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Changes of the Cu electrode real surface area during the process of electroless copper plating

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Abstract The surface area (nanoscale roughness) of copper coatings deposited from electroless plating solutions containing Quadrol, L(+)- and DL(±)-tartrate as Cu(II) ion ligands was measured using underpotential deposition thallium monolayer formation. Surface roughness of Cu coatings depends on the plating solution pH and the Cu(II) ligand, and varies over a wide range. In L(+)-tartrate and Quadrol solutions (pH 12.5–13.3) the roughness factor R_f is low and is equal to 2–3 and 4–6, respectively (substrate: electrodeposited Cu; $R_f = 2.2$). Cu coatings of higher surface area are obtained in DL(±)-tartrate (pH 12.3–12.7) and Quadrol (pH 12.0) solutions: R_f reaches 20–30. The correlation between R_f and Cu deposition rate was found in L(+)-tartrate solution. The Cu surface area changes are discussed in terms of partial electrochemical reactions of the autocatalytic Cu deposition process, and the decisive role of cathodic Cu(II) reduction from adsorbed Cu(II) complex species.

Key words Electroless plating · Copper electrode · Real surface area · Thallium underpotential deposition

Introduction

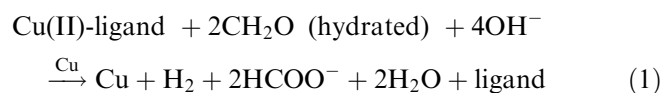
The process of electroless copper plating is used for decorative and functional purposes, e. g. for deposition of a metal layer on dielectrics or on conductors having a complicated configuration [1–5]. This process is most widely applied in the manufacture of integrated circuits, through hole plating.

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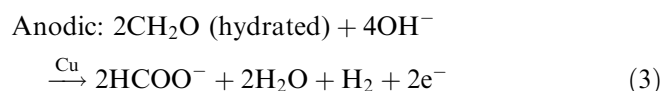
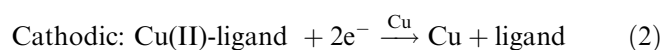
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In general, electroless metal deposition processes are considered as the coupling of the cathodic reduction of metal ions and the anodic oxidation of the reducing agent occurring simultaneously on the metal surface.

In the case of the conventional alkaline formaldehyde-containing solutions the total process of autocatalytic Cu(II) reduction occurs as follows:



The two partial reactions are:



The electrons produced in the course of the anodic oxidation of formaldehyde are transferred through the metallic copper surface to Cu(II) ions, and the autocatalytic reduction of Cu(II) occurs. Copper is a catalyst of partial reaction (3) of the electrocatalytic oxidation of formaldehyde. This reaction rate was shown to be sensitive to Cu surface structure: the Cu(110) plane was more active compared with the Cu(100) and Cu(111) planes [6]. Since anodic formaldehyde oxidation under the conditions of electroless plating is not limited by diffusion, its rate is proportional to the catalyst (Cu surface) area. Therefore knowledge of the surface area of electrolessly deposited Cu is important for understanding the autocatalytic deposition process kinetics and mechanism. Data on surface roughness are important also for copper coating characterization in practical applications.

The real surface area (S_R) usually differs from the geometrical surface area (S_G , for the surface with no roughness). For characterization of heterogeneous (surface) reactions the surface area at the atomic (nanoscale) level should be known. From various methods of metal surface area determination at metal-

solution interfaces (for review of these methods, see [7]), the measurements of hydrogen overvoltage [8], double layer capacity [9–13], Cu₂O or Cu(OH) (adsorbed oxygen) monolayer [14–17] and metal monolayers formed in underpotential conditions [17, 18] have been used. Some measurements of the surface area of Cu coatings obtained by electroless deposition were carried out mostly using the double layer capacity method [10–14].

