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# Application of saccharose as copper(II) ligand for electroless copper plating solutions

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**Abstract**—Saccharose, forming sufficiently stable complexes with copper(II) ions in alkaline solutions, was found to be a suitable ligand for copper(II) chelating in alkaline ($\text{pH} > 12$) electroless copper deposition solutions. Reduction of copper(II)–saccharose complexes by hydrated formaldehyde was investigated and the copper deposits formed were characterized. The thickness of the compact copper coatings obtained under optimal operating conditions in 1 h reaches ca. 2 μm at ambient temperature. The plating solutions were stable and no signs of Cu(II) reduction in the bulk solution were observed. Results were compared with those systems operating with other copper(II) ligands.

*Keywords:* Saccharose; Ligand; Copper(II); Electroless copper deposition; Copper coatings; Surface roughness

## 1. Introduction

Electroless copper plating solutions are widely used in electronics for deposition of metallic copper layers on semiconductors or dielectrics (silicon wafers, resins, etc.).[1,2] The electroless deposition method uses a catalytic redox reaction between metal ions and dissolved reduction agent, and the main advantages of this technique is a possibility to plate nonconductive surfaces and to obtain metal coatings of the uniform thickness all over the plated object.

The overall process of electroless copper deposition is described by the following equation:

$$\text{Cu(II)–ligand} + 2\text{HCHO} + 4\text{OH}^- \xrightarrow{\text{Cu}} \text{Cu} + \text{H}_2 + 2\text{HCOO}^- + 2\text{H}_2\text{O} + \text{ligand} \quad (1)$$

In general, electroless metal deposition processes are recognized now to be electrochemical by nature and are supposed to result from the coupling of two partial electrochemical reactions—the cathodic reduction of metal ions and the anodic oxidation of the reducing agent. Electroless copper deposition process consists of anodic formaldehyde oxidation and cathodic Cu(II) reduction occurring simultaneously on the same copper surface; the electrons that appear in anodic oxidation of formaldehyde are transferred through the metallic copper to Cu(II) ions, and the autocatalytic deposition of Cu takes place.

Copper(II) ligands, along with hydrated formaldehyde as the reducing agent and a copper(II) salt as copper(II) ions source, are important components of autocatalytic copper deposition systems. Since these systems operate in alkaline milieu, the ligands used must meet several important requirements: these compounds must form copper(II) complexes that are stable enough to prevent precipitation of copper(II) hydroxide, and they should not react with formaldehyde nor retard the catalytic copper(II) reduction reaction. Ethylenediaminetetraacetic acid (EDTA) is currently the most widely used ligand in electroless copper plating technique due to its perfect chelating properties. However, there are attempts to replace EDTA, because it creates environmental hazards.

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Xylitol, D-mannitol and D-sorbitol were proposed recently as environmentally friendly alternate copper(II) ligands for electroless copper plating solutions.[3] The alditols mentioned showed good chelating properties for copper(II) ions in alkaline media ($pH > 11.5$).[4] Electroless copper plating solutions containing the chelators xylitol, D-mannitol and D-sorbitol are stable and, under optimal conditions, copper coatings up to 3 μm thick can be obtained in 1 h at ambient temperatures.[3]

The ability of polyols to chelate Cu(II) ions in alkaline solutions has been known since the 19th century, but quantitative data on the composition and stability of the complexes formed are sparse. Data on the interactions of saccharose (Sa) with Cu(II) ions in alkaline medium were published in the late 20th century.[5,6] It was found that the chelating ability of saccharose depends on solution pH and the concentrations of Cu(II) and saccharose. The pH-dependence is related to deprotonation of saccharose in alkaline solutions ($pK_a = 12.43$) and formation of the $Sa^-$ anion, which is the main chelator in the systems investigated. Generally, formation of soluble Cu(II)–saccharose compounds is observed at pH values > 10. This pH limit depends also on Cu(II) concentration and the degree of excess of saccharose. Three mononuclear copper(II)–hydroxy complexes were documented under conditions of saccharose excess: $CuSa(OH)_2^-$ ($\log\beta = 17.6$), $CuSa(OH)_3^{2-}$ ($\log\beta = 19.4$) and $CuSa_2(OH)_2^{2-}$ ($\log\beta = 19.6$).[5,6]

Since composition and stability of Cu(II) complexes with xylitol[4] are similar to those of Cu(II)–saccharose, the aim of the study presented herein was to evaluate the electroless copper deposition process in solutions containing saccharose as the Cu(II) ligand.

