

Comparative study of electroless copper deposition using different cobalt(II)-amine complex compounds as reducing agents

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For the first time, tetraethylenepentamine (Tetraen) and triethylenetetramine (Trien) were applied as ligands in electroless copper plating systems using Co(II)-amine complexes as reducing agents. The highest copper deposition rate (in 2 minutes) determined for tetraethylenepentamine (Tetraen) system was about $3.3 \mu\text{g cm}^{-2}$, whereas this rate for triethylenetetramine (Trien) system was lower being $2 \mu\text{g cm}^{-2}$. The processes of the dissolution of copper substrate taking place in the solutions of the mentioned amines at certain pH values are discussed. The amines under investigation were proposed as stabilizing agents or plating rate adjusters in electroless copper plating solutions containing other amines as ligands, e. g. ethylenediamine, propylenediamine or diethylenetriamine.

Key words: electroless copper deposition, cobalt(II) complexes, aliphatic amines

INTRODUCTION

The Co(III) / Co(II) redox couple, depending on the presence of ligands and values of solutions pH, provides a rather wide variety of its use as a strong oxidizing agent as well as a strong reducing agent. In the absence of ligands, the standard redox potential of hydrated cobalt ions is 1.86 V, showing very strong oxidizing properties (e. g. hydrated Co(III) ions can oxidize water); whereas in the presence of different ligands, the redox potential of the Co(III) / Co(II) couple shifts to the site of more negative values. This shift is noticeable for the systems containing aliphatic amines as Co(III) and Co(II) ligands: the redox potential can gather even negative values, Co(II) complexes being strong reducing agents able to reduce Cu(II) to the metallic state.

Primarily, ethylenediamine (En) was found to be a proper ligand for Co(II) and Co(III) redox couple, cobalt(II) complex with ethylenediamine being an effective reducing agent in the autocatalytic reduction of copper(II) to metal (electroless copper plating) [1]. The use of Co(III)–Co(II)–Cu(II)-ethylenediamine system for electroless copper deposition was

investigated in detail from both kinetic and thermodynamic standpoints [2–6].

The next amine with a longer $-\text{CH}_2-$ chain, namely propylenediamine, was also proposed as a ligand for Co(II) containing electroless copper deposition systems. It is worth to note that Co(II) complexes with the mentioned ligand were documented as sufficiently strong reducing agents allowing electroless copper deposition at room temperature as well as at elevated temperatures [7]. Later, the higher aliphatic amines were applied as ligands for Co(II) containing systems for electroless copper deposition. Promising results have been obtained using diethylenetriamine (Dien) $\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{NH}-\text{CH}_2-\text{CH}_2-\text{NH}_2$ [8, 9].

Finally, the results on investigation of Cu–Cu(II)–Co(II)–Co(III)-pentaethylenhexamine have been documented recently [10].

This work is aimed at an initial kinetic study of electroless copper deposition using Cu–Cu(II)–Co(II)–Co(III)-amine systems where amines were triethylenetetramine (Trien) and tetraethylenepentamine (Tetraen), that have never been used for such purposes. Additionally, the comparison of the systems investigated with those having other amines as ligands in electroless copper plating systems is presented.

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EXPERIMENTAL

Triethylenetetramine and tetraethylenepentamine were from Aldrich. Analytical grade chemicals and triply distilled water were used to prepare solutions. The solutions contained: $\text{CuCl}_2 - 0.05$, $\text{CoCl}_2 - 0.15$, amine $- 0.4 \text{ mol l}^{-1}$. Solution pH was adjusted by adding of HCl. The solutions were purged from air oxygen by using Ar.

Microgravimetric studies were performed with a Quartz Crystal Microbalance QCM922 (Princeton Applied Research, USA), two digital voltmeters B7-46/1 connected to a PC through the GPIB-USB-B controller cable (National Instruments, USA). A programming potentiostat PI-5-1 and a sweep generator PR-8 (Russia) were used. AT-cut quartz crystals of 6 MHz fundamental frequency (from Intellectrics Ltd., UK) sputtered by gold from both sides were used. The geometric area of the working electrode was 0.636 cm^2 . The sensitivity constant with respect to the piezoelectric-active area of the electrode was 7.8 ng Hz^{-1} . A standard three electrode configuration was employed with one side of the quartz crystal as a working electrode, an $\text{Ag} / \text{AgCl} / \text{KCl}_{\text{sat}}$ electrode as a reference and a Pt-wire as a counter electrode. The measured electrode potential, the current and the frequency were transferred to the PC every 1.0 s. The electrode potential is quoted *versus* a standard hydrogen electrode (SHE). All the cyclic voltammograms and microgravimetric scans were measured at a scan rate of 5 mV s^{-1} and were swept in the cathodic direction from its stationary value.