The aim of this work was to investigate the changes of the Cu coating surface during the process of electroless copper plating from solutions containing the widely used Cu(II) ligands Quadrol [*N,N,N',N'*-tetrakis(2-hydroxypropyl)ethylenediamine], L(+)-tartrate (Rochelle salt), or DL(±)-tartrate.

The method of thallium monolayer formation in underpotential deposition conditions [17] was used. This surface area determination method seems to be the most simple and convenient, giving reproducible results.

Experimental

Chemicals and solutions

“Chemical pure” grade chemicals from Reachim were used; Quadrol was of a practical grade from Fluka, and the formaldehyde source was pharmaceutical formalin (37% CH₂O) solution. Carbonate-free NaOH solutions were prepared using the method described [19]. The pH of the solutions was measured at 20 °C using an EV-74 pH meter (Belarus).

Treatment of the electrodes and electroless copper plating

The substrate was a Pt sheet (1 × 1 cm, geometrical surface area $S_G = 2 \text{ cm}^2$) freshly electroplated with Cu from an acid electrolyte (1.0 M CuSO₄ + 0.5 M H₂SO₄) at 15 mA cm⁻² for 20 min. Before the electroless plating, the electroplated substrate was activated for 10 s in acid PdCl₂ solution (1 g l⁻¹), then rinsed with distilled water and immersed into the electroless plating solution.

The electroless plating was carried out for 15, 30, 45 and 60 min at 20 °C in 50 ml of the solution containing: 0.05 M CuSO₄; 0.1–0.2 M Cu(II) ligand [Quadrol, L(+)-tartrate, or DL(±)-tartrate]; 0.15 M formaldehyde; NaOH (up to pH value needed).

Determination of the real surface area of the Cu electrode

The method is based on the underpotential deposition of the thallium monolayer on the Cu electrode surface and is described elsewhere [17]. Standard electrochemical equipment and procedures were used. Cyclic voltammetric curves were obtained by a programming potentiostat PI-50, sweep generator PR-8 and xy-recorder H-307 (Russia), thermostatted electrochemical cell JES-1 (Belarus), and thermostat UH-4 (Germany). The solutions were deaerated by Ar. The auxiliary electrode was Pt foil, and the reference electrode was Ag/AgCl with a saturated KCl solution.

The measurements were carried out at 25 °C in 1 M Na₂SO₄ solution containing 1 mM TlNO₃. Before the measurements copper oxides were removed from the surface: the working Cu electrode was kept at –0.80 for 5 s. Then the electrode was kept at +0.15 V for 5 s (for dissolving the bulk Tl deposit). A Tl monolayer was formed at –0.49 V for 200 s. Then the Tl monolayer was dissolved using anodic scanning of the potential up to –0.1 V (scanning rate 50 mV s⁻¹). By integration of the potentiodynamic curve obtained

(in the range –0.39 to –0.10 V), the quantity of electricity (Q , μC) used for anodic dissolution of the Tl monolayer was calculated.

The real surface area (nanoscale roughness) of the Cu electrode ($S_{R,Cu}$) was calculated using the equation:

$$S_{R,Cu} = Q/Q_T \quad (4)$$

where Q_T is the quantity of electricity necessary to form a Tl monolayer on 1 cm² of polycrystalline Cu: 112 μC cm⁻² [17].

Results and discussion

Initial Cu electrode surface

The measured real surface area of the electroplated Cu electrode which was used as the substrate for electroless plating ($S_{R0,Cu}$) was found to be 4.4 cm², i.e. the surface roughness factor R_f (ratio $S_{R0,Cu}/S_G$) was 2.2. The initial substrate (Pt foil surface) roughness factor according to the standard electrochemical hydrogen adsorption method was (for various samples) 2.0–2.5. Obviously, Cu electroplating did not change the surface morphology appreciably.

L(+)-Tartrate- and DL(±)-tartrate-containing electroless plating solutions

Although the values of the stability constants for Cu(II) complexes with L(+)- and DL(±)-tartrate are similar and the degree of Cu(II) ion complexation is practically the same in both cases [20], the real surface area changes in the process of Cu deposition from these solutions as well as the copper plating rate and its dependence on the pH of the solution (12.0 ≤ pH ≤ 13.3) differ considerably (Figs. 1, 2).

