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The influence of 2,2′-dipyridyl on non-formaldehyde electroless copper plating

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Abstract

High electroless copper deposition rates can be achieved using hypophosphite as the reducing agent. However, the high deposition rate also results in dark deposits. In the hypophosphite baths, nickel ions (0.0057 M with Ni^{2+}/Cu^{2+} mole ratio 0.14) were used to catalyze hypophosphite oxidation. In this study, additives (e.g. 2,2′-dipyridyl) were investigated to improve the microstructure and properties of the copper deposits in the hypophosphite (non-formaldehyde) baths. The influence of 2,2′-dipyridyl on the deposit composition, structure, properties, and the electrochemical reactions of hypophosphite (oxidation) and cupric ion (reduction) have been investigated. The electroless deposition rate decreased with the addition of 2,2′-dipyridyl to the plating solution and the color of the deposits changed from dark brown to a semi-bright with improved uniformity. The deposits also had smaller crystallite size and higher (1 1 1) plane orientation with the use of 2,2′-dipyridyl. The resistivity and nickel content of the deposit were not affected by 2,2′-dipyridyl additions to the bath. The electrochemical current–voltage results show that 2,2′-dipyridyl inhibits the catalytic oxidation of hypophosphite at the active nickel site. This results in a more negative electroless deposition potential and lower deposition rate.
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Keywords: 2,2′-Dipyridyl; Hypophosphite; Electroless copper plating; Copper

1. Introduction

Electroless copper plating using sodium hypophosphite as the reducing agent in place of formaldehyde is attractive because of its low pH, low cost, and relative safety, compared with high pH formaldehyde-based solutions [1,2]. However, the hypophosphite-based electroless copper plating process is complicated because copper is not a good catalyst for the oxidation of hypophosphite resulting in little or no plating on a pure copper surface. One approach to catalyze the oxidation of the reducing agent is to add nickel ions (or other metal ions) to the bath, resulting in a very small amount of co-deposited nickel in the copper deposit. The nickel serves to catalyze the oxidation of hypophosphite enabling continuous copper deposition [2–5].

Previous studies have shown that accelerators, such as formamidine disulfide, and nickel are essential to the electroless copper plating bath to maintain an autocatalytic surface [6,7]. The autocatalytic surface results in a high deposition rate. It was shown that electroless copper plating occurred at a low deposition rate in the absence of the accelerators in the bath, even though adequate nickel(II) was in the bath. When the Ni^{2+}/Cu^{2+} mole ratio in the bath is low, the deposition rate of the copper plating decreased with time and finally stopped because the surface catalytic activity was not replenished. Thus, it was necessary to maintain the Ni^{2+}/Cu^{2+} mole ratio above a critical value in the bath to sustain the deposition rate. However, the copper deposit properties were degraded and the deposit appearance became darker with increased Ni^{2+}/Cu^{2+} mole ratio in the bath. Consequently, it is important to improve the microstructure and properties of the copper deposit while maintaining the nickel(II) concentration in the electroless copper plating bath.

2,2′-Dipyridyl has been used in formaldehyde-based electroless copper plating baths to improve the physical properties of the copper deposits [8]. When an optimum amount of 2,2′-dipyridyl was added into the solution, the copper deposit had a glossy appearance and good ductility [9]. 2,2′-Dipyridyl has also been used as a stabilizer in the formaldehyde-based electroless copper plating

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because it can inhibit the autocatalytic deposition process [10]. In this study, the influence of 2,2′-dipyridyl on the hypophosphite-based electroless copper process has been investigated. The microstructure and properties of the copper deposits obtained at different 2,2′-dipyridyl concentrations in the bath are reported along with voltametric analysis of its role.

