Electroless Deposition of Bright/Black Pure Nickel Films from Simple Solution Consists of Nickel Acetate and Hydrazine

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We 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 luster of deposits. In this study, it is found that a simple solution consists of nickel acetate and hydrazine that can deposit black nickel films stably. The deposition rate is 0.75 nm/s. The addition of a small amount of formaldehyde to the plating solution gives bright nickel films. The purity of the deposited nickel is higher than 99.7%. Its electric conductivity increases with the purity. The microstructure of the deposits was observed using a transmission electron microscope.

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Introduction

The autocatalytic electroless plating of nickel is widely used in various industries. In general, autocatalytic electroless nickel films include phosphorus or boron from a reducing agent such as phosphinic acid or dimethylamine-borane. These impurities affect properties of deposited nickel films such as electric conductivity and adhesion with solder. Thus, electroless pure nickel plating is attracting much attention in the electronic industries. Several solutions for electroless pure nickel plating using hydrazine[1-5], Ti^{3+} ion[6] or Co^{2+} ion[7] as a reducing agent have been reported. None of the solutions previously reported produced all of the three desired properties, i.e., high stability of solution, high deposition rate and high luster of the deposits. Recently, we developed a solution for electroless pure nickel plating that has all of the three desired properties[8-10]. The solution consists of nickel acetate, hydrazine, ethylendiaminetetraacetic acid (EDTA) and lactic acid. Hydrazine in plating solution works not only as a reducing agent but also as a complexing agent. Very recently, we found that a simple solution consisting of only nickel acetate and hydrazine can be used as a solution for autocatalytic electroless pure nickel plating[11]. The present paper reports the solution composition dependence of the brightness, deposition rate, microstructure, impurity content and electric conductivity of the electroless pure nickel deposits.

Experimental

Polished copper plates (20 x 25 x 0.2 mm) were used as the substrates. The autocatalytic deposition was started by a galvanic initiation. The volume of the plating solution was 0.20 dm^3. Distilled water and reagent-grade chemicals were used in all the experiments. The initial solution pH was measured with a pH meter (Horiba, F-21 or F-55). The solution was heated with a water bath. The solution was not stirred during the deposition. The thickness of the deposited films was measured using the gravimetric procedure with a 8.9 g cm^{-3} density of pure bulk nickel. The reflectance of the 1-μm thick films was measured using a spectrophotometer (Shimadzu, UV-360) in the specular reflection mode with an aluminum vacuum-coated mirror reference (Shimadzu). The cross-sectional structure of the films was inspected with a transmission electron microscope (JEOL, JEM-200CX). The cross sections of the films were prepared by an ultra-microtome (LEICA, ULTRACUT UCT). The surface inspection was performed with a tapping-mode atomic force microscope (TM-AFM, Digital Instruments Nanoscope IIIa). The contents of carbon, sulfur and nitrogen in the films were measured with gas analyzers (Horiba, EMIA-820 and EMGA-2200). The electric conductivity of the 5-μm thick films on aluminum oxide substrates was measured by a four-point probe method (Daiainstruments, Loresta-GP). A sensitization-activation method was used to start the deposition onto the aluminum oxide substrates[12].

Results and Discussions

Figure 1 shows the solution pH at ordinary temperature and the deposition rate of the nickel films at the solution temperature of 345 K as a function of nickel acetate concentration of the plating solution. The color of the solutions was blue and deepened with nickel acetate concentration. The pH increased with hydrazine concentration and decreased with nickel acetate concentration. All solutions were stable for longer than three hours at 345 K. The deposition rate increased with nickel acetate concentration except at the high nickel acetate concentration range of 0.1 and 0.2 mol dm^{-3} hydrazine. The deposited films were black or dark gray. The deposition rate is plotted as the ordinate and the pH as the abscissa for each hydrazine concentration in Fig. 2. The figure shows peaks at a pH between 8 and 9. Hydrazine's ability as a reducing agent, complexing agent and base is concerned with these changes of rate. Nickel ion and hydrazine form the following complex.