In the case of L(+)-tartrate (Rochelle salt) solutions the real surface area of the Cu coatings at pH 12.5–13.3 (Cu deposition at pH 12.0 is inhibited by the passivation of the copper surface owing to Cu₂O formation [21]) is similar to that of the electroplated copper substrate and the surface area changes in the course of the deposition process are not large: the surface roughness factor $R_f = 2.1–3.1$ (Fig. 1a). Similar results were obtained earlier using double layer capacity measurements [10, 11].

When using DL(±)-tartrate as the Cu(II) ion ligand in electroless copper plating solutions, the coating surface area increases significantly in the plating process (except for coatings deposited at pH 13.3) (Fig. 1b). Especially high surface roughness (R_f up to 20) is obtained at a solution pH of 12.3–12.5.

When comparing the Cu surface area (Fig. 1) with the Cu deposition kinetics (Fig. 2) it is possible to conclude:

1. In the case of low surface roughness [L(+)-tartrate solutions], a copper deposition rate increase with solution pH is observed (Fig. 2a); this effect is well known and is explained by the increase in formaldehyde oxidation – partial reaction (3) of the electroless copper plating process – rate with increasing solution pH.

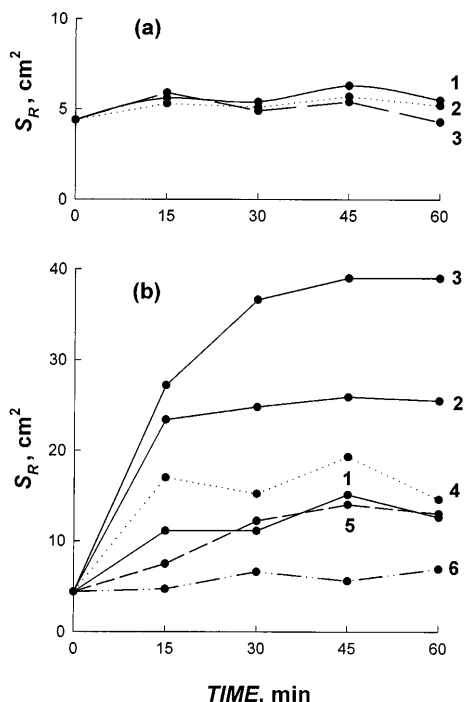


Fig. 1 Dependence of the real surface area of the Cu electrode on time during the process of electroless copper plating in solutions containing L(+)-tartrate (a) and DL(\pm)-tartrate (b) as Cu(II) ion ligands. Solution composition 0.05 M CuSO_4 , 0.15 M CH_2O , 0.15 M tartrate. Solution pH: a 1 12.5, 2 13.0, 3 13.3; b 1 12.0, 2 12.3, 3 12.5, 4 12.7, 5 13.0, 6 13.3

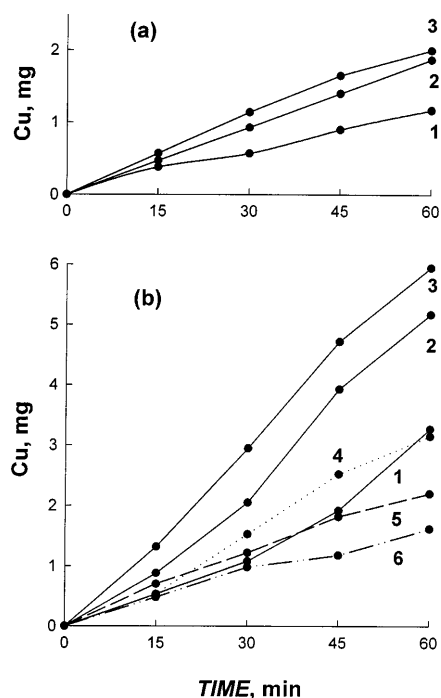


Fig. 2 Dependence of the Cu deposition rate on time in electroless copper plating solutions containing L(+)-tartrate (a) and DL(\pm)-tartrate (b) as Cu(II) ion ligands. Solution composition 0.05 M CuSO_4 , 0.15 M CH_2O , 0.15 M tartrate. Solution pH: a 1 12.5, 2 13.0, 3 13.3; b 1 12.0, 2 12.3, 3 12.5, 4 12.7, 5 13.0, 6 13.3