2. Experimental

The electroless copper plating bath contained: 0.04 M copper sulfate, 0.0057 M nickel sulfate, 0.28 M sodium hypophosphite, 0.051 M sodium citrate, 0.485 M boric acid, 250 ppm accelerators (formamidine disulfide) [6,7], and 0–50 ppm 2,2′-dipyridyl. Deionized water was used to prepare the solutions. The pH was adjusted using NaOH or H_2SO_4 to a final value of 9.0–9.3. The temperature was held at $70 \pm 0.5\,^{\circ}C$.

Plating was performed in a 200 ml electroless copper solution with continuous stirring. Epoxy boards (area: $6\,cm^2$) or alumina sheets (area: $2\,cm^2$) were used as the substrates for the electroless copper plating. The substrates were activated by palladium in the sequence described in the Shipley process [6]. Copper deposition rates were determined by the change in weight of the epoxy boards after 30 min plating assuming uniform plating and bulk density. For via-hole plating, the copper surface was activated in a dilute acidic $PdCl_2$ solution for 1 min. The copper thickness was determined using a DekTeck profilometer and via cross-sections were observed using optical microscopy. The resistivity of the as-deposited and annealed copper were measured using a four-point probe. The copper was deposited on alumina sheets for annealing at high temperature. The annealing of the copper deposits was carried out in a tube furnace with nitrogen ambient. The temperature inside the furnace was controlled to $\pm 1.0\,^{\circ}C$. The crystal structure of the copper deposits was investigated using X-ray diffraction (XRD, Cu Kα radiation and graphite filter at 40 kV and 30 mA). Atomic force microscopy (AFM) was used to characterize the roughness of the deposits. The chemical composition of the copper deposits at the surface was determined by X-ray photoelectron spectroscopy (XPS). The analysis was performed after a brief sputter cleaning.

An EG & G PARC model 263A potentiostat was used for electrochemical measurements. The linear sweep voltammetry (LSV) and cyclic voltammetry (CV) experiments were carried out at 70 °C and at a scan rate of 10 mV/s. The working electrode was pure copper with $0.25\,cm^2$ surface area; the counter electrode was a platinum wire, and the reference electrode was a saturated calomel electrode (SCE). Prior to each test, the electrolyte was deaerated with nitrogen gas and the electrodes were immersed in the electrolyte until a steady open circuit potential (OCP) was reached.

3. Results and discussion

The effect of 2,2′-dipyridyl on the deposition rate and copper properties were investigated. The change in deposition rate of the electroless copper plating as a function of 2,2′-dipyridyl concentration is shown in Fig. 1. The nickel ion concentration in the bath was 0.0057 M and the Ni^{2+}/Cu^{2+} mole ratio was 0.14. The deposition rate of the electroless plating in the absence of 2,2′-dipyridyl was high and the deposits were dark. 2,2′-Dipyridyl had a significant affect on the copper deposition rate. The deposition rate decreased from 18 to 7 μm/h (as measured after 30 min plating) as the concentration of 2,2′-dipyridyl was increased from 0 to 20 ppm. The decrease in deposition rate with further additions of 2,2′-dipyridyl occurred more gradually. A similar effect on the deposition rate with 2,2′-dipyridyl addition to a formaldehyde-based electroless copper plating bath was observed previsously [8]. It is possible that the reduction in the deposition rate with the addition of 2,2′-dipyridyl results from its adsorption on the electrode surface causing a lower rate of electron transfer or nucleation. The effect slows with further added 2,2′-dipyridyl as the surface adsorption reaches saturation.

The color of the deposits changed from dark brown to a semi-bright with the addition of 2,2′-dipyridyl to the plating bath. AFM images and root mean square (RMS) roughness of the deposits versus 2,2′-dipyridyl concentration are shown in Figs. 2 and 3, respectively. The topography of the copper deposit in the absence of 2,2′-dipyridyl in the bath was rough. The deposits became smooth, and the RMS roughness of the deposits dropped from 398 to 200 nm with the addition of 2,2′-dipyridyl to the bath. A corresponding improvement in color of the deposit also occurred. The bright appearance of the deposit usually indicates better mechanical and physical properties. The XRD patterns of the copper deposits obtained at different 2,2′-dipyridyl concentrations are shown in Fig. 4. The deposits exhibited the characteristic peaks corresponding to (1 1 1) orientation. The copper oxide phase was not detected in the deposits. The effective crystallite size of the copper deposits can be estimated from the broadening of the diffraction peak from the (1 1 1) planes by the use of Scherrer's equation [11,12].