$$Ni^{2+} + 6\ N_2H_4 = [Ni(N_2H_4)_6]^{2+} \qquad (1)$$

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 1.24[13]. The common logarithm of the basic constant (K_b) of hydrazine is –6.01[13]. The anodic reaction of hydrazine is expressed by

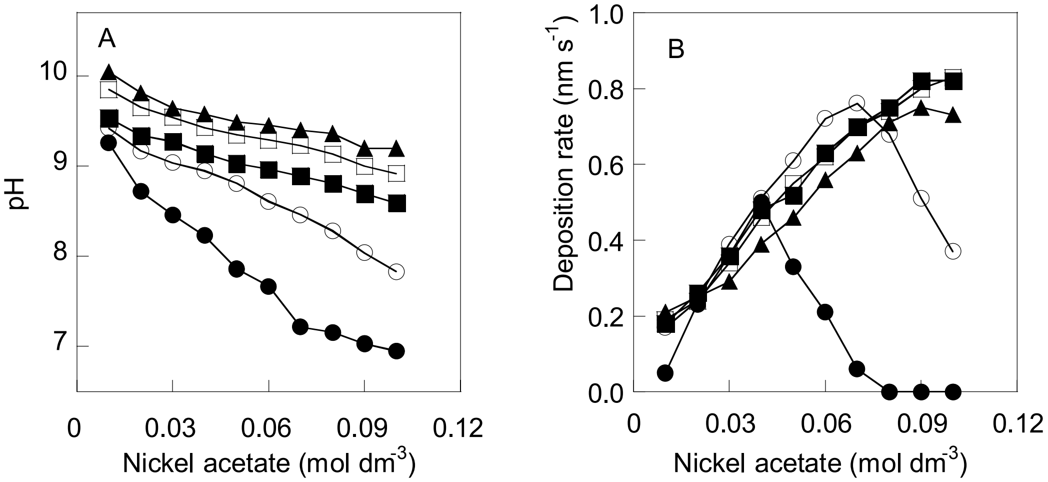

Figure 1 Solution pH at ordinary temperature (A) and deposition rate of nickel films at the solution temperature of 345 K (B) as a function of nickel acetate concentration of the plating solution. The hydrazine concentration is 0.1 (●), 0.2 (○), 0.3 (■), 0.4 (□), and 0.5 (▲) mol dm^{-3}.

$$N_2H_4 + 4OH^- = N_2 + 4H_2O + 4e^- \qquad E^0 = -1.16\ V\ vs.\ SHE \qquad (2).$$

In the conditions of Figs. 1 and 2, the increase in hydrazine concentration leads to an increase in not only the reducing agent but also the nickel-hydrazine complex and pH. Thus, the free nickel ion, i.e., the potential of nickel deposition, decreases while the reducing power increases with hydrazine concentration. When the concentration of nickel acetate increases, the free nickel ion and the complex increase. Thus, the free hydrazine, pH and reducing power decrease with nickel acetate concentration. This relativity increased the deposition rate and pH with a decrease in the nickel acetate concentration in the low hydrazine concentration cases by an increase of free hydrazine, as shown in the lower pH region in Fig. 2. The relativity leads to a decrease in the deposition rate with an increase of nickel acetate concentration and pH in other cases by a decrease in free nickel ion. Two kinds of deposition rate changes are balanced and give a peak of the deposition rate where the hydrazine/nickel acetate concentration ratio is about 3.

Formaldehyde and saccharin sodium were added to the plating solution to improve the brightness of the deposited films. Formaldehyde reduced the deposition rate, and accordingly the solution temperature was increased to 361 K. The solutions without formaldehyde were decomposed in 30 minutes at 361 K.

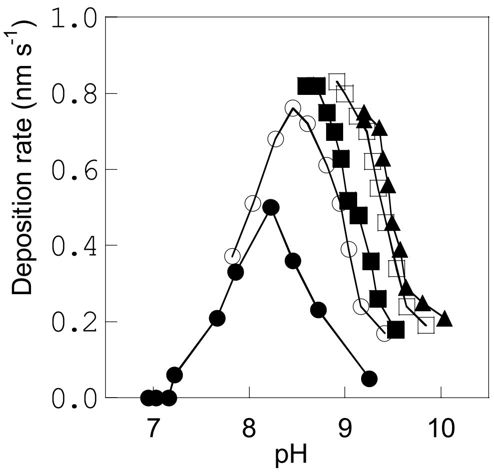

Figure 2 Deposition rates of nickel films as a function of plating solution pH re-plotted from Fig. 1. The symbols represent the same hydrazine concentrations as Fig. 1.