2. In the case of DL(\pm)-tartrate solutions, a correlation between the Cu surface area and the Cu coating deposition rate exists: the higher Cu surface area achieved in the plating process, the higher Cu plating rate is observed (compare Figs. 1a and 2a). In some cases, the Cu deposition rate is increasing during the plating process when the surface area of the coating is increasing sharply (curves 1–3 on Figs. 1 and 2). The high Cu deposition rate in DL(\pm)-tartrate solutions is apparently the result of the higher area of the catalytic Cu surface. The rate of both partial reactions of the electroless plating process – Cu(II) reduction (Eq. 2) and CH_2O oxidation (Eq. 3) – should be sensitive to the electrode area. In the case of DL(\pm)-tartrate solutions pH 12.3–12.7, the anodic partial reaction (Eq. 3) is accelerated by the surface area increase more than the cathodic one, and the coating potential shifts to more negative values by 100–150 mV compared with other solutions [including plating solutions containing L(+)-tartrate].

Quadrol-containing electroless plating solutions

The surface area of Cu coatings during their deposition in Quadrol solutions (pH 12.5–13.0) increases up to $R_f = 4$ –6 (Fig. 3). Different behavior is observed at lower solution alkalinity (pH 12.0) when the surface roughness factor increases to very high values: up to 20–30 (curve 1 in Fig. 3a, b).

In contrast to DL(\pm)-tartrate solutions, the Cu coating with the highest surface area does not correspond to the highest Cu deposition rate from Quadrol plating solutions: the plating rate is the lowest in this case (Fig. 4). Obviously, the Cu surface obtained at the plating process at pH 12.0 is less catalytically active compared with the Cu surface deposited at higher solution pH values. A possible explanation of this phenomenon could be a low rate of formaldehyde oxidation at this solution alkalinity, and the resulting reduction of Cu(II) is not completely to the metallic state but to Cu_2O (a similar situation with the prevailing formation of Cu_2O is observed in Rochelle salt solutions at the same pH).

Comparison of various plating solutions

Electroless plating experiments in this study were carried out in solutions containing the same concentration of the main reactants, Cu(II) and formaldehyde. The only variation was the Cu(II) ligand. Therefore the differences in Cu coating formation should be related mostly to the cathodic partial reaction of the autocatalytic Cu(II) reduction process, i.e., cathodic reduction of various Cu(II) complexes. Although two partial reactions (2) and (3) of the autocatalytic process are not independent, and rather large effects of anodic CH_2O oxidation (3) on the rate of Cu(II) reduction reaction (2)