$$D = \frac{0.89\lambda}{\beta_{1/2}\cos\theta} \tag{1}$$

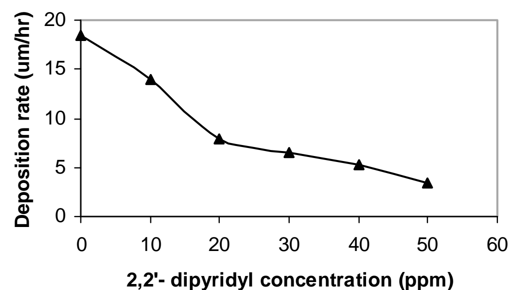

Fig. 1. The change in deposition rate of the electroless copper plating as a function of 2,2′-dipyridyl concentration.

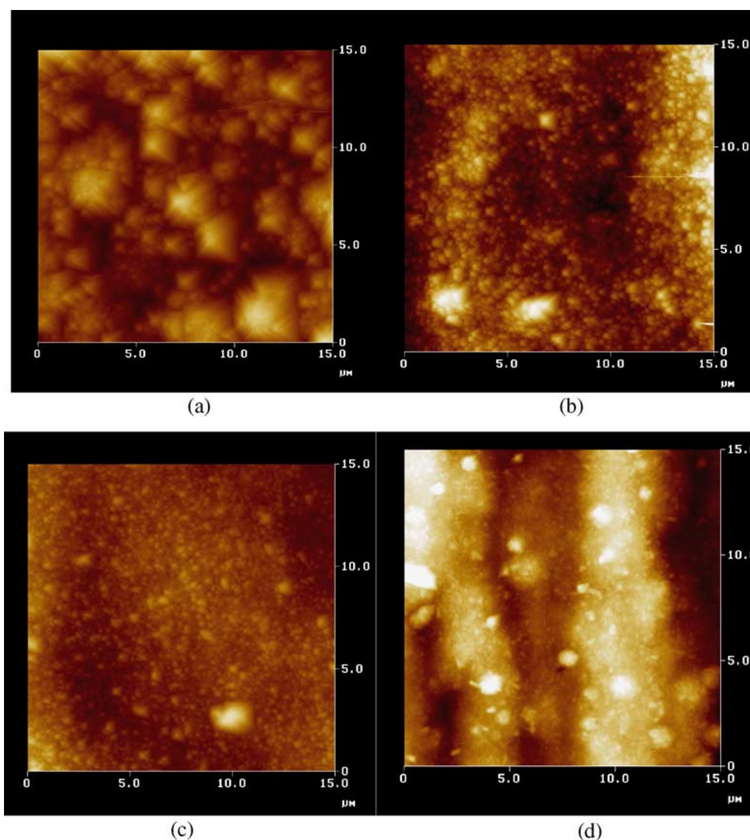

Fig. 2. AFM images of copper deposits from different 2,2′-dipyridyl concentration bath: (a) 0 ppm; (b) 5 ppm; (c) 10 ppm; (d) 20 ppm.

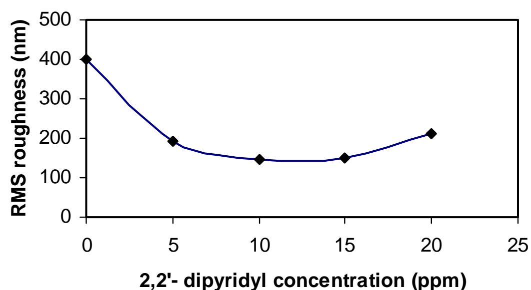

Fig. 3. Dependence of RMS roughness of copper deposits on 2,2′-dipyridyl concentration.

