$, $K_5 = 1.55$ and $K_6 = 1.2412$. The common logarithm of the basic constant (K_b) of hydrazine is $\text{D}6.01^{12}$. The anodic reaction of hydrazine is expressed by:



As noted in Figs. 1 and 2, the increased hydrazine concentration led to an increase not only in the reducing agent but also in the nickel-hydrazine complex and pH. Thus, the free nickel ion concentration, and therefore the nickel deposition potential, decreased while the reducing power increased with hydrazine concentration. When the concentration of nickel acetate increased, the concentrations of free nickel ions and the complex increased. Thus, the free hydrazine, pH and reducing power decreased with nickel acetate concentration. This relationship increased the deposition rate and pH with decreasing nickel acetate at low levels of hydrazine via an increase in free hydrazine, as shown in the lower pH region of Fig. 2. At other pH values, the relationship led to a decrease in the deposition rate and an increase of pH with decreasing nickel acetate. The two deposition rate changes are balanced and correspond to a maximum deposition rate where the hydrazine/nickel acetate concentration ratio is about 3.0.

Formaldehyde and saccharin sodium were added to the plating solution to improve the brightness of the deposits. Formaldehyde reduced the deposition rate, and accordingly the solution temperature was increased to 88°C (190°F). Without formaldehyde, the solutions decomposed within 30 min at 88°C (190°F). The stability and the brightness increased with formaldehyde concentration. Increasing the hydrazine concentration dulled the surface while increasing the deposition rate. The addition of saccharin sodium to the formaldehyde-containing solution improved the brightness. The composition of three typical solutions and the properties of the deposited films are given in Table 1.

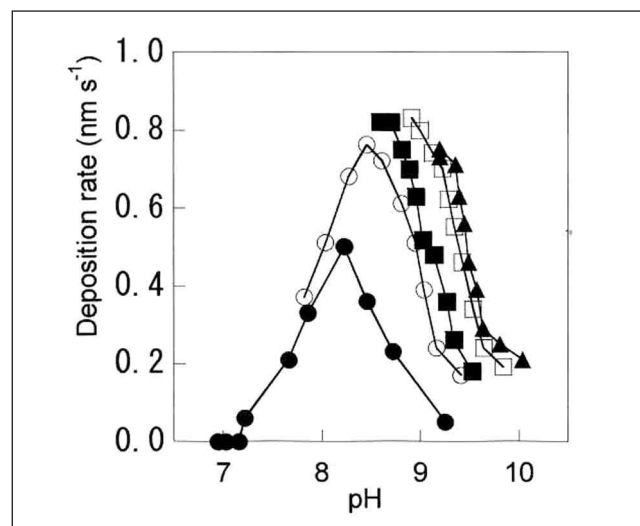


Figure 2—Deposition rates of nickel films as a function of plating solution pH re-plotted from Fig. 1. The symbols represent the same hydrazine concentrations as used in Fig. 1.

Table 1
Composition of typical plating solutions and properties of the deposited films

	Composition, mol/dm ³				pH	T, °C(°F)	ρ, %	R _a , nm	v, nm/ sec	Composition, wt%			σ×10 ⁶ S/m
	Ni Acetate	N ₂ H ₄	HCHO	Saccharin						C	S	N	
A	0.07	0.2	0	0	8.46	72(161)	2.3	46	0.8	0.053	0.0023	0.130	5.5
B	0.06	0.5	0.068	0	9.02	88(190)	48	24	0.3	0.180	0.0006	0.089	4.4
C	0.06	0.5	0.068	0.002	9.02	88(190)	59	15	0.3	0.220	0.0099	0.066	3.3

T = solution temperature; ρ = reflectance at 550nm; R_a = average surface roughness; v = deposition rate and σ = electrical conductivity.

Figure 3 shows the reflectance spectra of the deposits. The reflectance of the black film deposited from solution A, which included no brightener, was only 2.3% at 550 nm. Solution C, which included both formaldehyde and saccharin sodium, significantly improved the reflectance of the deposits to a level higher than that of typical electroless Ni-P films.

In the present study, only formaldehyde and saccharin sodium were examined as brighteners. Further investigation should find other effective brighteners for this solution, particularly in regard to the fact that formaldehyde has environmental and safety problems that restrict its use in commerce.

Figure 4 shows the atomic force microscope (AFM) images of films deposited from solutions A, B and C. The black film deposited from solution A shows a spiky surface morphology with an average roughness (R_a) of 46 nm. The bright films deposited from solutions B and C had smoother surfaces than the film deposited from solution A. Their roughness (24 and 15 nm, respectively) was much lower than that of the film from solution A.