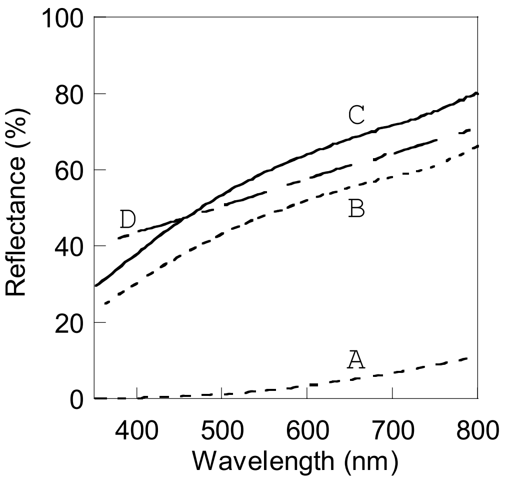

Figure 3 Reflectance spectra of electrolessly-deposited nickel films. Curves A, B and C are for films deposited from solutions A, B and C listed in Table 1, respectively. Curve D is for an electroless Ni-P film deposited from conventional plating solution.

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

	Composition (mol dm^{-3})				pH	T (K)	ρ (%)	R_a (nm)	v (nm s^{-1})	Contents (mass%)			σ ($\times 10^6$ Sm^{-1})
	Ni acetate	N_2H_4	HCHO	Saccharin						C	S	N	
A	0.07	0.2	0	0	8.46	345	2.3	46	0.8	0.053	0.0023	0.13	5.50
B	0.06	0.5	0.068	0	9.02	361	48	24	0.3	0.18	0.0006	0.089	4.40
C	0.06	0.5	0.068	0.002	9.02	361	59	15	0.3	0.22	0.0099	0.066	3.30

T: solution temperature, ρ: reflectance at 550nm, R_a: average surface roughness,
v: deposition rate, σ: electric conductivity.

The stability and the brightness increased with the formaldehyde concentration. The increase of hydrazine concentration dulled the surface of the deposited films while it increased the deposition rate.