The calibration constant $37 \text{ Hz s}^{-1} \text{ mA}^{-1}$ of the EQCM system used was found for the cathodic copper deposition from Cu(II) and both amines solutions and was used for converting the counted frequency change to current units. Partial currents of Co(II) oxidation and Co(III) reduction were calculated as the difference between the measured current and that found from the EQCM data.

Prior to the measurements, a copper layer was electrodeposited on a gold sublayer onto quartz crystals installed at the bottom of the cell from solution containing $1.0 \text{ mol l}^{-1} \text{ CuSO}_4$ and $0.5 \text{ mol l}^{-1} \text{ H}_2\text{SO}_4$ for 2 min. Electroless copper was deposited for 2 min from $\text{Cu(II)}-\text{Co(II)}$ -amine solutions with an electrochemically formed copper coating. The solutions contained (mol l^{-1}): $\text{Cu(II)} - 0.05$, $\text{Co(II)} - 0.15$, amine $- 0.4$ and various amounts of HCl. The experiments were carried out at $20 \pm 1 \text{ }^\circ\text{C}$.

In some longer time experiments, the amount of copper deposited on the surface to be plated (Pt sheet electroplated with copper) was determined by simple weighing with the precision scale.

RESULTS AND DISCUSSION

In the case of two redox couples, namely $\text{Cu(II)}/\text{Cu}$ and $\text{Co(III)}/\text{Co(II)}$, in the presence of amines as ligands there are three main pH-dependent variations (Fig. 1). The redox potential of $\text{Co(III)}/\text{Co(II)}$ remains more positive than that of

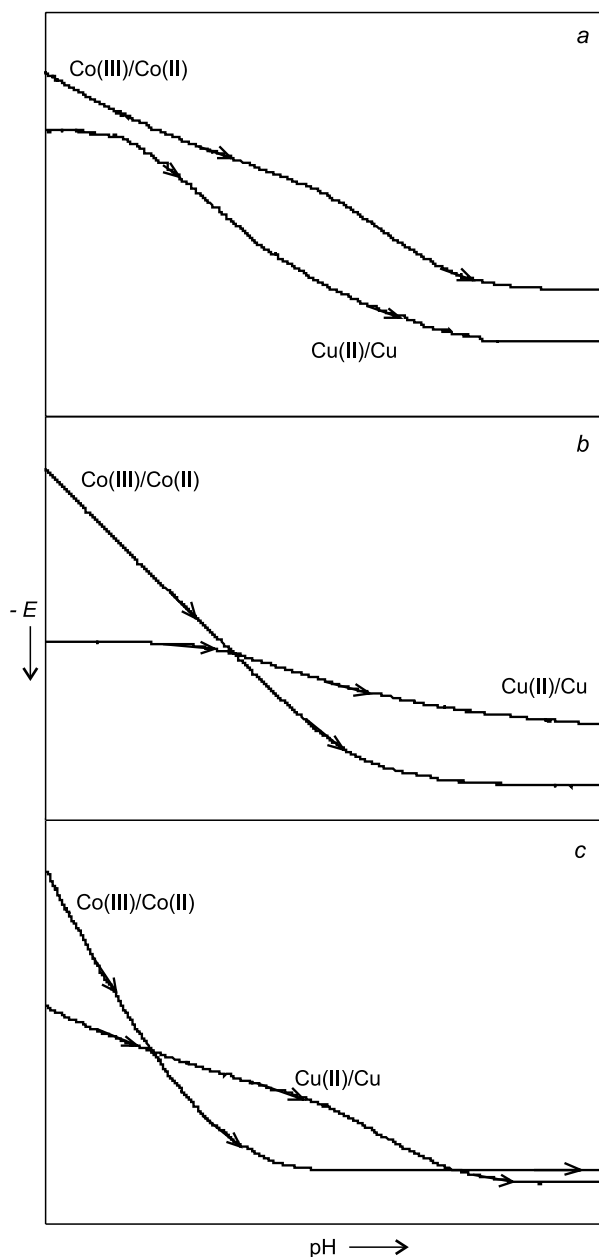


Fig. 1. Schematic dependencies of redox potentials on solution pH in amine-containing solutions

$\text{Cu(II)}/\text{Cu}$ in all pH region and Cu(II) reduction to the metallic state is not possible thermodynamically (Fig. 1a). Fig. 1b represents the case, when under certain conditions the values of the potential of the $\text{Co(III)}/\text{Co(II)}$ redox couple become more negative comparing with the potential of $\text{Cu(II)}/\text{Cu}$ redox couple. Consequently, Co(II) is thermodynamically able to reduce Cu(II) to Cu under the conditions mentioned. It is worth noting that our case is connected with a theoretical thermodynamical possibility. In the real systems, the kinetical limitations could be of great importance, e. g. for the realization of autocatalytic copper(II) reduction the difference between the mentioned redox couples should be negative enough etc.