Figure 5(a) shows the transmission electron micrographs and electron diffraction pattern of the film deposited from solution A. The film was comprised of many crystallites less than 20 nm in

size. The surface had many needle-like artifacts. Solutions B and C produced microstructures quite different from those from solution A [Figs. 5(b) and (c)]. These films exhibited a large columnar structure that consisted of upright crystallites larger than 50 nm in width and 100 nm in length. The film thickness of 1.1 μm (43.3 μ-in.), determined gravimetrically, was in accord with the micrographs.

The total amount of carbon, sulfur and nitrogen in the deposits was less than 0.3 wt%. The carbon content of the films was increased by the addition of brightener to the plating solutions. Sulfur originated with the addition of saccharin to the solution. We can infer that these impurities were included in films by the adsorption of brightener molecules on the film surface during deposition. Adsorbed molecules inhibited the nucleation of nickel, thus leveling the surface, decreasing the deposition rate and increasing the solution stability. Therefore, the brightness and crystallite size of the deposited films was increased.

The electrical conductivity value of 5.5 × 10⁶ S/m for the deposits from solution A was higher than the 2.0 to 4.0 × 10⁶ S/m for conventional electroless Ni-P or Ni-B. However, it was not as high as 11.3 × 10⁶ S/m, the highest value reported for deposits from our previously-reported solution including complexing agents such as EDTA and lactic acid.⁷⁻⁹ The electrical conductivity of films deposited from those solutions increased with decreasing carbon content.

The carbon content of the film with the highest conductivity was 0.0092 wt%, much lower than the 0.053 wt% for the deposit from solution A. The films deposited from solutions B and C had a higher carbon content and lower electrical conductivity than those from solution A. These results show that the carbon content was more closely related to the electrical conductivity of electroless pure nickel films in this study than was the crystallite size.

In the case of the adhesion strength measurements, none of the nickel films deposited from solution A, B or C peeled from the copper substrates. This indicates that the adhesion strength of the films on the copper substrates was higher than the adhesion strength of the adhesive tapes to the films. The adhesion strength values for the tapes were about 640, 330 and 360 N/m for the films deposited from solutions A, B and C, respectively. The black dendritic films deposited from solution A gave much higher strength values than the bright smooth films from solutions B or C. These results indicate that the needle-like structures of the films from solution A had enough strength to exert an anchor effect.

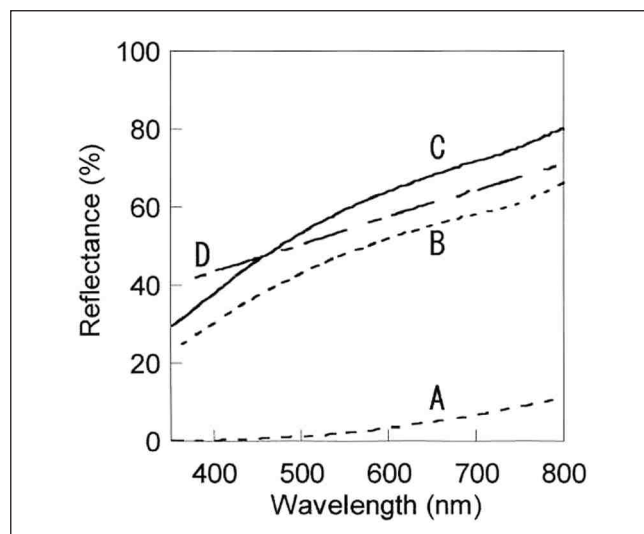


Figure 3—Reflectance spectra of electroless nickel films. Curves A, B and C are for films deposited from solutions A, B and C listed in Table 1, respectively. Curve D is for an electroless Ni-P film deposited from a conventional plating solution.