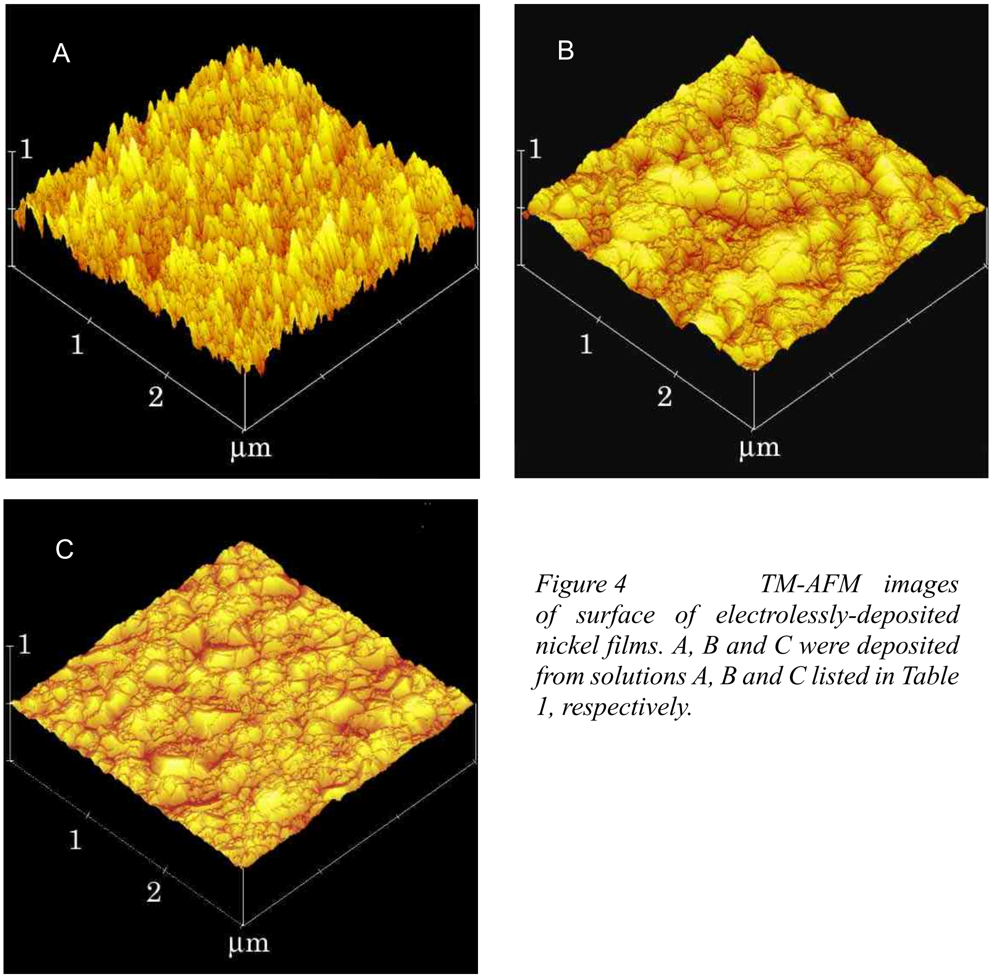

Figure 4 TM-AFM images of surface of electrolessly-deposited nickel films. A, B and C were deposited from solutions A, B and C listed in Table 1, respectively.

The addition of saccharin sodium to the solution including formaldehyde improved the brightness of the deposits. The composition of the three typical solutions and properties of the deposited films are listed in Table1. Figure 3 shows the reflectance spectra of the deposited films. 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, amazingly improved the reflectance of the deposited films to higher than that of common electroless Ni-P films. 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 has a spiky surface morphology with an average roughness (R_a) of 46 nm. The bright films deposited from solutions B and C have blocky but smoother surfaces than the film deposited from solution A. Their roughness (24 and 15 nm, respectively) is much lower than that of the film from solution A. Figure 5A shows the transmission electron micrographs and electron diffraction pattern of the film deposited from solution A. The film is comprised of many crystallites smaller than 20 nm in size. The surface has many needle-like structures. Solutions B and C produced different microstructures of films from solution A (Fig. 5B and C). These films have a large columnar structure that consists of upright crystallites larger than 50 nm in width and 100 nm in length. The film thickness of 1.1 µm obtained by the gravimetric procedure accords with the micrographs. The total contents of carbon, sulfur and nitrogen of the deposited films are less than 0.3 mass%. The carbon content of the films was increased by the addition of brightener to the plating solutions. Sulfur was contained by the addition of saccharin to the solution. It is inferred that these impurities are included in films by the adsorption of brightener molecules on the film surface during deposition. Adsorbed molecules inhibit the nucleation of nickel, thus leveling the surface of the deposited films, decreasing the deposition rate and increasing the solution stability. Therefore, the brightness and crystallite size of the deposited films are increased. The 5.5 x 10^6 S m^{-1} electric conductivity of films deposited from solution A is higher than the 2-4 x 10^6 S m^{-1} of conventional electroless Ni-P or Ni-B films, but is not higher than 11.3 x 10^6 S m^{-1}, the highest value of films deposited from our previously reported solution including complexing agents such as EDTA and lactic acid[8-10]. The electric conductivity of films deposited from our previously reported solutions increased with decreasing carbon content of the films. The carbon content of the film having the highest conductivity is 0.0092 mass%, much lower than the 0.053 mass% of the film deposited from solution A. The films deposited from solutions B and C gave a higher carbon content and lower electric conductivity than those of films from solution A. These results show that the carbon content relates closer to the electric conductivity of electrolessly-deposited pure nickel films in this study than the crystallite size.

