VILNIUS UNIVERSITY
CENTER FOR PHYSICAL
SCIENCES AND TECHNOLOGY

KĘSTUTIS PRUŠINSKAS

INVESTIGATION OF THE AUTOCATALYTIC Cu(II) REDUCTION PROCESSES IN THE SYSTEMS WITH NATURAL POLYHYDROXYLIC COMPOUNDS AS LIGANDS

Summary of Doctoral Dissertation
Physical Sciences, Chemistry (03P)

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VILNIAUS UNIVERSITETAS
FIZINIŲ IR TECHNOLOGIJOS MOKSLŲ CENTRAS

KĘSTUTIS PRUŠINSKAS

AUTOKATALIZINIŲ Cu(II) REDUKCIJOS PROCESŲ TYRIMAS CHEMINIO VARIAVIMO SISTEMOSE LIGANDAIS NAUDOJANT GAMTINIUS POLIHIDROKSILIUS JUNGINIUS

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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.). The electroless deposition method uses a catalytic redox reaction between metal ions and dissolved reduction agent, and the main advantages of this technique are a possibility to plate non-conductive surfaces and to obtain metal coatings of the uniform thickness all over the object plated.

The overall process of alkaline formaldehyde-containing electroless copper deposition is described by following equation:

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

In general, electroless metal deposition processes are recognized now to be electrochemical by nature and 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 is consisting of anodic formaldehyde oxidation and cathodic Cu(II) reduction occurring simultaneously on the same copper surface; the electrons appeared 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 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 do not react with formaldehyde, do not 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.

The aim of the study presented herein was to investigate the electroless copper deposition process in solutions containing saccharose and glycerol as Cu(II) ligands.

Ultrasound (US) provides a large amount of energy for chemical reactions which taking place in the liquid phase. This is the result of an ultrasound induced physical phenomenon known as cavitation. Fluid flow formed and directed into the solid phase during implosion of cavities near surface. The flow speed can reach 400 km/h. Surfaces exposed to an enormous force and surface impacts leads a formation of active reactions points after bubble implosion. Organic compounds and water molecules exposed to ultrasound can be divided into radicals resulting formation of new forms, also unusual molecular clusters can be created, homogeneous catalysis can be initiated. Since data on effects of ultrasonic radiation on parameters of electroless copper deposition are very limited and sometimes rather contradictory, the aim of the study presented herein was to clarify general effects of ultrasound on the process of electroless copper deposition.

The aim of the work is to investigate the electroless copper plating processes in the systems using natural polyhydroxylic ligands – saccharose and glycerol – as Cu(II) ligands as well as to determine the impact of ultrasound different copper plating systems of different types.

Main tasks:

1. To calculate and to analyze formation and distribution of the copper(II) among complexes with polyhydroxylic compounds – saccharose and glycerol – in the alkaline medium.
2. To investigate the influence of solution pH on electroless copper deposition process for the systems with formaldehyde as reducing agent.
3. To measure the roughness of copper surfaces electrolessly deposited from the systems with ligands saccharose and glycerol.
4. To perform studies of formaldehyde anodic oxidation the studies on electrolessly deposited copper coatings.
5. To determine the influence of ultrasonic irradiation on the processes electroless copper plating systems.

Novelty and actuality of the work

With the development of modern industry and technology, the growth in consumption of environmental resources rises heavily, while there is also the problem of various wastes. In order to reduce the negative environmental impact, industry is looking for the possibilities to use renewable sources of energy and materials, also looking for technologies which reduces the harmful environmental impact of products, it is searching for products that would make it easier to recycle. This work investigates polyhydroxylic alcohols – glycerol and saccharose – as an alternative ligand for electroless copper plating systems using formaldehyde as reducing agent. Natural polyhydroxylic alcohols are environmentally friendly, easily bio-degradable materials, but have not been studied enough for suitability for electroless copper plating systems. In order to increase of the efficiency, the electroless copper plating was investigated in ultrasonic environment, to observe how ultrasound impacts the electroless copper plating rate and properties of the coatings obtained.

2. EXPERIMENTAL

2.1. Chemicals and solutions

The solutions were prepared from "Fluka" analytical grade reagents. For preparation of solutions three times distilled water was used. Measurements of pH were achieved using a EV-74 pH-meter and a ESL 63-07 glass electrode.

2.2. Formation of copper surface elektrode

The substrate for experiments was a smooth Pt sheet (1×1 cm) electroplated with Cu for 20 min from acid copper solution (1.0 mol l^{-1} $CuSO_4$ + 0.5 mol l^{-1} 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 (saccharose) and 30 min (glycerol) at 20 °C in 50 ml of the solution containing (mol l^{-1}): $CuSO_4 \cdot 5H_2O$ – 0.05; formaldehyde – 0.15; saccharose – 0.10 or glycerol – 0.25, 0.50, 1.00; 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. The electroless copper deposition in the environment of ultrasonic irradiation was carried out in the Elma D-78224 ultrasonic bath (Germany), using ultrasound with frequencies of 35 kHz and 130 kHz.

2.3. Determination of the real surface area of the Cu coatings obtained

The determination of copper surface is based on the method of underpotential deposition of the thallium monolayer on the Cu electrode surface. The measurements were carried out at 25 °C in 1 mol l^{-1} Na_2SO_4 solution containing 1 m mol l^{-1} $TlNO_3$. 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 μC cm^{-2} :

$$S_R = Q/Q_{\mathrm{Tl}} \qquad (2)$$

The surface nano-scale roughness factor R_{f} is calculated as a ratio of real and geometric surface areas:

$$R_{\mathrm{f}} = S_R / S_G \qquad (3)$$

2.4. 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 and thermostat Julabo ED-F12). 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 curve was recorded in the range from –1.0 to +0.5 V at potential scanning rate 5 mV s^{-1}. All potentials are presented in reference to SHE.

3. RESULTS AND DISCUSSION

3.1. Equilibria in alkaline copper(II)–saccharose solutions

Data on the interactions of saccharose (Sa) with Cu(II) ions in alkaline medium were published in the late 20th century. 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 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)-saccharose-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). The values of stability constants of Cu(II)-saccharose complexes lead to a prediction that at the Cu(II) concentration (0.05 mol l^{-1}) 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 mol l^{-1} Cu(II) sufficiently to prevent $Cu(OH)_2$ precipitation at pH values > 12. That is, calculated pCu values are higher than those necessary to prevent precipitation of copper(II) hydroxide, and $Cu(OH)_2(s)$ should not form. 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. 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. 1). 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 $CuSa_2(OH)_2^{4-}$ complex, which clearly predominate at higher pH values.