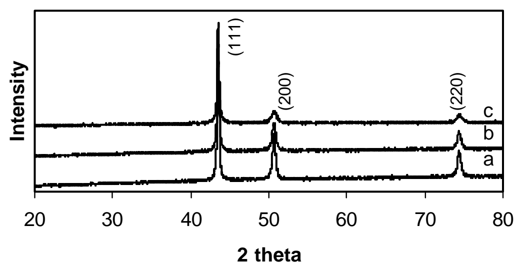

Fig. 4. XRD patterns of copper deposits from different 2,2′-dipyridyl concentration bath: (a) 0 ppm; (b) 20 ppm; (c) 40 ppm.

where λ is the wavelength of Cu Kα, $\beta_{1/2}$ the half width of diffraction line, and θ the diffraction angle. The calculated effective crystallite size of the copper deposits and relative intensities of the diffraction peaks from the (1 1 1), (2 0 0), and (2 2 0) planes are listed in Table 1. It can be seen that the copper deposit has a decreased crystallite size and intensified (1 1 1) plane orientation with the addition of 2,2′-dipyridyl to the plating bath. The concentration of impurities at the surface of the copper deposits as a function of 2,2′-dipyridyl concentration in the bath was investigated using XPS. The deposit surface consisted mainly of copper with a trace of nickel as given in Table 2. The nickel concentration was 4–7 at.% and was unaffected by 2,2′-dipyridyl in the plating bath.

Table 1
Characteristic peak relative intensities and crystallite size of the copper deposits from the bath with different 2,2′-dipyridyl concentrations

Copper deposits	2,2′-Dipyridyl concentration (ppm)	Crystallite size	I (1 1 1)	I (2 0 0)	I (2 2 0)
1	0	5.272	100	25.5	9.6
2	20	5.271	100	21.2	9.3
3	40	3.076	100	14.4	6.2

Table 2
The nickel content in the copper deposits from the bath with different 2,2′-dipyridyl concentrations

Copper deposits	2,2′-Dipyridyl concentration (ppm)	Ni (at.%)
1	0	6.19
2	10	4.04
3	20	6.99
4	40	5.15

Nickel ions are required in the hypophosphite-based electroless copper plating bath to maintain the deposition rate. Nickel catalytically participates in the oxidation of hypophosphite. The copper deposition rate increased with nickel ion concentration [7]. At 0.0057 M nickel ion concentration in the bath without 2,2′-dipyridyl, the copper deposition rate was very high resulting in large crystallite with poor microstructure due to the rapid nucleation and growth [13]. This poor microstructure is consistent with the high RMS roughness of the copper deposit observed when 2,2′-dipyridyl was absent from the bath. In addition, nickel atoms in the copper lattice increase the crystal defects with the copper deposit. Consequently, the poor quality copper deposits produced in the absence of 2,2′-dipyridyl in the bath have higher resistivity. The resistivity of the as-plated copper deposits versus 2,2′-dipyridyl concentration is shown in Fig. 5a. It can be seen that the resistivity of the copper deposits were higher than those deposited from formaldehyde-based electroless copper plating baths (2.0 to 3.0 $\times 10^{-6}$ Ω cm) [14]. The resistivity of the copper deposits did not change with the addition of 2,2′-dipyridyl to the plating bath, even though the deposit microstructure improved with addition of 2,2′-dipyridyl. Normally, the deposit resistivity increases with decreasing crystallite size due to electron scattering from grain boundaries. The resistivity of the copper deposits (20 ppm 2,2′-dipyridyl) annealed at different temperatures for 1.5 h in nitrogen ambient is shown in Fig. 5b. The reduction in the resistivity occurred with a 300 °C anneal and the resistivity reached a minimum (4.7 $\times 10^{-6}$ Ω cm) with a 400 °C anneal. The reduction in the resistivity after the 300 °C anneal is caused by recrystallization in the deposit, which is accompanied by crystallite growth, and crystal defect and micro-void annihilation.