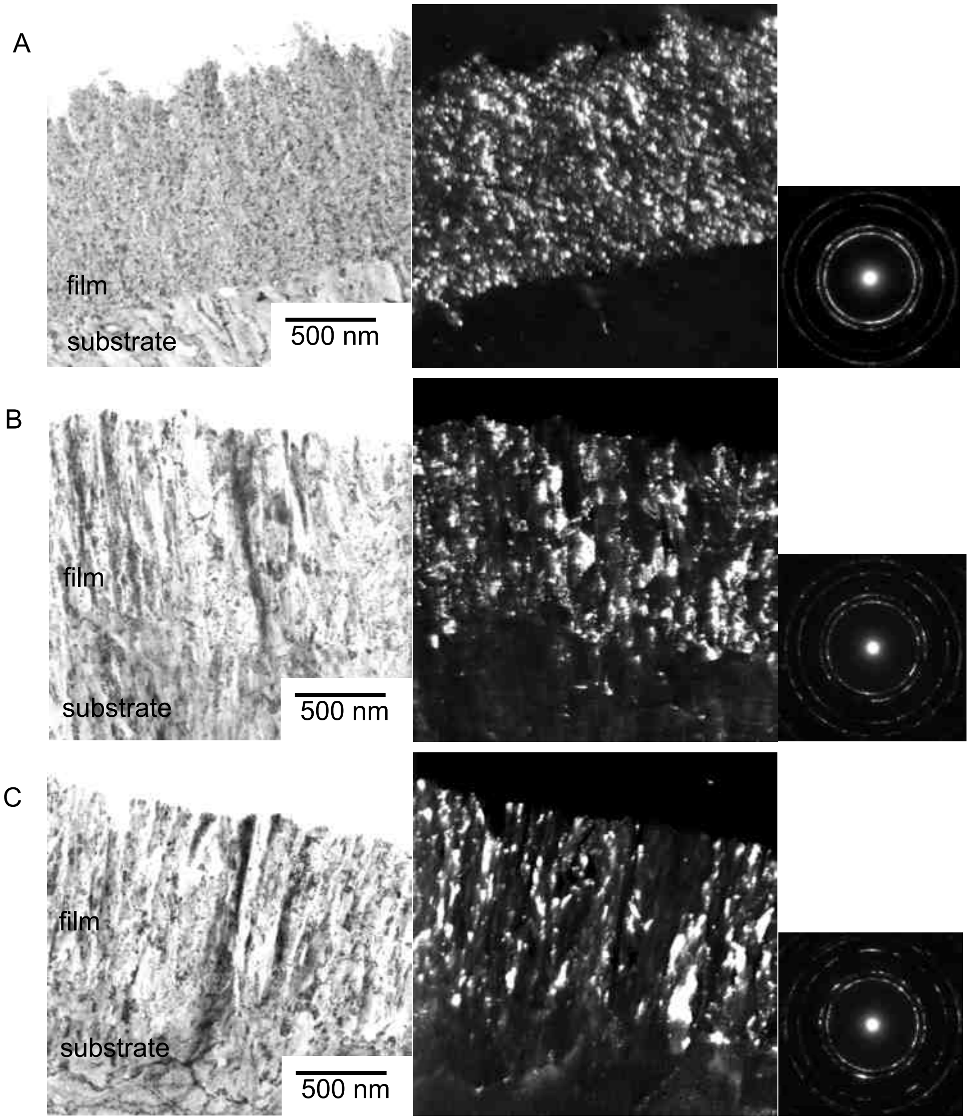

Figure 5 *Transmission electron micrographs (left: bright-field, center: dark-field) and electron diffraction pattern (right) for the same area of the cross section of the electrolessly- deposited nickel films. A, B and C were deposited from solutions A, B and C listed in Table 1, respectively.*

In conclusion, we developed a solution for autocatalytic electroless pure nickel plating. The solution is comprised of only nickel acetate and hydrazine. The brightness (i.e., surface micro-morphology) of the films can be changed from black (dendritic surface) to metallic bright (blocky smooth surface) by the addition of a small amount of brightener to the solution. The high purity of deposited nickel films (99.8 mass%) from the simple solution gave an electric conductivity of 5.5×10^6 S m^{-1}, which is higher than that for conventional electroless Ni-P and Ni-B films.

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