## 2. Results and discussion

### 2.1. Equilibria in alkaline copper(II)–saccharose solutions

The values of stability constants of Cu(II)–saccharose complexes lead to a prediction that at the Cu(II) concentration (0.05 M) commonly used in electroless copper plating solutions, saccharose should be able to adequately chelate Cu(II) ions under conditions of saccharose excess. Calculations indicate that saccharose is able to chelate 0.05 M Cu(II) sufficiently to prevent $Cu(OH)_2$ precipitation at pH values >12. That is, calculated pCu (i.e., negative logarithm of uncomplexed Cu(II) ions) values are higher than those necessary to prevent precipitation of copper(II) hydroxide, and $Cu(OH)_2(s)$ should not form (Fig. 1). Experiments confirmed these predictions—no $Cu(OH)_2(s)$ precipitate was observed at pH values >12 and solutions became dark blue, whereas at lower pH values formation of $Cu(OH)_2(s)$ is clearly visible.

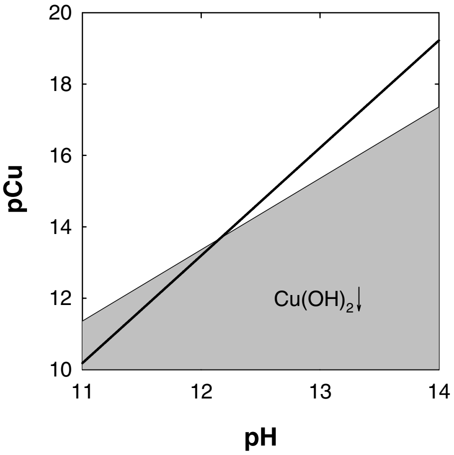

**Figure 1.** Relationships of pH to pCu in saccharose containing solutions. Solution composition (M): $[Cu(II)]_0 = 0.05$; $[Sa]_0 = 0.10$. Filled areas represent regions of $Cu(OH)_2$ precipitate formation.

Calculations of the distribution of Cu(II) among the complexes with saccharose show that a mixture of Cu(II)–saccharose complexes is formed in the solution (Fig. 2). No predominate species is observed in pH region from 12.25 to 13, whereas at pH 13, ca. 50% of Cu(II) is in the form of the $CuSa(OH)_3^{2-}$ complex, which clearly predominate at higher pH values.

### 2.2. Electroless copper deposition from solutions containing saccharose as Cu(II) ion ligand

In solutions with an excess of saccharose (Cu(II)/saccharose molar ratio 1:2), autocatalytic reduction of Cu(II) by formaldehyde starts at pH (Fig. 3). The plating rate near the lower pH limit (pH 12.25) is ca. 0.5 μm $h^{-1}$. With further increase in solution pH, the plating rate rises sharply reaching maximum values at a pH near 12.75, and then decreases as the pH is further elevated.

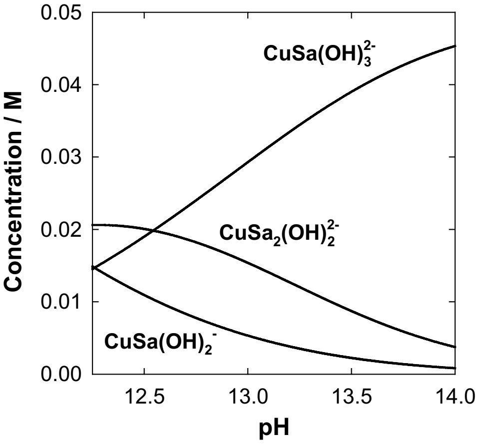

**Figure 2.** Distribution of Cu(II) among the complexes in solution containing (M): $[Cu(II)]_0 = 0.05$; $[Sa]_0 = 0.10$.