According to the mixed potential theory of electroless plating [15,16], the overall reaction of the electroless process is determined by the two half-reactions on the same electrode, i.e. the reduction of cupric ions and the oxidation of the reducing agent. Consequently, studying the effects of 2,2′-dipyridyl on the half-reactions can help understand the function of 2,2′-dipyridyl in the electroless copper plating bath.

Fig. 6 shows the LSV (from OCP positively to −0.100 V) for hypophosphite oxidation on the copper electrode in an electrolyte containing 0.28 M sodium hypophosphite, 0.051 M sodium citrate, 0.485 M boric acid with and without 0.0057 M nickel ions. It can be seen that the addition

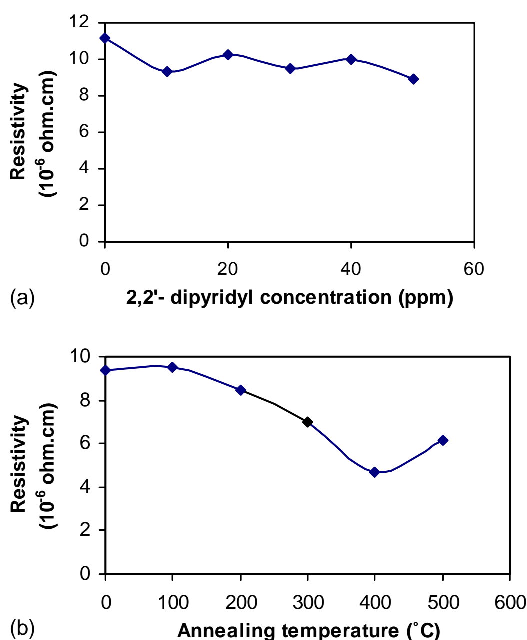

Fig. 5. Resistivity of the copper deposits: (a) dependence of the resistivity of copper deposits on 2,2′-dipyridyl concentration; (b) dependence of copper deposit resistivity (20 ppm 2,2′-dipyridyl) on annealing temperature.

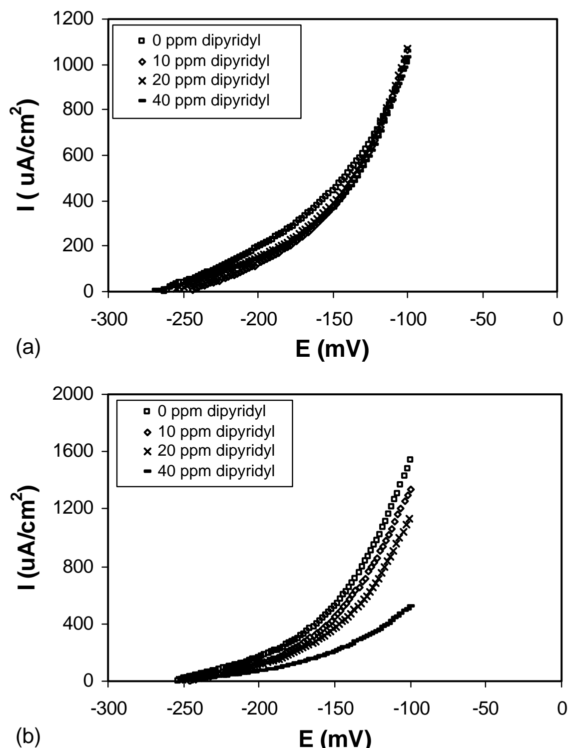

Fig. 6. Current–potential curves for the oxidation of hypophosphite with different 2,2′-dipyridyl concentrations in the electrolyte containing 0.28 M sodium hypophosphite, 0.051 M sodium citrate, 0.485 M boric acid: (a) without nickel ions; (b) with 0.0057 M nickel ions.