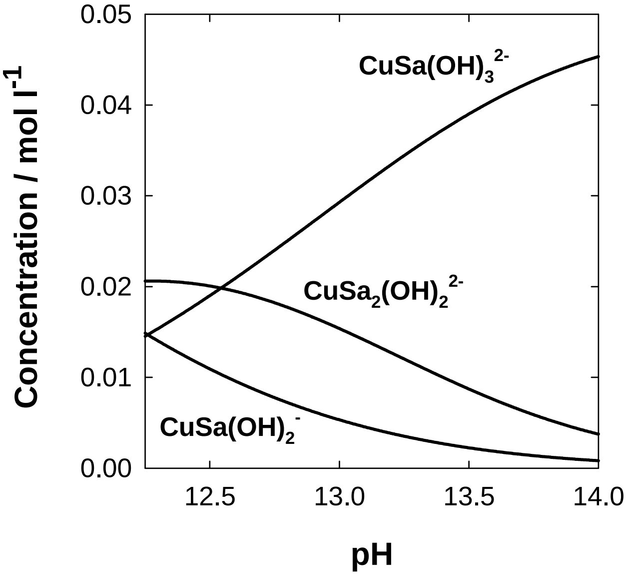

Figure 1. Distribution of Cu(II) among the complexes in solution containing (mol l^{-1}): $[Cu(II)]_0 = 0.05$; $[Sa]_0 = 0.10$.

3.2. Electroless copper deposition from solutions containing saccharose as Cu(II) 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 12.25 (Fig. 2a). The plating rate near the lower pH limit 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. The thickness of the compact copper coatings obtained under optimal operating conditions in 1 h reaches ca. 2 μm (Fig. 2a). The plating solutions are stable and no signs of Cu(II) reduction in the bulk solution were observed.

The electroless copper deposition process also can be characterized by the overpotential of copper electrode overpotential. In our system, the overpotential (ΔE) represents the difference between the measured mixed potential of the copper electrode (E_{mix}) and the equilibrium potential of a Cu^{2+}/Cu 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.

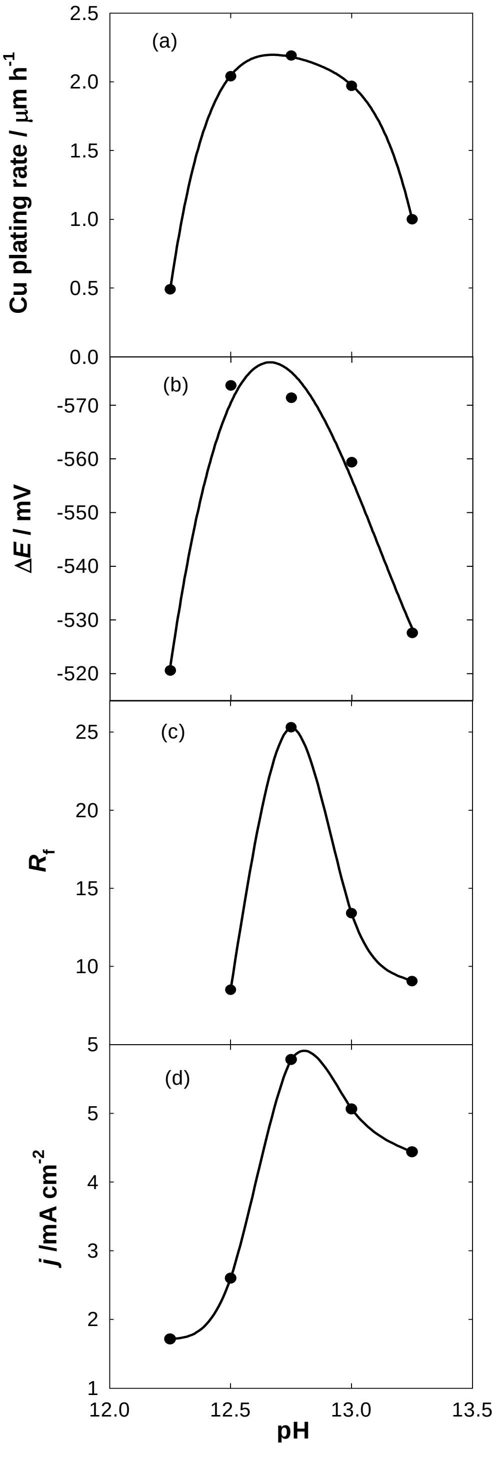

Figure 2. Dependence of copper plating rate (a), overpotential of the copper electrode (b), copper surface roughness factor (c) and HCHO anodic oxidation current peak density (d) on pH. Solution composition (mol l^{-1}): (a), (b), (c) – $[Cu(II)]_0 = 0.05$; $[Sa]_0 = 0.10$; $[HCHO]_0 = 0.15$ and (d) – given in Fig. 3f–j.

Fig. 2b 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 Figs. 2a and 2b, 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.

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. 2c). 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. Figs. 2a–c). These correlations correspond to the well-known general trends in the effects of overpotential on metal nucleation during copper electrodeposition, i. e. the formation of smoother metal deposits at lower deposition rates.

3.3. 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.

In the first series of experiments we tried to detect an effect of saccharose on the electrochemical behavior of copper electrodes in solutions with a variety of pH values (Figs. 3a–e). Consider first the data obtained with the electroplated electrode (dashed lines). No effects were observed at pH 12.25-12.5 (Figs. 3a, b). With further pH elevation a peak of anodic current appears at potential of about –50 mV (Figs. 3c, 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. 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.

