Effect of Isomeric Dipyridyls On Electroless Copper Deposition from EDTA Solutions

By L.L. Duda

The effect of 2,2'-, 2,4'- and 4,4'-dipyridyl on the rate of electroless copper deposition from EDTA solutions was examined. It was found that, of all dipyridyls examined, only 2,2'-dipyridyl increases the copper plating rate at concentrations of 5×10^{-5} to 8×10^{-4} mol/dm³. The results were compared to those obtained by chronovolt-amperometric method from solutions of similar composition and pH.

Alkaline electroless copper plating baths contain strong Cu(II) complexing ligands and various additives, needed to improve the quality of the deposited copper film, prevent decomposition of the bath, and increase the plating rate. The concentration of the additives in the bath is two to four orders of magnitude lower than that of the copper ions and of the major complexing agent. The use of the relevant additives makes possible implementation of the process in printed circuit production, as well as in other applications, such as functional plating on plastics (EMI shielding), molded interconnect devices and decorative plating on plastics.^{1,2}

The heterocyclic amines, for example, 2,2'-dipyridyl, 1,10fenantroline,^{3,4} cyanides and ferrous- and nickel-cyanides,⁵ 2-mercaptobenzothiazole,⁶ thiourea⁷ and others, that form stable complexes with Cu(I) ions and adsorb easily on the surface being coated, have been used most often. Some additives, such as HIQSA (8-hydroxy-7-Iodo-5-quinoline sulfonic acid),⁸ cyanidine hydroxychloride,⁷ adenine and guanine⁹ and 2,2'-dipyridyl¹⁰ also, stabilize the bath and increase the copper deposition rate in some concentration ranges as well.

In this paper, the effects of adding isomeric dipyridyls (2,2'-, 2,4'- and 4,4'-dipyridyl) on the rate of copper deposition from alkaline EDTA solutions are examined and discussed. The dipyridyls studied are adsorbed on the metal surface in similar ways, but they are distinctly different in their way of complexing copper ions and in the stability of the complexes formed. Only 2,2'-dipyridyl forms stable chelate complexes with Cu(I) and Cu(II) ions. To examine the influence of isomeric dipyridyls on copper deposition processes, chronovoltamperometric and gravimetric methods were applied.

Experimental Procedure

Electroless Copper Deposition

The experiments were performed in a 250-cm³ Erlenmeyer flask. The copper coating solution was prepared with analytical grade reagents. The basic solution contained Cu⁺², 8.0 x 10^{-3} mol/dm³; EDTA, 1.4×10^{-2} mol/dm³; formaldehyde, 0.2 mol/dm³; and Na₂SO₄; 0.5 mol/dm³. The dipyridyl concentration was being changed in a broad range from 5 x 10^{-6} to 1.0 x 10^{-2} mol/dm³. NaOH solution was used to maintain the pH value of the bath at 12.5. Copper was deposited on Pt plates, $30 \times 30 \times 0.1$ mm. First, each plate was etched in a mixture of

concentrated phosphoric, acetic and nitric acids (0.5:0.35:0.15), then carefully rinsed, activated in 0.01 mol/dm³ PdCl₂ solution for 10 sec and, finally, pre-covered with a thin copper film by immersing it for 5 min in a bath containing Cu⁺², 8.0 x 10⁻³ mol/dm³; EDTA, 1.4 x 10⁻² mol/dm³; HCHO, 0.2 mol/dm³; and 2.2'-dipyridyl, 1.0 x 10⁻³ mol/dm³. The temperature of the bath was maintained at 60 °C and pH 12.5. Next, the plates were rinsed and weighed. Such pretreatment procedure was to assure sufficient repeatability of results.

The basic copper coating was deposited at 60 \pm 0.5 °C for 20 to 30 min, using magnetic stirring of the bath. Upon completion, the test plate was carefully rinsed and weighed to determine the copper plating rate. During the process, the mixed potential vs. SCE was measured.^{11,12}

Electrochemical Experiments

The plating solutions were prepared from the same reagents as the solution for electroless copper deposition. The basic composition of the bath was: Cu^{+2} , $1.0 \times 10^{-3} \text{ mol/dm}^3$; EDTA, 2.0 x 10^{-3} mol/dm^3 ; 2,2'-dipyridyl, $1.0 \times 10^{-3} \text{ mol/dm}^3$ to $1.0 \times 10^{-2} \text{ mol/dm}^3$; NaClO₄, 0.5 mol/dm³. All solutions were deaerated with argon before use. The measurements were conducted at ambient temperature.