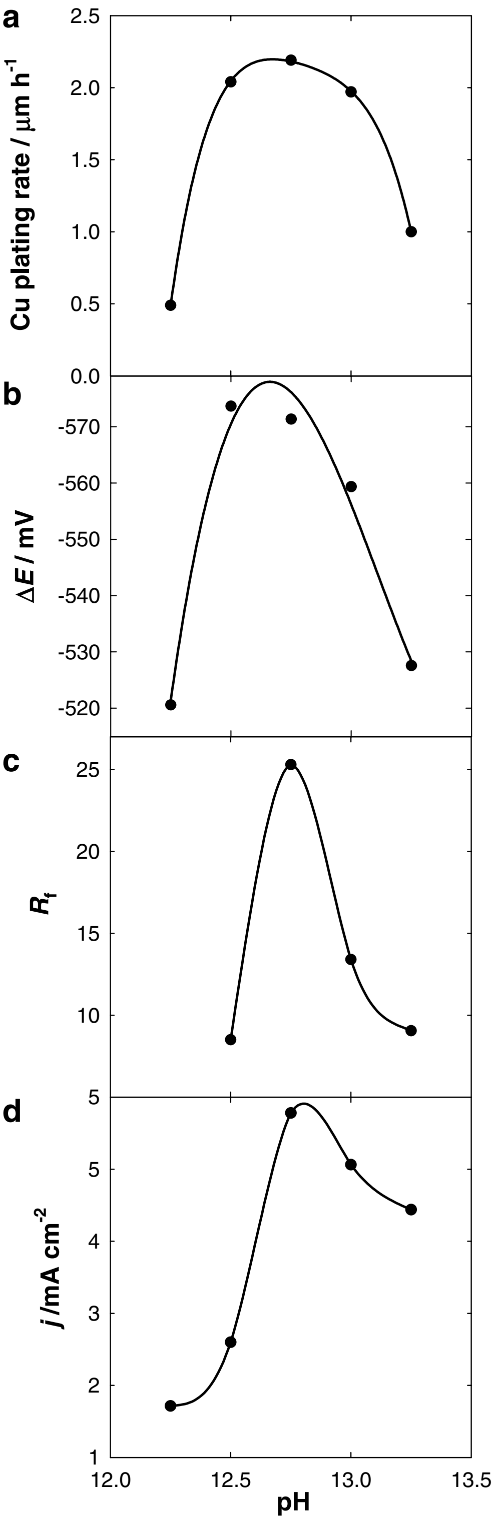

**Figure 3.** Dependence of copper plating rate (a), overpotential of the copper electrode (b), copper surface roughness factor (c) and HCHO anodic oxidation current peak density (d) on pH. Solution composition (M): (a)–(c) $[Cu(II)]_0 = 0.05$; $[Sa]_0 = 0.10$; $[HCHO]_0 = 0.15$ and (d) given in Figure 5f–j.

The thickness of the compact copper coatings obtained under optimal operating conditions in 1 h reaches ca. 2 µm (Fig. 3a). The plating solutions are stable and no signs of Cu(II) reduction in the bulk solution were observed.

Comparison of the Cu deposition rate data with the Cu(II) distribution among the complexes with saccharose (Fig. 2), indicates that the acceleration of the plating process (until the maximum rate is reached) could be related to an increase in the concentration of the $CuSa(OH)_3^{2-}$ complex as pH is elevated. This suggests that the $CuSa(OH)_3^{2-}$ complex is the principal electroactive species in the catalytic reaction investigated (Eq. 2):

$$CuSa(OH)_3^{2-} + 2HCHO + OH^- \xrightarrow{Cu} Cu + H_2 + 2HCOO^- + 2H_2O + Sa^- \qquad (2)$$

If this is the case, then the observed decrease in plating rate at higher pH values warrants additional discussion. As the pH is increased above the observed rate maximum, no changes in copper or formaldehyde speciation are expected, that is, $CuSa(OH)_3^{2-}$ and the methanediol anion form of formaldehyde should continue to dominate the speciation.[7,8] This suggests that solution conditions may not be the cause of the observed rate decrease. Alternatively, the decrease in plating rate could be caused by changes in the catalytic surface state. The real surface area of the deposited copper decreases considerably at pH 13 and greater (Fig. 3c), and the catalytic reaction rate in the simplest case should decrease correspondingly. In addition, other characteristics of the Cu surface obtained at higher pH values may be important. For example the surface may be less catalytically active due to the formation of Cu(I) species. The formation of Cu(I) species during electroless copper deposition processes is documented.[9,10] The Cu(I) species slow down the autocatalytic reduction of Cu(II) by formaldehyde (Eq. 1) through retardation of anodic formaldehyde oxidation on the Cu surface.[11]

The open-circuit potential of copper in the course of electroless deposition varies over a rather wide range of values depending on solution pH (Fig. 4). As the process of autocatalytic copper(II) reduction (electroless metal deposition) is generally accepted to be electrochemical by nature (the electrons appearing in formaldehyde anodic oxidation are transferred through metallic copper to copper(II) ions), the open-circuit potential in this case is a mixed one ($E_{mix}$). The potential is established as a result of two reactions occurring simultaneously on the same copper surface—cathodic reduction of Cu(II) ions and anodic oxidation of formaldehyde.[12–14] The time-dependence curves of $E_{mix}$ are typical for alkaline formaldehyde-containing electroless copper plating solutions.[15] During the initial period (i.e., in the first 1–2 min) $E_{mix}$, reaches its most negative value, later shifting to more positive potentials and after 20–40 min it remains practically constant due to the establishment of quasi-stationary plating conditions.