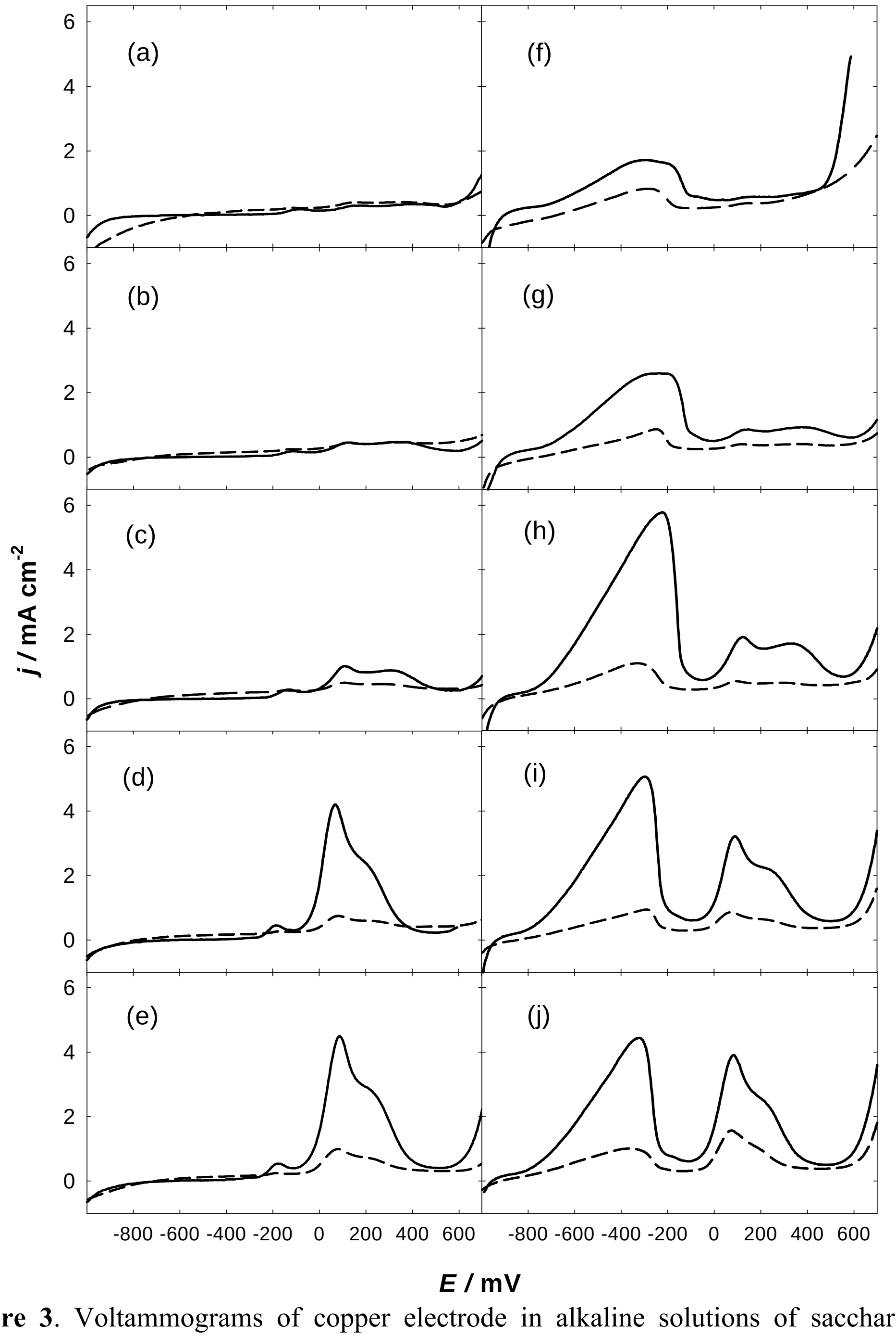

Figure 3. Voltammograms of copper electrode in alkaline solutions of saccharose (a-e) and saccharose and formaldehyde (f-j). Scanning rate 5 mV s^{-1}, solution composition (mol l^{-1}): [Sa]$_0$ = 0.10; [Na_2SO_4]$_0$ = 0.10; [HCHO]$_0$ = 0.15 (f-j). Solution pH values: a, f – 12.25; b, g – 12.5; c, 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).

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 (Figs. 3b–d; solid lines). These augmentations (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. 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 (Figs. 3b–d; solid lines). According to the literature data and our electrochemical experiments in the absence of saccharose (not presented here), this oxidation 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), 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 less developed surfaces (Figs. 3f–j). An anodic current is observed in the potential range ca. –800 to ca. –100 mV; this current is known to be a result of formaldehyde anodic oxidation. 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, e. g. saccharose, due to the formation of more soluble copper(II) species.

As can be seen from the voltammograms (Figs. 3b–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 correlation was observed when analyzing the pH–dependencies: the formaldehyde anodic oxidation rate (Fig. 2d) depends on solution pH in the same manner as the electroless copper plating rate, the copper deposition overpotential and the surface roughness factor (cf. Figs. 2a–d). The highest observed values of the electroless plating rate, overpotential and surface roughness correspond to the highest formaldehyde oxidation rate (pH 12.75).

3.4. Equilibria in alkaline copper(II)–glycerol solutions

The data on use of glycerol (1,2,3-propanetriol) as copper(II) ligand in solutions for copper deposition are not numerous. Glycerol (Gl) contains three hydroxyl groups which theoretically might be deprotonated, but no data was found about deprotonation of more than one OH-group of glycerol. For our further calculations of equilibria in alkaline copper(II)-glycerol solutions we chose the pK_{a1} value equal to 13.99, since the same value was used when calculating stability constants of copper(II) complexes with glycerol. Generally, formation of soluble Cu(II)–glycerol compounds is observed at pH values higher than 10.6. This pH limit depends also on Cu(II) concentration and the degree of excess of glycerol. Two mononuclear copper(II)-hydroxy complexes were documented under conditions of glycerol excess: $CuGl(OH)_3^{2-}$ ($\log\beta$ = 20.2) and $CuGl_2(OH)_2^{2-}$ ($\log\beta$ = 21.1). The data on glycerol deprotonation and composition and stability of copper(II)-glycerol complexes lead to a prediction that at the Cu(II) concentration (0.05 M) commonly used in electroless copper plating solutions, glycerol should be able to adequately chelate Cu(II) ions under conditions of glycerol excess. Calculations indicate that glycerol is able to chelate 0.05 mol l^{-1} Cu(II) sufficiently to prevent $Cu(OH)_2$ precipitation at pH values above 12.0, depending on concentration of glycerol. 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. The overall shape of the dependence of Cu(II) distribution among the complexes on pH and glycerol concentration is shown in Fig. 4. According to the calculated data it is seen that the concentration of glycerol has main influence on distribution of Cu(II) among complexes, whereas the influence of pH is less expressed and is evidenced only at higher pH values (pH > 13). The $CuGl(OH)_3^{2-}$ complex predominates in the region of lower glycerol concentrations (up to 0.2 mol l^{-1}). Further increase in glycerol concentration (> 0.2 mol l^{-1}) leads to prevailing of the $CuGl_2(OH)_2^{2-}$ complex (Fig. 4).

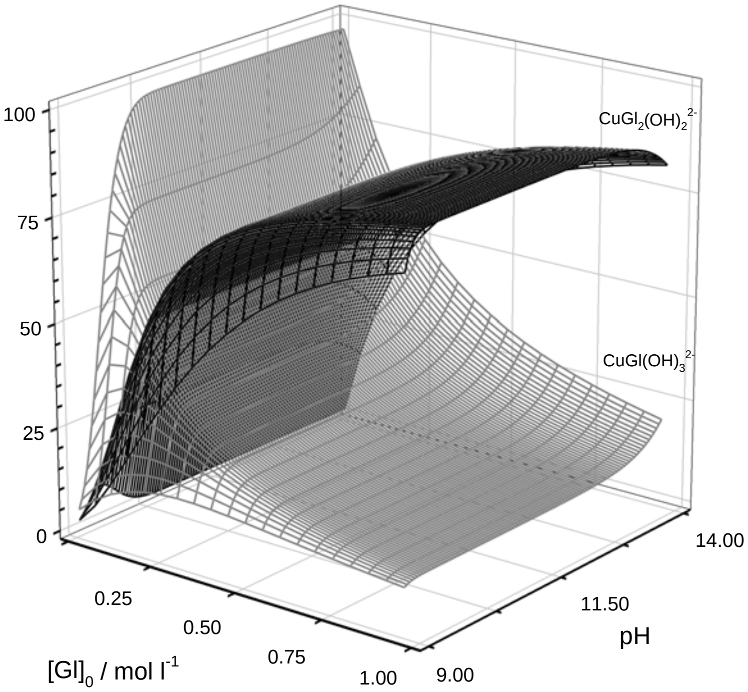

Figure 4. Dependence of Cu(II) distribution among the complexes with glycerol on glycerol concentration and pH. $[Cu(II)]_0 = 0.05$ mol l^{-1}.