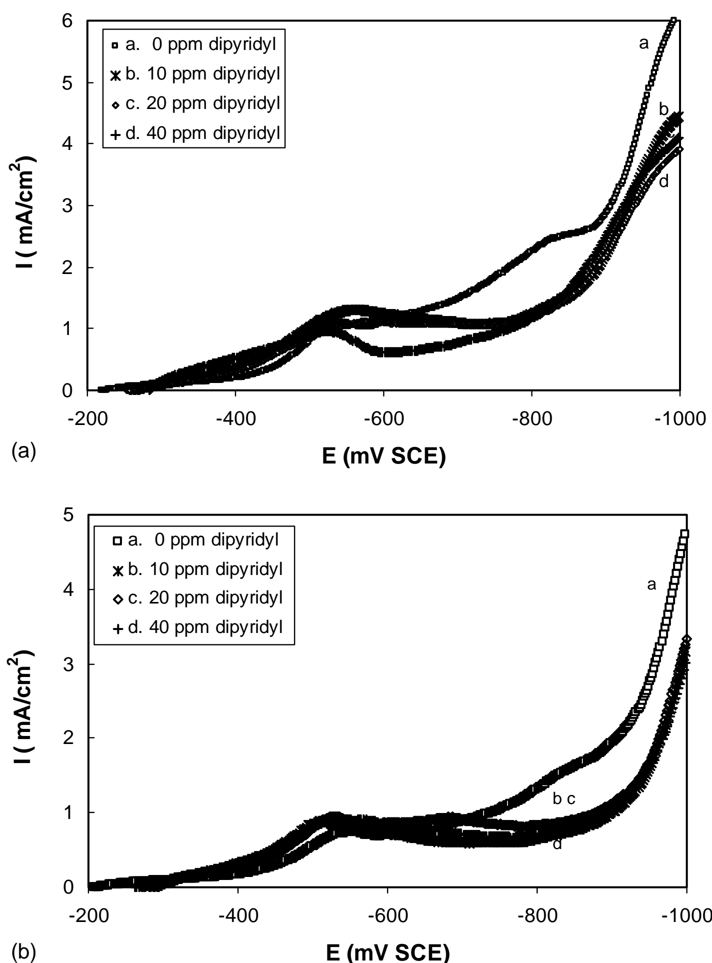

Fig. 7. Current–potential curves for the reduction of cupric ion with different 2,2′-dipyridyl concentrations in the electrolyte containing 0.04 M copper sulfate, 0.051 M sodium citrate, 0.485 M boric acid: (a) without nickel ions; (b) with 0.0057 M nickel ions.

of 2,2′-dipyridyl to the electrolyte without nickel ions had little effect on the oxidation of hypophosphite (Fig. 6a). The presence of 0.0057 M nickel ions in the electrolyte facilitated the oxidation of hypophosphite in the absence of 2,2′-dipyridyl (Fig. 6b). The oxidation of hypophosphite on the copper electrode was lowered by the addition of 2,2′-dipyridyl resulting in a decrease in the oxidation current with 2,2′-dipyridyl. Thus, 2,2′-dipyridyl effects the oxidation of hypophosphite in the presence of nickel ions in the plating bath. The reduction of cupric ions on the copper electrode was also investigated versus nickel ion and 2,2′-dipyridyl concentration by LSV in an electrolyte containing 0.04 M $CuSO_4{\cdot}5H_2O$, 0.051 M sodium citrate, 0.485 M boric acid, as shown in Fig. 7. The addition of 10 ppm (or greater) 2,2′-dipyridyl to the electrolyte caused a decrease in the magnitude of the cathodic current at the more negative potentials. There was little difference in the cathodic current at higher 2,2′-dipyridyl concentrations. This shows that 2,2′-dipyridyl increases the overpotential for the reduction of cupric ions or hydrogen evolution. The presence of nickel ions in the electrolyte had no effect on the cupric ion reduction and the effect of 2,2′-dipyridyl on the cupric ion reduction was not dependent on the presence of nickel ion in the electrolyte.