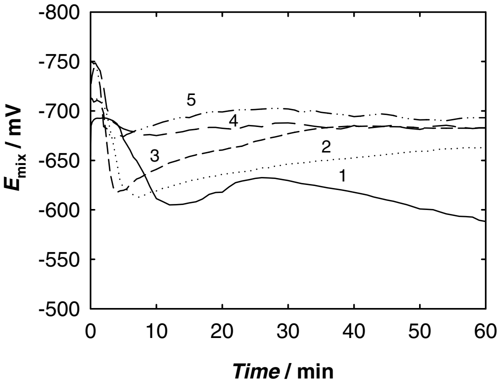

**Figure 4.** Time dependence of mixed potential of copper electrode ($E_{mix}$) during electroless copper plating. Solution composition (M): $[Cu(II)]_0 = 0.05$; $[Sa]_0 = 0.10$; $[HCHO]_0 = 0.15$. Solution pH: (1) 12.25, (2) 12.5, (3) 12.75, (4) 13.0, (5) 13.25.

The mixed potential, shifts continuously to more negative values with the rise in solution pH, corresponding to the shift of the potential regions in both the electrochemical half-reactions of the catalytic process.

The electroless copper deposition process can also be characterized by the copper electrode overpotential. In our system, the overpotential ($\Delta E$) represents the difference between the measured mixed potential of the copper electrode ($E_{mix}$) and the equilibrium potential of a $Cu/Cu^{2+}$ electrode ($E_{equil}$) calculated according to the Nernst equation using data on mass balance and the stability constants of the Cu(II) complexes existing in the solution.

From the calculated $E_{equil}$ and measured $E_{mix}$ values, the $\Delta E$ values were obtained. Figure 3b shows the dependence of the overpotential of the copper electrode (the $E_{mix}$ values were taken after 60 min from the beginning of electroless copper deposition) on solution pH. When comparing Figure 3a and b, an obvious correlation between copper plating rate and the overpotential for copper deposition is seen: the highest plating rates are observed at most negative values of the overpotential.

The real surface areas (nano-scale roughness) of the copper coatings obtained were characterized using the thallium underpotential deposition method described below. The roughness factor ($R_f$) of the electroplated copper electrode (which was used as the substrate for electroless plating) was found to be relatively low −2.2, whereas copper coatings deposited by the electroless technique have more developed surfaces and $R_f$ values that vary widely, from ca. 8 up to 25 (Fig. 3c). If one observes the pH-dependence in the $R_f$ of the copper deposits, the interrelationships among $R_f$ and copper plating rates and the overpotentials of copper electrodes are evident (cf. Fig. 3a–c). These correlations correspond to the well-known general trends in the effects of overpotential on metal nucleation during copper electrodeposition, that is, the formation of smoother metal deposits at lower deposition rates.

## 2.3. Voltammograms of copper electrode in alkaline solutions of saccharose and formaldehyde

Voltammograms were recorded using two different types of copper electrodes. The surface of the first electrode type was formed by electroplating from an acid copper(II) sulfate electrolyte, whereas those of the second type were prepared by an electroless plating technique from solutions containing saccharose as the Cu(II) ligand at pH values corresponding to those of solutions under electrochemical investigations (see Section 4.2).

In the first series of experiments we tried to detect an effect of saccharose on the electrochemical behaviour of copper electrodes in solutions with a variety of pH values (Fig. 5a–e). Consider first the data obtained with the electroplated electrode (dashed lines). No effects were observed at pH 12.25–12.5 (Fig. 5a and b). With further pH elevation, a peak of anodic current appears at a potential of about −50 mV (Fig. 5c and d). Peaks similar to these are known from earlier investigations of Cu in alkaline solutions and are attributed to copper anodic dissolution which is enhanced by the presence of ligands that form soluble copper(II) complexes.[11,16–18] The rise in peak current density values with pH elevation (from 0.5 mA $cm^{-2}$ at pH 12.75 up to 1.0 mA $cm^{-2}$ at pH 13.25) is explained by an increase in the complexing ability of saccharose due to its deprotonation as well as by increased Cu(II) complex stability at higher concentration of $OH^-$ ions which participate in Cu(II) complex formation with saccharose.

The currents of copper anodic dissolution in the presence of saccharose are much more pronounced when using electrolessly plated copper electrodes, and peak current densities range from 0.5 to 4.5 mA $cm^{-2}$ depending on solution pH (Fig. 5b–d; solid lines). These augmentatios (compared with those obtained on electroplated copper electrode) of copper anodic dissolution current in potential range from −100 to +450 mV, are explained by the much higher surface roughness of electrolessly deposited copper coatings. At constant pH values, the copper anodic dissolution peak current density has been reported to vary linearly with copper electrode surface roughness factor.[11] In our series, the linear dependence is not observed, apparently because our solutions had different pH values from those reported in Ref. 11.