Chronovoltamperometry on solid electrodes in a threeelectrode system with separated cathode and anode compartments was adopted as a test method. The working copper electrode of 0.152 cm^2 was electrolytically copper-plated in standard conditions before each experiment. The working electrode potential was measured against the silver chloride electrode. The auxiliary electrode was made of a Pt plate of about 2 cm² and polarization was changed within the range 0.025 to 0.35 V/sec, using a potentiostat. The results were calculated by computer, using special software.

Results

The influence of the concentration of 2,2'-, 2,4'- and 4,4'dipyridyl on the electroless copper deposition from alkaline EDTA solutions is shown in Fig. 1, which reveals that only addition of 2,2'-dipyridyl in the range of concentration 5×10^{-5} to 10^{-3} mol/dm³ results in an increase of the deposition rate. The other pyridyls show inhibiting action on the copper deposition process in the entire concentration range; when their concentration exceeds 10^{-4} mol/dm³, decomposition of the bath takes place with precipitation of the copper compounds within 30 min or an even shorter time.

The influence of 2,2'-dipyridyl concentration on the rate of electroless copper deposition, as measured by the gravimetric method, is shown in Fig. 2. The influence of the 2,2'dipyridyl concentration on the peak value of the current is seen in the same figure. That dependence was studied chronovoltamperometrically. The results obtained by both methods were compared. The X-coordinate is the negative



Fig. 1—Influence of isomeric dipyridyl concentration on the copper deposition rate and of the 2,2'-dipyridyl concentration on the $-E_m$ value. Composition of solution: Cu^{+2} , 0.008 mol/dm³; EDTA, 0.014 mol/dm³; HCHO, 0.2 mol/dm³; (\bigcirc) 2,2'dipy; (\triangle) 2,4'dipy; (*) 4,4'dipy; (\square) - E_m .

log of the quantity of 2,2'-dipyridyl added per cm² of the plated surface. The Y-coordinate, left, is the copper film deposition rate in μ m/hr, and right, the current peak values, in mA/cm², respectively. The maximum plating rate and the maximum current peak value appear at the same quantity of 2,2'-dipyridyl added per unit surface being copper-plated. Both curves were developed at the same pH of 12.5 and Cu/EDTA concentration ratio of 1:2. Moreover, the value of the mixed potential vs. SCE depends on the quantity of 2,2'-dipyridyl added to the bath. Results of the measurement are also shown in Fig. 1. The mixed potential changed step-wise with increase in 2,2'-dipyridyl concentration, from -740 mV at concentration 1.0 x 10⁻⁵ mol/dm³ to -624 mV at 1.0 x 10⁻² mol/dm³.

During the copper plating process, the color change of the baths with dipyridyl concentration higher than 5 x 10^{-3} mol/dm³ was observed: from blue to green and even green-brown, for dipyridyl concentrations greater than 10^{-2} mol/dm³. The reason was the presence of the red-brown Cu(dipy)_x⁺ complex, which was confirmed by absorption spectrum analysis. Formation of such a complex was observed only when copper plating was performed in the presence of oxygen. No formation of a complexed Cu(I) with 2,2'-dipyridyl occurred in the argon atmosphere, which may suggest that the Cu(dipy)_x⁺ complex appears as a result of copper dissolution by 2,2'-dipyridyl in the presence of oxygen. The latter was investigated by the author, with the results to be presented in a separate paper.¹³

Discussion

The rate of electroless copper deposition from alkaline solutions of EDTA is predominantly dependent on the Cu-EDTA complex concentration and on the concentration of various additives. The rate of Cu deposition rises linearly with increasing Cu-EDTA concentration,¹⁴ whereas the increase of the ligand-to-copper-concentration ratio results in a slight decrease of the deposition rate. An excessive concentration (within some range) of triethanolamine (TEA) or triisopropanolamine (TIPA), vs. the Cu(II) concentration, contributes to a very distinct rise in the deposition rate.^{15,16} According to the works cited, the reason is greater adsorption ability of TEA and TIPA on an active surface than that of EDTA. At similar copper and ligand concentrations, pH and temperature, the adsorption equilibrium constant (K) is 1.10^{-2}



Fig. 2—Dependence of electroless copper deposition rate and peak current value on concentration of 2,2' dipyridyl added to the bath: $(\bigcirc) i_p$; (\Box) deposition rate.

mol⁻¹dm³ for EDTA and 1.10¹ mol⁻¹dm³ for TEA. According to the same sources, the Cu-EDTA complex adsorbs much better than the Cu-TEA complex on bare, active surfaces. Corresponding adsorption equilibrium constants are 1.10⁴ and 2.10¹ mol⁻¹dm³, respectively. Because the K value is the same (1.10¹ mol⁻¹dm³ for both complexes), 2,2'-dipyridyl can be adsorbed as well as TEA on surfaces being copper-plated.