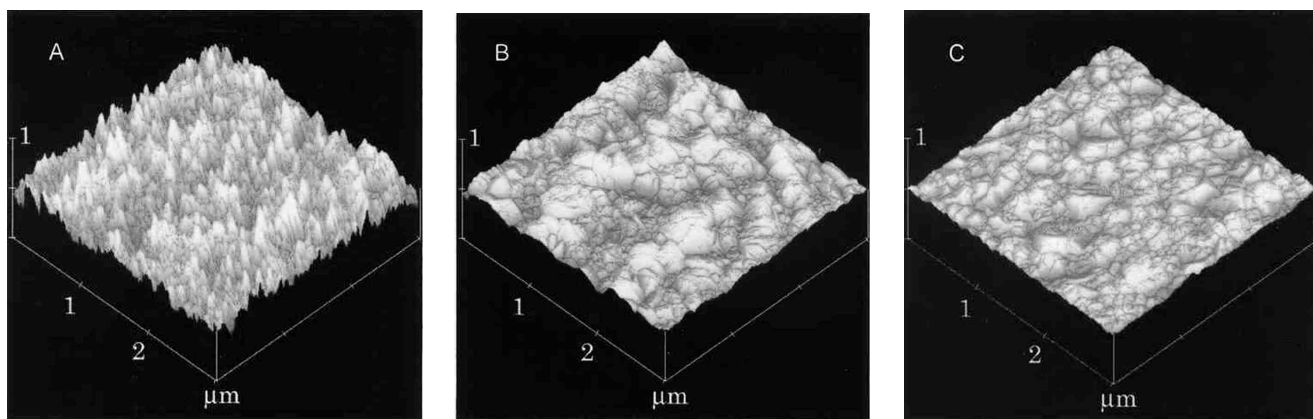


Figure 4—TM-AFM images of surface of electroless nickel films. A, B and C were deposited from solutions A, B and C listed in Table 1, respectively.

Conclusion

In conclusion, we have developed a solution for the autocatalytic electroless plating of pure nickel. The solution is comprised of only nickel acetate and hydrazine. The brightness of the films could be changed from black (dendritic surface) to bright metallic

(smooth surface) by the addition of a small amount of brightener to the solution. The high purity of the nickel films (99.8 wt%) from the simple solution gave an electrical conductivity of 5.5×10^6 S/m, which was higher than that for conventional electroless Ni-P and Ni-B films.

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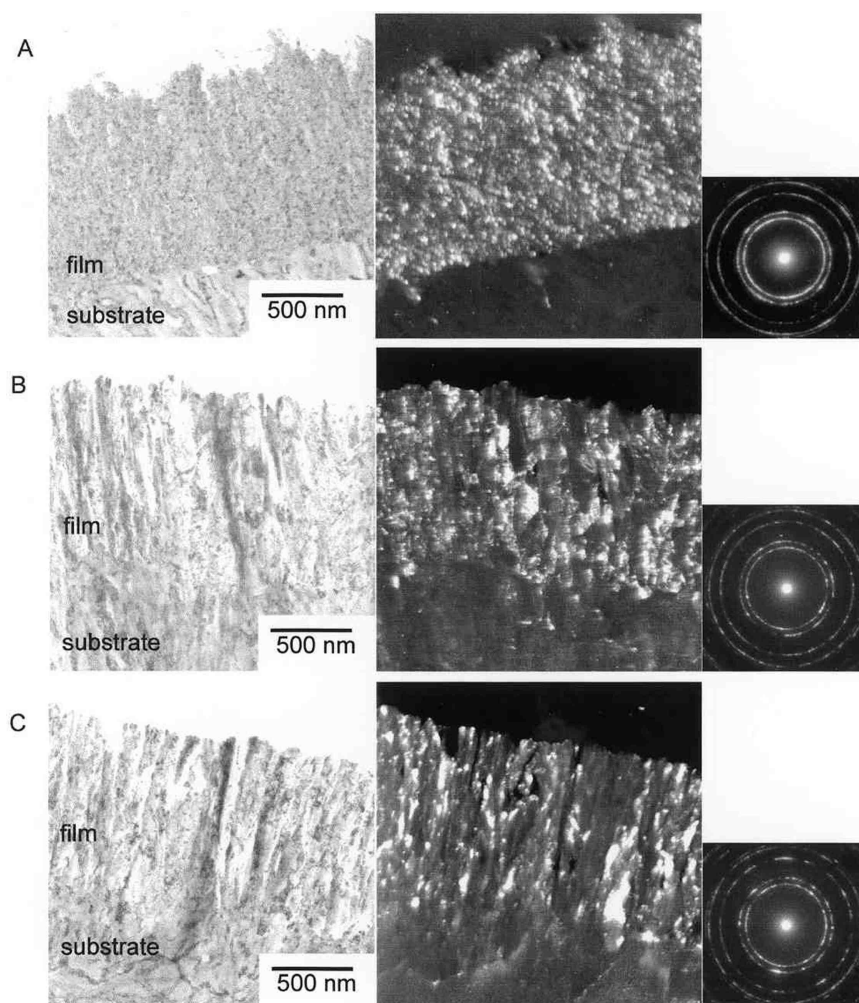


Figure 5—Transmission electron micrographs (left: bright field; center: dark field) and electron diffraction pattern (right) for the same area of the cross section of the electroless nickel films. A, B and C were deposited from solutions A, B and C listed in Table 1, respectively.

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