3.5. Electroless copper deposition from solutions containing glycerol as Cu(II) ion ligand

In solutions with an excess of glycerol, autocatalytic reduction of Cu(II) by formaldehyde starts at pH > 13.00 (Fig. 5, Table 1). The copper plating rate in range from 1.8 μm h^{-1} (pH 13.00, $[Gl]_0 = 0.50$ mol l^{-1}) to 3.8 μm h^{-1} (pH 13.00, $[Gl]_0 = 0.25$ mol l^{-1}). The plating solutions are stable and no signs of Cu(II) reduction in the bulk solution were observed during plating.

In our system with glycerol as Cu(II) ligand, the ΔE values obtained are represented in (Fig. 5, Table 1). Copper coatings deposited by the electroless technique from alkaline solutions with the ligand glycerol have less developed surfaces and R_f values vary not widely, from ca. 2.6 up to 4.3 (Fig. 5, Table 1). If one observes the pH-dependence in the R_f of the copper deposits, the interrelationships among R_f and the overpotentials of copper electrodes are evident. (Fig. 5). These correlations correspond to the well-known general trends in the effects of overpotential on metal nucleation during copper electrodeposition, i. e. the formation of smoother metal deposits at lower deposition rates.

Table 1. Characteristics of the process of electroless copper deposition from glycerol-containing solutions at 20 ºC. Composition of electroless copper deposition solutions (mol l^{-1}): $[Cu(II)]_0 = 0.05$, $[HCHO]_0 = 0.15$; $[Gl]_0$ and pH – variable.

$[Gl]_0$ (mol l^{-1})	pH	v, (µm h^{-1})	R_f	Most negative value of E_{mix} (mV)	E_{mix} (mV) after 30 min	E_{equil} (mV)	ΔE (mV)
0.25	13.00	3.8	3.4	-548	-249	-153	-96
0.25	13.25	2.7	3.0	-596	-254	-181	-73
0.25	13.50	3.2	2.7	-607	-275	-208	-67
0.25	13.75	3.0	2.8	-621	-289	-234	-55
0.50	13.00	1.8	3.2	-553	-278	-172	-106
0.50	13.25	2.0	2.6	-598	-295	-200	-95
0.50	13.50	3.4	3.0	-615	-302	-226	-76
0.50	13.75	2.2	2.3	-677	-320	-251	-68
1.00	12.75	3.5	4.6	-552	-293	-98	-195
1.00	13.00	2.7	4.3	-528	-292	-127	-165
1.00	13.25	2.5	4.2	-590	-336	-155	-181
1.00	13.50	1.5	3.5	-622	-365	-182	-183
1.00	13.75	1.7	3.1	-600	-352	-209	-143

3.6. Voltammograms of copper electrode in alkaline solutions of glycerol and formaldehyde

The peaks obtained in range -100 – 400 mV 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 (Fig. 6). The rise in peak current density values with pH elevation is explained by an increase in the complexing ability of glycerol 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 glycerol. 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 metallic Cu, anodic processes proceedings on copper electrodes in alkaline solutions containing formaldehyde and glycerol are of interest. An anodic current is observed in the potential range ca. –800 to ca. –200 mV; this current is known to be a result of formaldehyde anodic oxidation (Fig. 6).

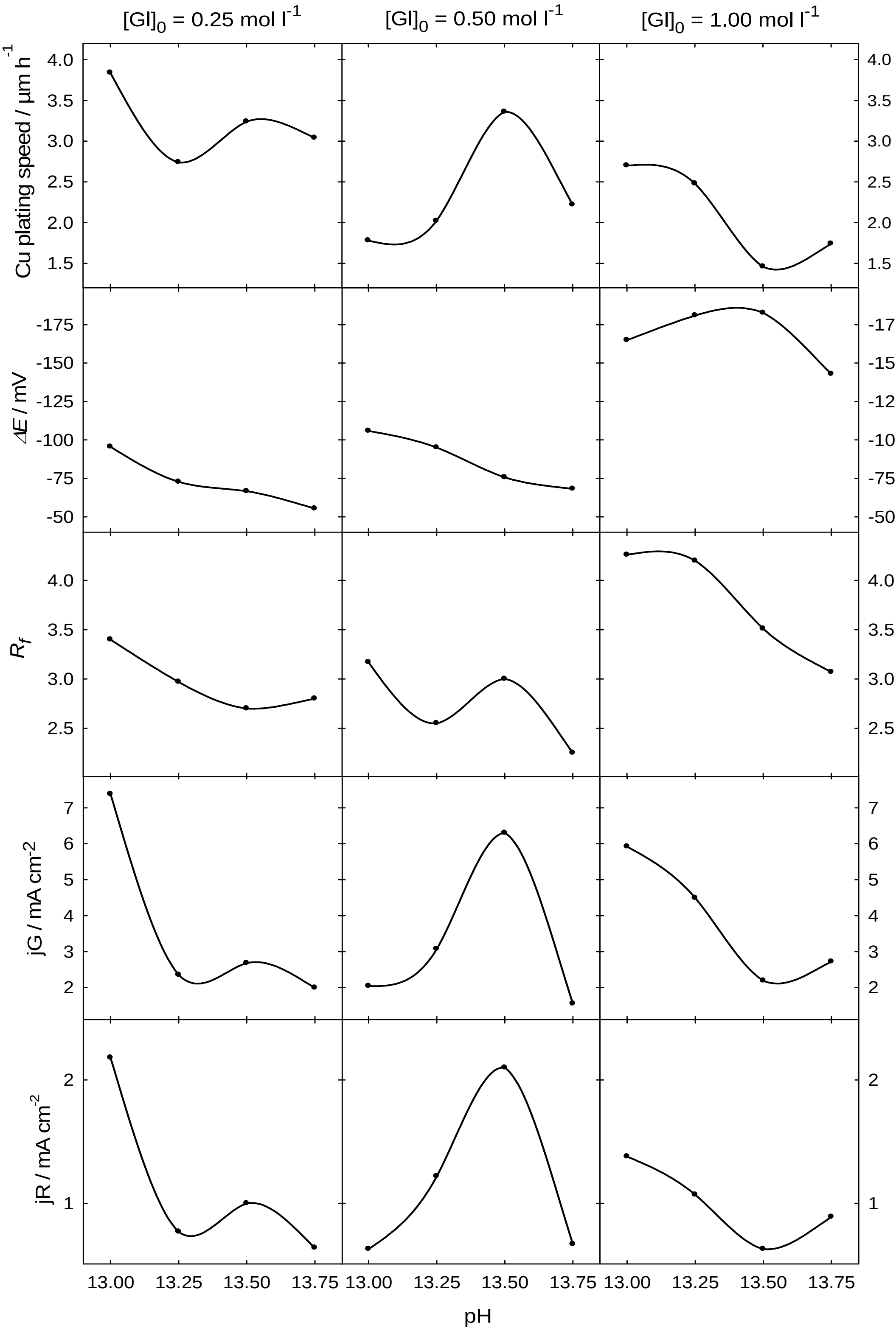

Figure 5. Dependence of copper plating speed, overpotential *ΔE* of the copper electrode, copper surface roughness factor R_f and HCHO anodic oxidation current peak density (jG according geometrical size of electrode, jR according real surface of coating obtained) on pH and concentration of glycerol Solution composition (mol l^{-1}): $[Cu(II)]_0 = 0.05$; $[HCHO]_0 = 0.15$.