Fig. 1c shows the case where Cu(II) reduction by Co(II) is thermodynamically feasible in a specific pH range, where the

Co(III)/Co(II) redox couple potential becomes more negative than that of the Cu(II)/Cu redox couple. Thus reduction of Cu(II) by Co(II) is possible only in the pH region discussed, taking into account kinetical limitations given above.

Summarizing the data presented in Figs. 1a, c, it can be noted that the shape of the dependences shown depends on the nature of amine used (i. e. on amine protonation constants values, composition and stability constants of Cu(II), Co(II) and Co(III) complexes with amine), solution pH, temperature, anions presented in solution and concentrations of reacting species.

Unfortunately, no literature data were found on protonation constants as well as on the composition and stability constants of Cu(II), Co(II) and Co(III) complexes with triethylenetetramine (Trien) and tetraethylenepentamine (Tetraen). Therefore in the case of the amines mentioned, our study will be restricted to electrochemical and kinetic data without a deeper thermodynamical analysis.

It should be pointed that anions play a very important role in the systems under investigation. In the case of the amines used (Trien and Tetraen), no Cu(II) reduction was observed when Cu(II) and Co(II) nitrates or sulphates were applied. Detectable reduction of Cu(II) to the metallic state was achieved only when chlorides were used. It can be noted that such phenomenon was documented in the first paper published concerning electroless copper deposition using Co(II)-ethylenediamine (En) complexes as a reducing agent [1] and discussed later [11, 12]. The assumption was made that mixed Cu(II)-En-Cl⁻ complexes are formed in solution adsorbing on the surface, and, subsequently, reduction of the mentioned complex occurs through a chloride "bridge" [12].

When investigating the effect of anions on electroless copper plating with Co(II)-En complex compounds as a reducing agent, it was found that chlorides and especially bromides have a very high accelerating effect on the copper deposition rate in sulphate and nitrate solutions [11]. By contrast, using Trien and Tetraen as ligands, no viewable copper(II) reduction was observed even after additions of chlorides and bromides.

Therefore the systems composed of Cu(II) and Co(II) chlorides were investigated in the present study. When Trien was applied as a ligand, the measurements carried out in the wide pH range (from 4.6 to 9.0) using EQCM showed three processes taking place in the system under investigation. At lower pH values (pH 4.6 and 5.0), definite dissolution of electrode copper substrate occurs (Fig. 2b). Taking into account that the measured values of the open-circuit are comparatively positive, the dissolution of metallic copper can be accounted for the presence of chlorides in the solution forming Cu(I)-chloride complex compounds:



This assumption is confirmed by the fact that the dissolution of copper is not observed in chloride-free solutions, e. g. in sulphate or nitrate solutions. Such dissolution of copper

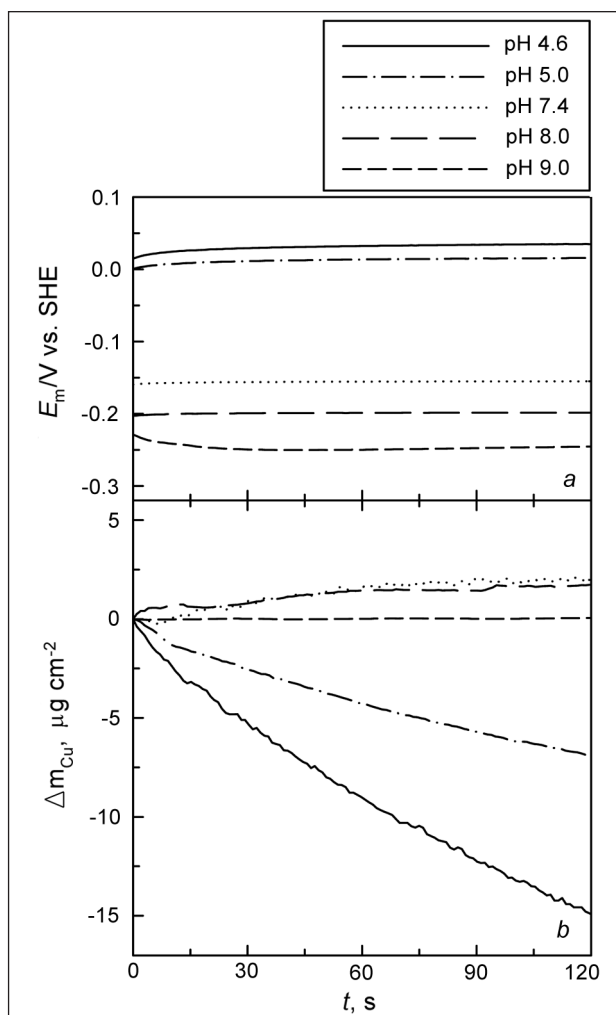


Fig. 2. Kinetics of electroless copper deposition (dissolution) at different solution pH: open-circuit potential (a), copper mass change (b). Solution composition (mol l⁻¹): CuCl₂ – 0.05, CoCl₂ – 0.15, triethylenetetramine (Trien) – 0.4. 20 °C