It can be noted that when using electrolessly plated copper electrodes with high surface roughness, a new oxidation current peak at ca. −180 mV is detected (Fig. 5b–d; solid lines). According to the literature data[11,16–18] and our electrochemical experiments in the absence of saccharose (not presented here), this oxida-

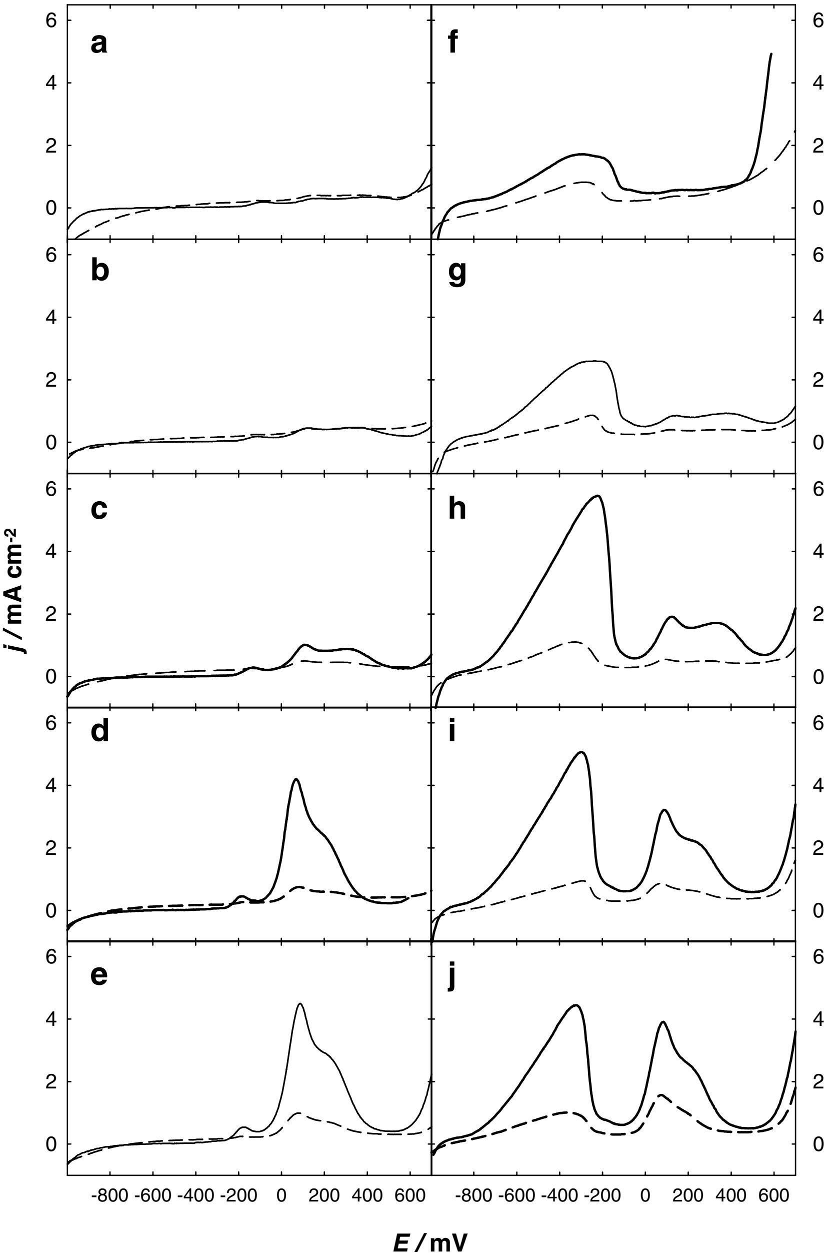

**Figure 5.** Voltammograms of copper electrode in alkaline solutions of saccharose (a–e) and saccharose and formaldehyde (f–j). Solution composition (M): $[Sa]_0 = 0.10$; $[Na_2SO_4]_0 = 0.10$; $[HCHO]_0 = 0.15$ (f–j). Solution pH values: (a, f) 12.25; (b, g) 12.5; (c, h) 12.75; (d, i) 13.0; (e, j) 13.25. Copper electrode surfaces were formed by electroplating (dashed lines) and by electroless plating from solutions containing saccharose as the Cu(II) ligand at respective pH values (solid lines).

tion current can be attributed to initial anodic oxidation of the copper surface to form Cu(I) species.