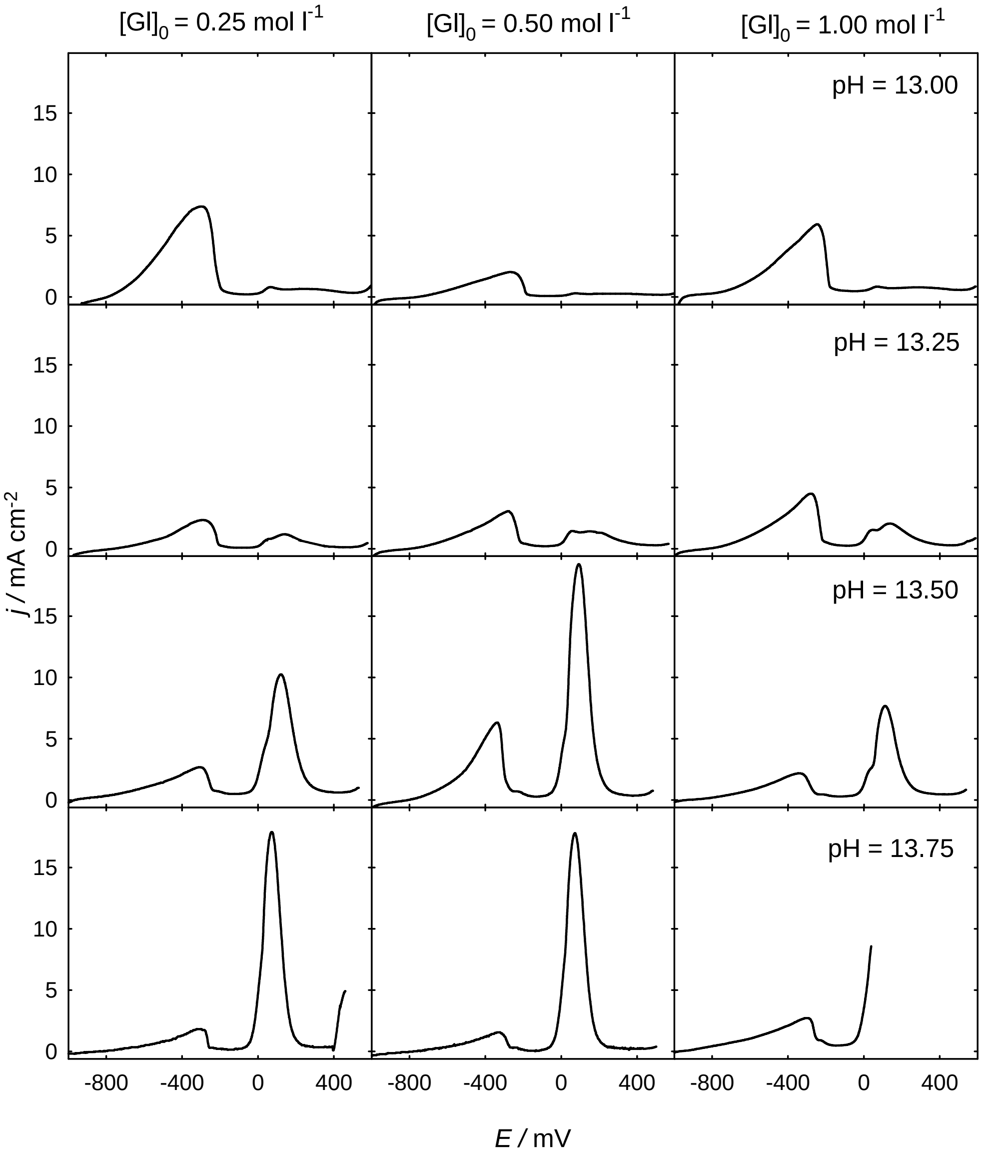

Figure 6. Voltammograms of copper electrode in alkaline solutions of formaldehyde and glycerol. Solution composition (mol l^{-1}): $[Sa]_0 = 0.10$; $[Na_2SO_4]_0 = 0.10$; $[HCHO]_0 = 0.15$.

It can be noted that, like in system with ligand glycerol, the changes in the copper electrode surface state also influence the process of formaldehyde anodic oxidation: the anodic current drops abruptly at potentials ca. –200 mV as a result of copper surface oxidation to form initially the monolayer of Cu(I) derivatives 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, e. g. glycerol, due to the formation of soluble copper(II) species.

As can be seen from the voltammograms (Fig. 6), 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 glycerol concentration. A correlation was observed when analyzing the pH–dependencies: the formaldehyde anodic oxidation rate (Fig. 5) depends on solution pH in the same manner as the electroless copper plating rate. The higher observed values of the electroless plating rate correspond to the higher formaldehyde oxidation rates. Current density of formaldehyde anodic oxidation on electrolessly coated copper electrode (using glycerol as ligand) range from 1.5 to 7.4 mA cm^{-2} (Table 1) depending on the pH of the solution and glycerol concentrations.

3.7. Comparison of saccharose and glycerol as Cu(II) ligands for electroless copper plating systems with systems operating with other Cu(II) ligands

For comparative purposes, we have selected literature data on electroless Cu plating rates obtained under similar experimental conditions (20ºC temperature, concentrations copper(II) salt and formaldehyde equal to 0.05 mol l^{-1} and 0.15 mol l^{-1}, respectively) but using different ligands.

The rate of copper deposition in saccharose-containing electroless copper solutions under optimal operating conditions reaches about 2 μm h^{-1} and 3.8 μm h^{-1} in glycerol-containing solutions. 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. The almost two times higher plating rates (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. 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). 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. Thus, saccharose- or glycerol-containing electroless copper plating solutions give rates of copper deposition that are comparable to other ligands.

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 on real catalytic surface area in great extent, 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 ($R_f = 124$), 4-hydroxypyridine-2,6-dicarboxylic acid ($R_f = 35$) and Quadrol ($R_f = 23$). In the case of use of EDTA, L-tartrate and DL-tartrate the values of R_f are lower and do not exceed 18. Our experiments show that rather high surface roughness values ($R_f = 25$) are obtained during electroless copper deposition using saccharose as Cu(II) ligand, whereas low surface roughness (2.6 – 4.3) obtained from solutions with ligand glycerol.

Finally it is worth noting that copper recovery from the used electroless copper plating solutions containing saccharose and glycerol as the Cu(II) ligands is much less complicated than that form solutions using conventional ligands such as EDTA, tartrates or Quadrol, since the Cu(II) complexes with saccharose or glycerol 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 or glycerol are environmentally benign, i. e. it do not form complexes with heavy metals under natural conditions and are easily biodegraded.