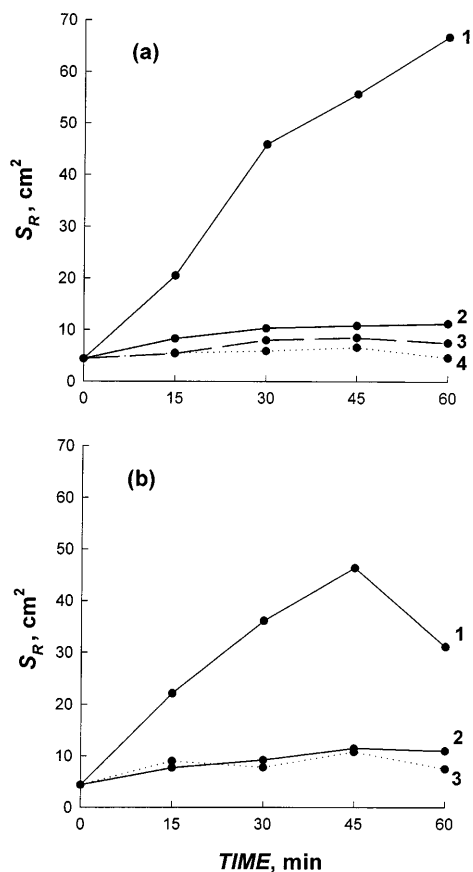


Fig. 3a, b Dependence of the real surface area of the Cu electrode on time during the process of electroless copper plating in solutions containing Quadrol as the Cu(II) ion ligand. Solution composition 0.05 M CuSO_4 , 0.15 M CH_2O , 0.10 M Quadrol (a) and 0.20 M (b). Solution pH: a 1 12.0, 2 12.5, 3 13.0, 4 13.3; b 1 12.0, 2 12.5, 3 13.0

are observed (for a discussion of these effects see, for example, [22]), electrocrystallization of Cu from adsorbed Cu(II) complex species should be mostly responsible for the Cu coating morphology. The effect of free ligand adsorption seems to be less significant: the free Quadrol concentration change has little effect on the Cu deposition rate and surface area (Figs. 3 and 4), and the adsorption behavior of L(+)- and D(-)-tartrate should be not different.

Unexpected large differences between the morphology of the Cu coatings deposited in L(+)- and DL($\bar{\text{T}}$)-tartrate solutions are apparently connected with different structures of the Cu(II) complexes. The complexes CuT_2^{4-} and $\text{CuT}_2(\text{OH})_2^{6-}$ (T = tartrate) are present in electroless plating solutions at pH 12–13 [20]. Complexes with two L(+)- or D(-)-tartrate ligands probably have the same properties, but a complex containing one L(+)- and one D(-)-tartrate ion could be of different structure; indications of this are the different light absorption spectra of Cu(II) complexes with L(+)- and DL($\bar{\text{T}}$)-tartrate [20]. Probably the adsorption behavior of these complexes is different and so the electrocrystallization situation may be different.

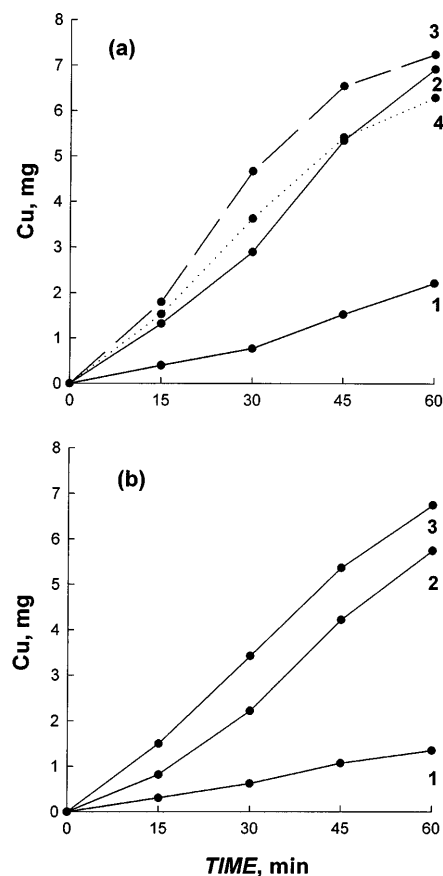


Fig. 4a, b Dependence of the Cu deposition rate on time in electroless copper plating solutions containing Quadrol as the Cu(II) ion ligand. Solution composition: 0.05 M CuSO_4 , 0.15 M CH_2O , 0.10 M Quadrol (a) and 0.20 M (b). Solution pH: a 1 12.0, 2 12.5, 3 13.0, 4 13.3; b 1 12.0, 2 12.5, 3 13.0

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