Since formaldehyde as a reducing agent is a significant component of electroless plating solutions and electrons appearing during its anodic oxidation reduce copper(II) ions to Cu(0) (Eq. 1), anodic processes proceeding on copper electrodes of both types were investigated in alkaline solutions containing formaldehyde and saccharose. The same processes are observed on both electroplated and electrolessly plated copper electrodes, the anodic current being low for electroplated copper electrodes because they are less developed surfaces (Fig. 5f–j). An anodic current is observed in the potential range ca. −800 to ca. −100 mV; this current is known to be the result of formaldehyde anodic oxidation:[11–15,17,18]

$$HCHO + 2OH^- \overset{Cu}{\rightarrow} HCOO^- + H_2O + 1/2H_2 + e^- \quad (3)$$

In the absence of formaldehyde, only small currents of initial anodic oxidation of the copper surface are observed in this potential region (Fig. 5b–d; solid lines).

It can be noted that changes in the copper electrode surface state also influence the process of formaldehyde anodic oxidation: the anodic current drops abruptly at potentials ca. −100 mV or more positive as a result of copper surface oxidation to form a $Cu_2O$ monolayer which inhibits HCHO oxidation. The anodic currents at potentials more positive than 0 mV correspond to deeper Cu oxidation, with the formation of Cu(II) oxy- and hydroxy-compounds; the anodic current in this potential region is enhanced in the presence of a Cu(II) ligand, for example, saccharose, due to the formation of more soluble copper(II) species.

As can be seen from the voltammograms (Fig. 5b–d), the maximum formaldehyde oxidation rate (i.e., the current density of the anodic oxidation peak) varies over a wide range depending on solution pH and method of preparation of copper surface. An interesting correlation was observed when analyzing the pH–dependencies: the formaldehyde anodic oxidation rate (Fig. 3d) depends on solution pH in the same manner as the electroless copper plating rate, the copper deposition overpotential and the surface roughness factor (cf. Fig. 3a–d). The highest observed values of the electroless plating rate, overpotential and surface roughness correspond to the highest formaldehyde oxidation rate (pH 12.75).

The specific activity of the copper surface (formaldehyde anodic oxidation peak current per unit of real surface area) was calculated from the data in Figure 3 for comparing the electrocatalytic properties of various Cu layers obtained by electroless deposition technique using saccharose as the Cu(II) ligand. The values obtained (0.33, 0.23, 0.39 and 0.49 mA $cm^{-2}$ at pH 12.5, 12.75, 13.0 and 13.25, respectively) demonstrate that the specific activity of copper surface in anodic formaldehyde oxidation is not directly correlated with values of the real copper surface area. A possible explanation of this data could be the presence of differing catalytic activities in different regions of the copper surfaces, that is, not all of the surface is involved in the anodic oxidation of formaldehyde.

### 2.4. Comparison of saccharose-containing electroless copper plating systems with systems operating with other Cu(II) ligands

For comparative purposes, we have selected literature data for electroless Cu plating rates obtained under similar experimental conditions (20 °C temperature, 1 h plating time, concentrations of copper(II) salt and formaldehyde equal to 0.05 and 0.15 M, respectively) but using different ligands.

The rate of copper deposition in saccharose-containing electroless copper solutions under optimal operating conditions (pH 12.75) reaches about 2 μm $h^{-1}$ (Fig. 3a). Very similar rates (2–2.5 μm $h^{-1}$) were determined using related compounds such as xylitol, D-mannitol and D-sorbitol as Cu(II) ligands, but required pH values were much higher and reached 13.5–13.8.[3] Plating rates that where almost two times higher (ca. 4 μm $h^{-1}$ at pH 13.0) were obtained from solutions with Quadrol (*N*,*N*,*N*′,*N*′-tetrakis(2-hydroxypropyl)ethylenediamine) as the Cu(II) ligand.[10] Also rather high plating rates were documented recently using novel ligands such as 4-hydroxypyridine-2,6-dicarboxylic and pyridine-2,6-dicarboxylic acids as the Cu(II) ligands. Copper plating rates with these ligands reached 2.8 μm $h^{-1}$ (pH 13.0) and 3.9 μm $h^{-1}$ (pH 12.7).[19] The use of L-tartrate and DL-tartrate gave interesting results: maximum plating rate of only about 1 μm $h^{-1}$ (pH 13.0) was observed in solutions with L-tartrate, whereas it reached ca. 3.5 μm $h^{-1}$ (pH 12.5) when using the racemic mixture of DL-tartrate.[10] Thus, saccharose-containing electroless copper plating solutions give rates of copper deposition that are comparable to other ligands.