3.8. Electroless copper plating under conditions of ultrasonic irradiation

Ultrasound (US) produces specific conditions for reactions in electroless copper plating systems. Electroless deposition of copper using the systems with different ligands (EDTA, saccharose, pentaethylenehexamine) and different reducing agents (formaldehyde, Co(II)/Co(III) redox couple) proceeds differently under ultrasonic irradiation. Depending on the plating system, the plating rate varies from modest decrease (or stopping of the process) to five or more times higher plating rate, comparing with conditions without ultrasound. The dependencies of the surface roughness of the copper coatings obtained on various factors (ultrasonic irradiation, pH, ligands etc.) were investigated and discussed.

3.8.1. Electroless copper deposition using formaldehyde as reducing and EDTA as Cu(II) ligand under conditions of ultrasonic irradiation

The conventional electroless cooper plating system with ligand EDTA was selected for primary investigation of the effects of ultrasound. Since ultrasonic cavitation exhibits also the mixing effects, additionally experiments were carried out with the same solutions with and without ultrasonic irradiation, but in later case, using mixing by magnetic stirrer or agitation by argon bubbles. The results obtained are presented in Figs. 7 and 8.

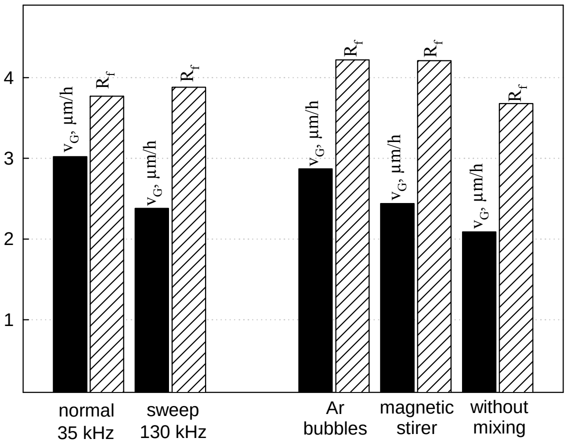

Figure 7. Dependence of characteristics of electroless copper plating on different solution agitation methods. Solution composition (mol l^{-1}): $[Cu(II)]_0 = 0.05$, $[EDTA]_0 = 0.055$, $[HCHO]_0 = 0.15$, pH 12.6; plating time 1 hour, 20 °C, ultrasonic bath power 100%

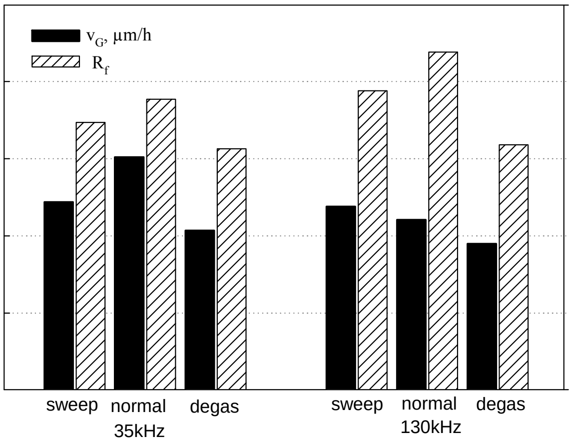

Figure 8. Dependence of characteristics of electroless copper plating on frequencies and modes of ultrasound. Solution composition (mol l^{-1}): $[Cu(II)]_0 = 0.05$, $[EDTA]_0 = 0.055$, $[HCHO]_0 = 0.15$, pH 12.6; plating time 1 hour, 20 °C, ultrasonic bath power 100%

Without additional agitation of solution, i. e. under conditions of natural convection, the rate of electroless copper deposition is the lowest and do not exceed ca. 2.1 µm/h (Fig. 7). The use of ultrasound or other agitation methods accelerate the plating rate to some extent. The acceleration of the electroless copper plating rate is observed in the following sequence: magnetic stirring < US (*sweep* mode, 130 kHz) < bubbling by Ar < US (*normal* mode, 35 kHz). The highest acceleration is observed using 35 kHz ultrasound and bubbling of Ar through the solution. In our opinion, both methods create the best conditions for removal from the surface to be plated of hydrogen formed during the autocatalytic reaction of electroless copper deposition using formaldehyde as reducing agent (2):

$$[\mathrm{CuEDTA(OH)}]^{3-} + 2\,\mathrm{HCHO} + 3\mathrm{OH}^- \overset{\mathrm{Cu}}{\rightarrow} \mathrm{Cu} + \mathrm{H}_2 + 2\mathrm{HCOO}^- + 2\mathrm{H}_2\mathrm{O} + \mathrm{EDTA}^{4-} \qquad (2)$$

Since the small hydrogen bubbles formed on the surface to be plated during the electroless copper deposition process block the part of the catalytic surface, their efficient removal determine higher rates of electroless copper deposition. As it is seen from Fig. 8, the deposition rate of electroless copper is higher under ultrasonic irradiation with lower frequency (35 kHz), i. e. with lower power, than under ultrasonic irradiation with higher frequency (130 kHz). Results obtained under conditions of different ultrasonic power are presented in Fig. 9. As can be seen from the results, the reduction of ultrasonic power up to ten times, results the decrease in the plating rate only by 10%. Meanwhile, the effect of the ultrasonic frequency can bee seen have a greater impact on the copper deposition rate. Different solution agitation methods have comparatively low influence on the R_f of coatings obtained – under the conditions of ultrasonic irradiation the values of R_f increase by ca. 2-3 %, whereas Ar bubbling and magnetic stirring enhances the surface development by 8-11 % comparing with the data obtained without mixing (Fig. 7).

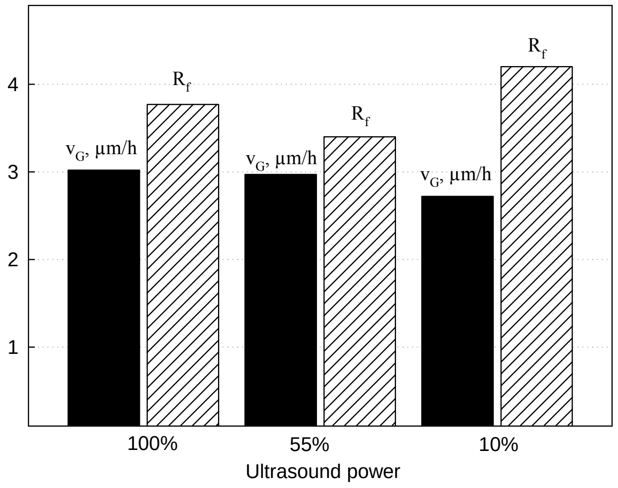

Figure 9. Dependence of characteristics of electroless copper plating on the ultrasonic power (35 kHz, normal). Solution composition (mol l^{-1}): $[\mathrm{Cu(II)}]_0 = 0.05$, $[\mathrm{EDTA}]_0 = 0.055$, $[\mathrm{HCHO}]_0 = 0.15$, pH 12.6; plating time 1 hour, 20 °C.