The cyclic voltammograms of a copper electrode in the electroless copper plating bath containing 2,2′-dipyridyl are shown in Fig. 8a. The cyclic voltammetry was performed starting from 0 V and going negative to −1.000 V. For comparison, the cyclic voltammetry of the electroless copper plating bath without nickel ions or 2,2′-dipyridyl is also shown in Fig. 8b. In the bath containing 0.0057 M nickel ions (Fig. 8a), an oxidation peak at −0.95 V was observed on the positive-going scan. It is interesting that the oxidation peak at –0.95 V occurred at a more negative potential than the reduction peaks at −0.54 and −0.90 V, respectively. This indicates that some of the nickel ions were reduced and co-deposited with copper on the electrode during the negative-going sweep, and the deposited nickel then catalyzed the oxidation of hypophosphite at −0.95 V. The peak current density for the oxidation of hypophosphite on the co-deposited nickel was higher in the absence of 2,2′-dipyridyl and decreased with 2,2′-dipyridyl concentration. Fig. 9 shows the current versus time on a copper electrode at −0.95 V in the electroless copper plating bath as a

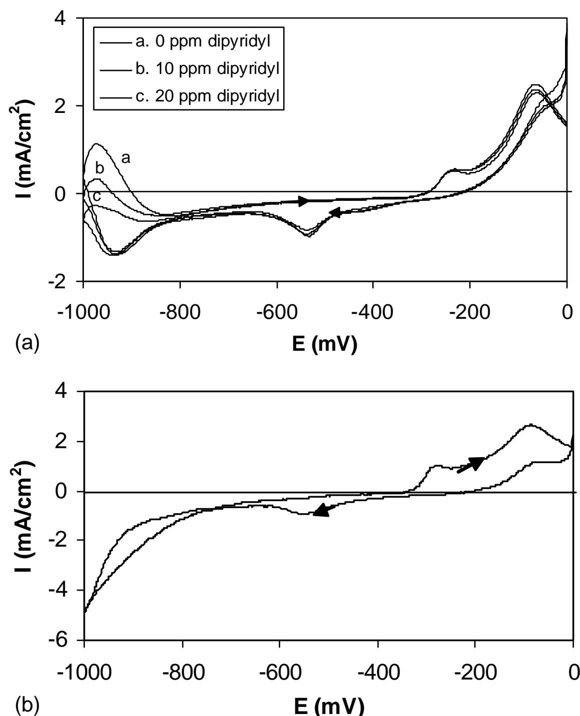

Fig. 8. Cyclic voltammograms for a copper electrode in the electroless copper plating: (a) with different 2,2′-dipyridyl concentrations and 0.0057 M nickel ions; (b) without 2,2′-dipyridyl and nickel ions.

function of 2,2′-dipyridyl concentration. The net current in the absence of 2,2′-dipyridyl was anodic, indicating the oxidation rate of hypophosphite was higher than the reduction rate of cupric and nickel ions. When 10 ppm 2,2′-dipyridyl was added to the bath, the oxidation rate of hypophosphite was lower and the net current became cathodic. The cathodic current increased slightly with 2,2′-dipyridyl concentration.

The adsorption of 2,2′-dipyridyl on the electrode inhibited the oxidation of hypophosphite presumably by decreasing the catalytic effect of nickel. The decrease in the oxidation of hypophosphite by 2,2′-dipyridyl was larger than the corresponding decrease in the reduction of cupric ions. The electroless deposition rate thus decreased significantly with the addition of 2,2′-dipyridyl in the solution and the copper crystallites became finer grain.