It should be noted that the process of electroless copper deposition from saccharose-containing solutions occurs at −600 to −750 mV, that is at relatively very negative open-circuit potentials ($E_{mix}$). Similarly negative values of $E_{mix}$ were observed only in systems with 4-hydroxypyridine-2,6-dicarboxylic and pyridine-2,6-dicarboxylic acids as the Cu(II) ligands.[19] Usually the values of $E_{mix}$ are in the range from −300 to −500 mV for systems with other ligands.[15]

Electroless copper deposition processes with saccharose as the Cu(II) ligand are characterized by very negative overpotentials ($\Delta E$), that is, −520 to −570 mV. With other ligands, the values of $\Delta E$ commonly do not go below −400 mV,[15,19] except in the case of pyridine-2,6-dicarboxylic acid, where $\Delta E$ was about −600 mV.[19] Obviously extremely negative $\Delta E$ values result in high surface roughness for copper coatings obtained.

Copper is an effective catalyst for anodic reduction of small organic molecules in alkaline solutions as well as for other catalytic processes. Since catalytic activity depends critically on real catalytic surface area, formation of copper surfaces with a high degree of roughness is of interest for practical purposes. Usually the surface roughness factor ($R_f$) of electrolessly deposited copper coatings exceeds those of Cu electroplated from an acid copper(II) sulfate bath ($R_f \sim 2.2$). Previously, copper coatings with the highest $R_f$ values were obtained from solutions containing the following Cu(II) ligands: pyridine-2,6-dicarboxylic acid ($R_f = 124$),[19] 4-hydroxypyridine-2,6-dicarboxylic acid ($R_f = 35$)[19] and Quadrol ($R_f = 23$).[11] In the case of use of EDTA, L-tartrate and DL-tartrate the values of $R_f$ are lower and do not exceed 18.[11] Our experiments show that rather high surface roughness values ($R_f = 25$) are obtained for copper deposition using saccharose as the Cu(II) ligand.

Finally it is worth noting that copper recovery from used electroless copper plating solutions containing saccharose as the Cu(II) ligand is much less complicated than for solutions using conventional ligands such as EDTA, tartrates or Quadrol, since the Cu(II) complexes with saccharose can be decomposed by simply lowering the solution pH to values less than 9 or 10. Copper(II) then precipitate in form of insoluble $Cu(OH)_2$. The remaining saccharose is environmentally benign, that is, it does not form complexes with heavy metals under natural conditions and it is easily biodegraded.

## 3. Conclusions

This study has shown the possibility of using saccharose as Cu(II) ligand in electroless copper plating systems. The autocatalytic reduction of Cu(II) by formaldehyde from solutions containing saccharose as the ligand begins at pH above 12, accelerates with a further increase in pH, reaches a maximum value at pH 12.75, then slows at higher pH values. The process of electroless copper deposition from saccharose-containing solutions occurs at relatively negative open-circuit potentials (−600 to −750 mV). Overpotential values are also exceptionally negative (ca. −520 to −570 mV).

Correlation among copper plating rates, overpotential, surface roughness values of the copper deposits formed and the concomitant anodic oxidation of formaldehyde have been established.

## 4. Experimental

### 4.1. Chemicals and solutions

Analytical grade reagents were used, and the formaldehyde source was formalin (37% HCHO) solution. Formaldehyde concentration in the stock solution was determined iodometrically. Measurements of pH were achieved using a Mettler Toledo MP 220 pH-metre and a Mettler Toledo InLab 410 glass electrode.

### 4.2. Copper surface formation

The substrate was a smooth Pt sheet (1 × 1 cm) electroplated with Cu for 20 min from acid copper solution ($1.0\ M\ CuSO_4 + 0.5\ M\ H_2SO_4$) at $1.5\ A\,dm^{-2}$. Before the electroless plating, the electroplated substrate was activated for 30 s in acid $PdCl_2$ solution ($1\ g\,L^{-1}$). The main electroless copper plating experiments were carried out for 60 min at 20 °C in 50 mL of the solution containing (M): $CuSO_4{\cdot}5H_2O$ −0.05; saccharose −0.1; formaldehyde −0.15; NaOH—up to pH needed. The amount of copper deposited was determined by mass difference. All measurements were repeated at least three times and mean value calculated.