3.8.2. Electroless copper deposition using formaldehyde as reducing agent and saccharose as Cu(II) ligand under conditions of ultrasonic irradiation

Experiments using saccharose as ligand were carried out under conditions of exposure in ultrasonic irradiation as well as under normal conditions, i. e. without additional impact. The highest electroless copper deposition rates derived using ultrasonic irradiation were more than five times higher than that obtained under conditions without ultrasound (Fig. 10). Without additional impact ca. 2 μm thick copper deposits were obtained in one hour, whereas at ultrasound frequency of 35 kHz the plating rate reached 10.6 μm/h (pH = 12.75).

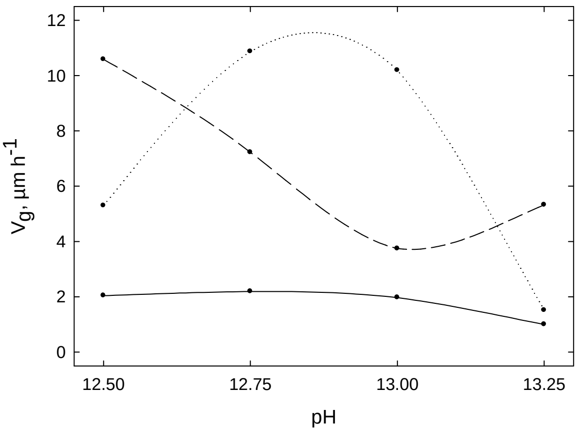

Figure 10. Dependence of electroless copper plating rate on solution pH. Solid line – without US, dashed – 130 kHz US, dotted – 35 kHz US, *sweep* mode. Solution composition (mol l^{-1}): [Cu(II)]$_0$ = 0.05, [Sa]$_0$ = 0.1, [HCHO]$_0$ = 0.15; plating time 1 hour, 20 °C

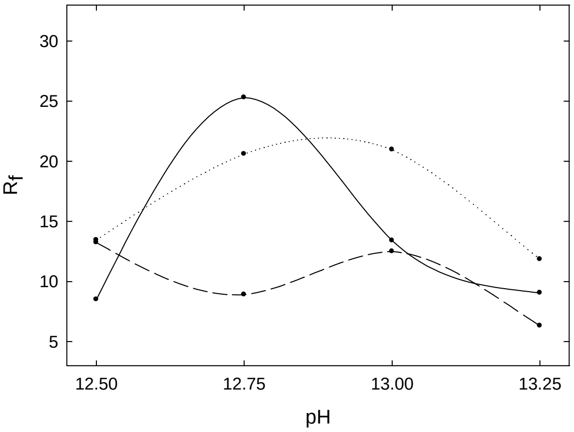

Figure 11. Dependence of surface roughness factor R_f on solution pH: solid line – without US, dashed – 130 kHz US, dotted –35 kHz US, *sweep* mode. Solution composition (mol l^{-1}): [Cu(II)]$_0$ = 0.05, [Sa]$_0$ = 0.1, [HCHO]$_0$ = 0.15; plating time 1 hour, 20 °C.

When using the ultrasonic irradiation the dependences of copper deposition rate on pH have extrema points, but the plating rate remains still higher than that without using of ultrasound (Fig. 10). According to the data obtained there is no linear relationship between the copper deposition rate and ultrasonic power. Higher deposition rates were obtained at lower power (35 kHz frequency), than at higher power (130 kHz frequency) of ultrasound. In our opinion, this indicates that the copper coating deposition rate is determined not only by US power, but also depends on the frequency of the ultrasound applied.

Surface roughness dependences on pH and US frequencies are represented in Fig. 11. At lowest pH limit (pH 12.5) and the highest pH limit (pH 13.25) investigated the roughness of the obtained copper coatings is very similar under conditions of ultrasonic irradiation as well as without using of US (Fig. 11), i. e. no considerable effects of US are observed. Substantial effect was obtained at pH 12.75 – the ultrasonic irradiation diminished the surface roughness factor by ca. 20-60 %. It can be also noted, that in all cases the surface roughness of copper coatings deposited from saccharose containing solutions is higher than that obtained using EDTA as Cu(II) ligand (cf. Fig. 7 and Fig. 8)

Worth to noting, that ultrasound affects the stability of electroless copper deposition solutions. After 45 minutes of electroless copper plating the signs of copper(II) reduction in the volume of solutions is observed, whereas the solutions remained stable more than one day in experiments without ultrasound.

3.8.3. Electroless copper deposition using Co(II) as reducing agent and pentaethylenehexamine as ligand

The influence of ultrasound on the parameters of electroless copper plating process has been studied also in the system of new type, where the reducing agent was a Co(III)/Co(II) redox couple, and pentaethylenehexamine (Penta) used as ligand for Cu(II), Co(II) and Co(III) ions. The reaction of Cu(II) reduction by Co(II) in acidic solutions of pentaethylenehexamine can be expressed as follows (3):

$$[\mathrm{CuPenta}]^{2+} + 2[\mathrm{CoPenta}]^{2+} + \mathrm{Penta} \xrightarrow{\mathrm{Cu}} \mathrm{Cu} + 2[\mathrm{Co(Penta)_2}]^{3+} \qquad (3)$$

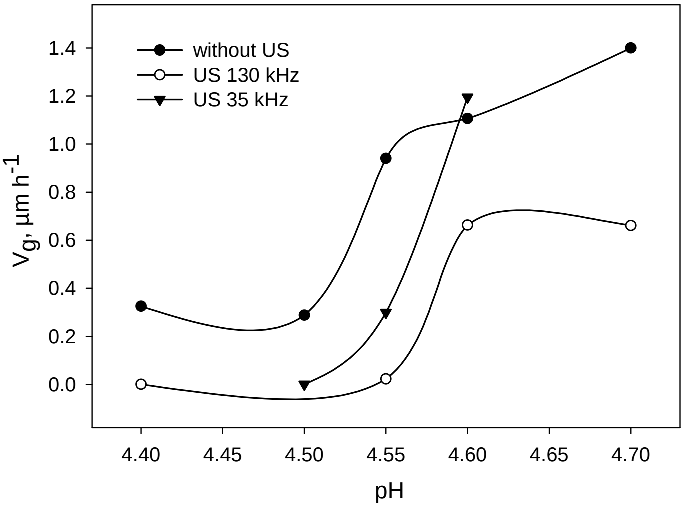

Figure 12. Dependence of electroless copper plating rate on solution pH. Solution composition (mol l^{-1}): $[\mathrm{Cu(II)}]_0 = 0.05$, $[\mathrm{Co(II)}]_0 = 0.15$, $[\mathrm{Penta}]_0 = 0.4$; plating time 1 hour, 20 ºC. *Sweep* mode of US.

As it is seen from Eq. (3), the reduction process occurs without formation of hydrogen, in opposite to the processes described above, where formaldehyde was used as reducing agent. Therefore the effects of ultrasound could be different for systems with hydrogen-containing reducing agents and systems of metal ions with different oxidation states as reducing agents with charge transfer. Generally, ultrasound retards (at lower pH's practically stops) the electroless copper plating process in the system with Co(II) as reducing agent (Fig. 12). This retardation is more expressed under conditions of ultrasonic irradiation with higher frequency (Fig. 12). The data obtained are in good agreement with earlier (this work) obtained results when using formaldehyde as reducing agent. In later case (Eq. (3)) no hydrogen bubbles are formed and therefore no acceleration effect is observed.