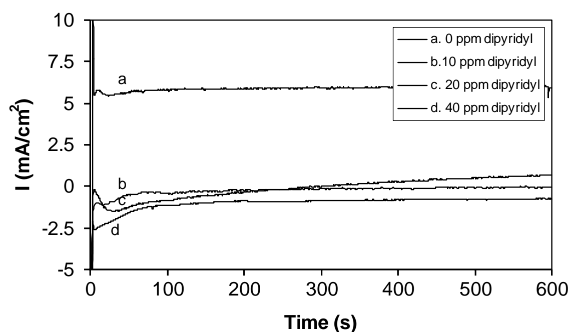

Fig. 9. Current–time curves on the copper electrode at −0.95 V in the electroless copper plating with different 2,2′-dipyridyl concentrations.

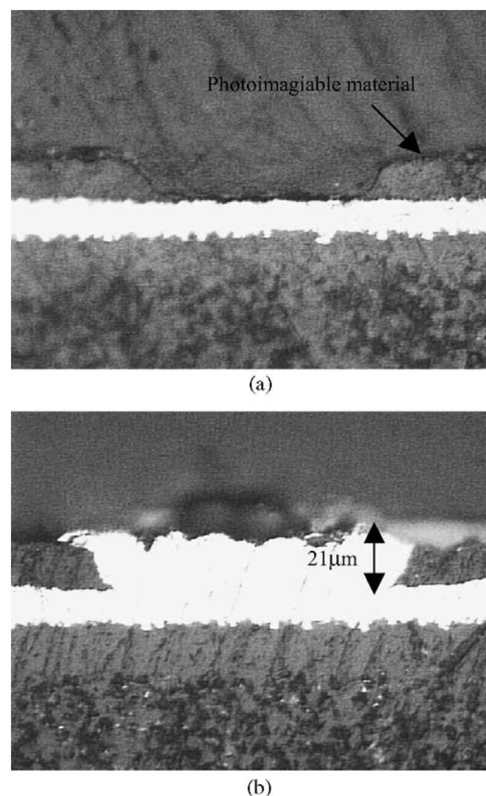

Fig. 10. Cross-section of via: (a) before plating; (b) after plating with total of 21 μm copper deposit.

The electroless copper plating bath with 20 ppm 2,2′-dipyridyl was used in via-hole plating on a printed circuit board. Formaldehyde-based electroless copper plating baths are often operated at a pH value above 11 and are not compatible with some photoimagiable materials used in the fabrication of high density printed circuit boards. Since the electroless copper plating solution using hypophosphite as a reducing agent with 20 ppm 2,2′-dipyridyl can be operated at pH of 9, and has a high deposition rate, it can be used for via-hole plating. Fig. 10 shows a cross-section of a via-hole before and after plating. The thickness of the plated copper was 21 μm. It can be seen that the photoimagiable material was stable during plating. The copper deposit in the via is uniform and compact. The average deposition rate was 3–4 μm/h.

4. Conclusions

2,2′-Dipyridyl improves the microstructure and properties of copper deposits obtained from electroless copper plating using hypophosphite as reducing agent. With the addition of 2,2′-dipyridyl to the plating bath containing 0.0057 M nickel ions, the color of the deposit changed from dark brown to a semi-bright and the deposits became uniform and compact. The deposits had a smaller crystallite size and higher (1 1 1) plane orientation with the addition of 2,2′-dipyridyl.

The electroless deposition rate decreased significantly with the addition of 2,2′-dipyridyl to the bath. Electrochemical measurements showed that 2,2′-dipyridyl inhibited the catalytic oxidation of hypophosphite at the active site of nickel on the deposit surface and increased the overpotential for reduction reaction (copper deposition or hydrogen evolution) by adsorption on the electrode, thus reducing the deposition rate and making the deposit finer in structure.

The resistivity and nickel content (4–7 at.%) of the deposit was not effected by the addition of 2,2′-dipyridyl in the plating bath. The resistivity of the as-plated deposit was higher than that of the deposits from formaldehyde-based electroless copper plating due to the presence of nickel. The resistivity of the deposit from baths with 0.0057 M nickel can be lowered to $4.7 \times 10^{-6}\ \Omega\,\mathrm{cm}$ by annealing at 300–400 °C.

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