### 4.3. Determination of the real surface area of the Cu coatings obtained

The copper surface determination method is based on the underpotential deposition of the thallium monolayer on the Cu electrode surface and is described elsewhere.[10,11,20] Briefly, the procedure was as follows. The measurements were carried out at 25 °C in 1 M $Na_2SO_4$ solution containing 1 mM $TlNO_3$. Before the measurements, copper oxides were removed from the surface: the working Cu electrode was kept at −0.80 V 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 from −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 (in nano-scale dimensions) of the Cu electrode ($S_R$, $cm^2$) was calculated using the Tl monolayer capacity $Q_{Tl}$ (the quantity of electricity necessary to form a monolayer on 1 $cm^2$ of electrode) equal in this case to $112\ \mu C\,cm^{-2}$:[20]

$$S_R = Q/Q_{Tl} \quad (4)$$

The surface nano-scale roughness factor $R_f$ is calculated as a ratio of real and geometric surface areas:

$$R_f = S_R/S_G \quad (5)$$

### 4.4. Voltammetric measurements

Voltammetric curves were obtained by standard electrochemical equipment (potentiostat PI-50, sweep generator PR-8, xy-recorder H–307, thermostatted electrochemical cell JES-1 (Belarus) and thermostat UH-4 (Germany). The solutions were dearated by Ar. The auxiliary electrode was Pt foil, and the reference electrode was Ag/AgCl with a saturated KCl solution. Voltammograms were recorded at 20 °C in 0.1 M $Na_2SO_4$ supporting electrolyte; the Cu electrode was potentiostated at −1.0 V and then the curve was recorded in the range from −1.0 to +0.3 V at potential scanning rate $5\ mV\,s^{-1}$. All potentials are presented in reference to SHE.

## Acknowledgement

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## References

1. Mallory, G. O.; Hajdu, J. B. *Electroless Plating: Fundamentals and Applications*; American Electroplaters and Surface Finishers Society: Orlando, 1990.
2. Vaškelis, A. In *Coatings Technology Handbook*; Satas, D., Tracton, A. A., Eds.; Marcel Dekker: New York, 2001; pp 213–225.
3. Norkus, E.; Vaškelis, A.; Jačiauskienė, J.; Vaičiūnienė, J.; Gaidamauskas, E.; Macalady, D. L. *J. Appl. Electrochem.* **2005**, *35*, 41–47.
4. Norkus, E.; Vaičiūnienė, J.; Vuorinen, T.; Gaidamauskas, E.; Reklaitis, J.; Jääskeläinen, A.-S.; Crans, D. C. *Carbohydr. Res.* **2004**, *339*, 599–605.
5. Norkus, E.; Vaškelis, A.; Vaitkus, R.; Reklaitis, J. *J. Inorg. Biochem.* **1995**, *60*, 299–302.
6. Norkus, E.; Vaškelis, A.; Reklaitis, J. *Koord. Khim.* **1988**, *14*, 325–327.
7. Norkus, E.; Pauliukaitė, R.; Vaškelis, A.; Butkus, E.; Jusys, Z.; Krenevičienė, M. *J. Chem. Res.(S)* **1998**, *N6*, 320–321.
8. Norkus, E.; Pauliukaitė, R. *J. Solution Chem.* **2001**, *30*, 55–66.
9. Vaškelis, A.; Norkus, E.; Juśkėnas, R.; Matulionis, E.; Stalnionis, G. *Galvanotechnik* **1995**, *86*, 2114–2123.
10. Norkus, E.; Vaškelis, A.; Stalnionienė, I. *J. Solid State Electrochem.* **2000**, *4*, 337–341.
11. Vaškelis, A.; Norkus, E.; Stalnionienė, I.; Stalnionis, G. *Electrochim. Acta* **2004**, *49*, 1613–1621.
12. Vaškelis, A.; Jačiauskienė, J. *Elektrokhimiya* **1981**, *17*, 1816–1821.
13. Wiese, H.; Weil, K. G. *Ber. Bunsen. Phys. Chem.* **1987**, *91*, 619–626.
14. Jusys, Z.; Stalnionis, G.; Juzeliūnas, E.; Vaškelis, A. *Electrochim. Acta* **1998**, *43*, 301–308.
15. Norkus, E.; Vaškelis, A.; Stalnionienė, I. *Galvanotechnik* **2004**, *95*, 2646–2655.
16. Dong, S.; Xu, Y.; Cheng, G. *Electrochim. Acta* **1992**, *37*, 17–22.
17. Jusys, Z. *J. Electroanal. Chem.* **1994**, *375*, 257–262.
18. Jusys, Z.; Vaškelis, A. *Electrochim. Acta* **1997**, *42*, 449–454.
19. Norkus, E.; Vaškelis, A.; Jačiauskienė, J.; Stalnionienė, I.; Stalnionis, G. *Electrochim. Acta* **2006**, *51*, 3495–3499.
20. Ramanauskas, R.; Stulgys, D. *Chemija (Vilnius)* **1990**, *N1*, 64–74.