CONCLUSIONS

1. The calculations of copper(II)-saccharose and copper (II)-glycerol complex formation equilibria showed that saccharose and glycerol provides sufficient capability to form complexes and prevent formation of copperCu(II) hydroxide and can be used as ligands in alkaline electroless copper plating solutions.

2. The autocatalytic reduction of Cu(II) starts from the pH > 12 when the saccharose as Cu(II) ligand was used. Under optimum operating conditions the copper deposition rate can reach 2.2 μm h^{-1} (pH 12.75). The mixed potential of copper electrode has relatively negative values (-600 mV - 750 mV) and the calculated overpotential values (-520 mV - 570 mV) are exceptionally negative for systems with Cu(II) ligand saccharose. Received copper coating roughness factor reaches quite high values (R_f = 25).

3. The voltamperic measurements have shown, that the current density of formaldehyde anodic oxidation range from 1.7 to 5.8 mA cm^{-2} on electrolessly coated copper electrode (ligand saccharose), and the dependence of anodic current density on pH is directly correlated with copper plating rate and surface roughness factor.

4. The studies have shown that glycerol can be used as ligand for electroless copper plating systems. The autocatalytic Cu (II) reduction starts from the pH > 13. Under optimal conditions, the copper deposition rate can reach 3.8 μm h^{-1} . The mixed potential of Cu electrode has relatively positive values (-250 mV - 350 mV); the overpotential values are low (-55 - 180 mV). Roughness factors of copper coatings obtained in the systems with ligand glycerol are relatively low (2.3 to 4.3), in some cases close to the electrochemically deposited copper coatings.

5. The current density of formaldehyde anodic oxidation on electrolessly coated copper electrode (using glycerol as ligand) range from 1.5 to 7.4 mA cm^{-2} depending on pH of the solution and glycerol concentrations. It was found that the shape of dependences of current density of anodic formaldehyde oxidation on pH is similar to dependences of overpotential and surface roughness factor for electroless copper plating system with glycerol as Cu(II) ligand.

6. The ultrasonic irradiation effects differently electroless copper plating systems. UG changes copper plating rates – depending on the copper plating system and ultrasonic frequency – copper deposition rate could fall (system with reducer Co(II), ligand pentaethylenehexsaamine), may increase to 1.44 times (system with reducing agent formaldehyde, ligand EDTA) or may increase 2-5 times up to 10.9 μm h^{-1} (system with reducing agent formaldehyde, ligand saccharose), Usually the coatings formed in ultrasound environment are more compact, smoother.

7. The data obtained suggest, that in the case of electroless copper plating it is difficult to predict and explain apparently the effects and mechanisms of ultrasound actions, including impact of characteristics of ultrasonic irradiation. Therefore it remains an area for further research.

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2. E. Norkus, I. Stankevičienė, A. Jagminienė, K. Prušinskas. *"Cu(II) complex formation with pentaethylenehexamine: determination of stability constants by the ligand displacement method"* Chemija, **22**, N2 (2011) 131-137.
3. K. Prušinskas, E. Norkus, I. Stalnionienė, I. Stankevičienė, *Application of ultrasound for the systems of electroless copper plating: Influence of ultrasonic irradiation on plating rate and coatings surface*, Chemija (2012) submited.

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2. K. Prušinskas, E. Norkus, J. Jačiauskienė, I. Stalnionienė. *"Application of enviromentally friendly ligands for alkaline electroless plating systems: Electroless copper deposition using glycerol as Cu(II) ligand".* 9-th conference of Lithuanian chemists "Chemistry 2009" dedicated for 110th anniversary of academician Juozas Matulis, Vilnius (2009) 76.
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4. K. Prušinskas, E. Norkus, A. Vaškelis, J. Jačiauskienė, I. Stalnionienė and D. L. Macalady. "*Electroless copper plating using saccharose as copper(II) ligand*". Conference "Chemistry and Technology of Chemistry" dedicated for 100th anniversary of academician Jonas Janickis, Kaunas (2006) 96-99.

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1. E. Norkus, I. Stankevičienė, L. Tamašauskaitė-Tamašiūnaitė, K. Prušinskas. *Comparative study of electroless copper deposition using different cobalt(II)-amine complex compounds as reducing agents.* Chemija, **23** N1 (2012) 1
2. I.Stankevičienė, A.Jagminienė, E.Norkus, K.Prušinskas. *Cu(II) complex formation with pentaethylenehexamine – determination of stability constants using the ligand displacement method.* 10th International conference of Lithuanian chemists dedicated to the International Year of Chemistry 2011, (2011) 103, Vilnius.

Autokatalizinių Cu(II) redukcijos procesų tyrimas cheminio variavimo sistemose ligandais naudojant gamtinius polihidroksilius junginius

REZIUMĖ

Šiame darbe tiriami polihidroksiliai alkoholiai sacharozė bei glicerolis, kaip ligandų alternatyvos cheminio variavimo sistemoms su reduktoriumi formaldehidu. Tai yra ekologiškos, biologiškai lengvai suyrančios medžiagos, tačiau mažai arba visiškai netirtas jų tinkamumas cheminio variavimo sistemose. Šiame darbe atlikti šių medžiagų kompleksų pusiausvyros skaičiavimai, eksperimentai parodantys sacharozės bei glicerolio praktinį pritaikomumą cheminio variavimo sistemose, atlikti įvairūs matavimai, atspindintys sistemų efektyvumą ir tinkamumą. Ultragarso poveikio cheminėms sistemoms dėsningumai dar nėra vienareikšmiškai ištirti ir suprasti. Siekiant padaryti cheminį metalų nusodinimą efektyvesniu pastaruoju metu cheminio metalizavimo procesuose taip pat bandoma taikyti ultragarsą.

Atlikti tyrimai parodė, kad naudojant sacharozę ir glicerolį ligandais cheminio variavimo tirpaluose vario nusėdimo greitis optimaliomis sąlygomis siekia atitinkamai 2,2 ir 3,8 μm/h, o chemiškai nusodinto vario paviršiaus šiurkštumo faktoriai varijuoja 8,5-25,3 ir 2,6-4,3 ribose. Analizuojant gautus duomenis stebimos koreliacijos tarp vario nusėdimo greičio, viršįtampio, paviršiaus šiurkštumo faktoriaus, formaldehido anodinės oksidacijos srovių maksimumų priklausomybių nuo pH.

Ultragarso panaudojimas cheminio variavimo sistemose keičia vario nusėdimo greičius. Priklausomai nuo pasirinktos cheminio variavimo sistemos, ultragarso dažnio ar jo skleidimo būdo vario nusėdimo greitis sumažėja iki visiško proceso sustabdymo arba gali padidėti 2-5 kartus ir pasiekti dideles vertes (10,9 μm/h). Ultragarso aplinkoje dažniausiai susiformuoja kompaktiškesnės, lygesnės cheminiu būdu nusodinto vario dangos lyginant su sistemomis be ultragarso.

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