In the solution of Cu⁺², EDTA and 2,2'-dipyridyl, both complexes, Cu-EDTA and Cu-2,2'-dipyridyl, can be adsorbed on the copper surface to a similar extent. The adsorption constants are 1.10⁴ mol⁻¹dm³ for both species.³ At low concentrations of 2,2'-dipyridyl (below 5 x 10⁻⁵ mol/dm³), the Cu-EDTA complex mainly adsorbs and its influence on the copper deposition rate is quite insignificant. The copper deposition rate then rises gradually at higher 2,2'-dipyridyl concentrations until reaching a maximum at 2.2'-dipyridyl concentration of about 2 x 10⁻⁴ mol/dm³ (Fig. 2). Such a relationship may suggest that 2,2'-dipyridyl adsorbed on the plated surface shows its complexing ability to copper ions bound in Cu-EDTA complexes by loosening the Cu-EDTA bond, which in turn facilitates the copper reduction and hastens the copper deposition process. Further addition of 2,2'-dipyridyl results in inhibiting action, and at a 2,2'dipyridyl concentration of about 1 x 10⁻² mol/dm3, the copper deposition rate becomes two times lower than that of a 2,2'dipyridyl concentration of 2 x 10⁻⁴ mol/dm³. The reason for that may be excess coverage of the catalytic copper surface with 2.2'-dipyridyl, up to multilayer coverage, ¹⁷ which makes the reduction of copper ions difficult or even impossible.

A similar effect of the concentration of 2,2'-dipyridyl upon the copper deposition rate has been observed in electrochemical studies. The maximum of the electroless copper deposition rate and the maximum of the cathodic current peak value fall in the same range of 2,2'-dipyridyl added per 1 cm² of the plated surface (Fig. 2), which may be considered confirmation of the proposed explanation for the 2,2'dipyridyl role in the copper reduction process.

Most studies of the influence of 2,2'-dipyridyl on electroless copper reduction from alkaline solutions confirm its positive effect on bath stability, the quality of the copper deposit^{3,4} and (within the range of 5×10^{-5} to 10^{-4} mol/dm³), on the copper deposition rate as well. All those positive effects of 2,2'-dipyridyl on electroless copper deposition may be assigned to adsorptive ability of the compound on plated surfaces and especially to its ability to form very stable chelate complexes with copper ions. The corresponding stability constants are: $-\log \beta_2 = 14.9$ for Cu(dipy)₂⁺² and $-\log \beta_2 = 12.9$ for Cu(dipy)₂^{+.18} The great stability of the compounds results from the fact that such ligands are good donors of electrons from σ orbitals of nitrogen atoms to the empty d (e_g), s and p orbitals of metal atoms. Moreover, these ligands may act as electron acceptors because of the presence of delocalized π orbitals of nitrogen atoms.

Other isomeric pyridyls studied do not form chelate-type complexes, because of the adverse location of nitrogen atoms. They can only form typical co-ordination compounds of significantly lower stability. Only 2,4-dipy complexes with Pd and Pt have been reported.¹⁹

All examined dipyridyls show similar adsorption abilities on metal surfaces. They depend on the composition of the electrolyte solution and its pH. The neutral dipyridyl particles adsorb from alkaline solutions much easier than from protonated ones.¹⁵ Adsorptive abilities of dipyridyls depend also (to some extent) on their structure. The surface activity increases in the sequence 2,2' > 4,4' > 3,3'-dipyridyls, but the differences are not significant.¹⁷

Conclusions

From the results of this investigation and citations from the literature, the following may be concluded:

- 1. Of isomeric dipyridyls studied, only 2,2'-dipyridyl shows a stabilizing effect on the bath. The other two dipyridyls make the bath decompose faster.
- 2. The stabilizing effect of the 2,2'-dipyridyl can be assigned to formation of stable complexes with Cu⁺ ions and, by that means, inhibiting Cu₂O formation.
- 3. Better quality of the copper surface obtained in the presence of 2,2'-dipyridyl^{3,4} can result from the ability of the 2,2'-dipyridyl to dissolve metallic copper. In the presence of 2,2'-dipyridyl, the reaction of copper deposition is accompanied by the dissolution reaction, inasmuch as it happens while depositing copper from solutions containing cyanide.
- 4. The increase in the copper deposition rate (in some range of 2,2'-dipyridyl concentrations) can be attributed to the ability of the 2,2'-dipyridyl to form quite stable complexes with the copper ions. The major factor of that increase may be the possibility of electron exchange between the metal surface, the adsorbed π -particles of 2,2'-dipyridyl and the Cu(II) complexes remaining in the solution.

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Continued from page 59

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