was also observed in ethylenediamine containing solutions, the open-circuit potential being slightly positive [4, 5]. In our case the open-circuit potential is also slightly positive, the values being close to those of ethylenediamine containing system (cf. Fig. 2a and Fig. 3a with Fig. 3 in [4]).

Further increase in solution pH results in the shift of the open-circuit potential to more negative values (Fig. 2a; Fig. 3a), and a modest copper mass gain (Fig. 2b; Fig. 3b) at pH equal to 7.4 and 8.0 is observed. Therefore the autocatalytic copper(II) reduction is realized (no copper(II) reduction in the solution bulk is observed), the copper plating rate being comparatively low. For instance, the highest copper mass gain (in 2 minutes) in pentaethylenhexamine containing solutions having the similar composition and close pH value is about 57 μg cm⁻² (Fig. 8 in [10]), whereas in the case of Trien it is only approx. 2 μg cm⁻² (Fig. 3b).

In solutions with pH 9, the open-circuit potential shifts farther to more negative potentials (Fig. 2a and 3a), whereas no copper deposition is detected (Fig. 2b; Fig. 3b). Such fact can be attributed to kinetic retardation, i. e. drop-off in the

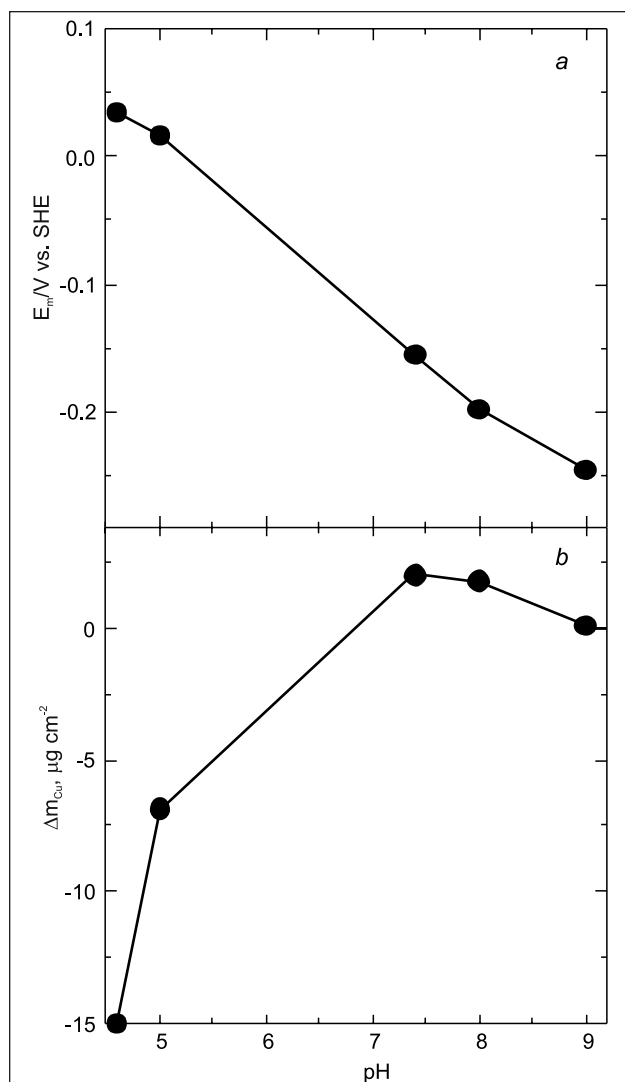


Fig. 3. Kinetics of electroless copper deposition (dissolution) at different solution pH: open-circuit potential (a), copper mass change (b). Solution composition (mol l^{-1}): $\text{CuCl}_2 - 0.05$, $\text{CoCl}_2 - 0.15$, triethylenetetramine (Trien) – 0.4. Deposition time – 120 s, 20 °C

difference between Co(III)/Co(II) and Cu(II)/Cu redox potentials at higher pH (like in the case of ethylenediamine system [4, 5]), or even to thermodynamical limitation, i. e. the redox potential of Co(III)/Co(II) couple being equal or more positive than that of Cu(II)/Cu (like in the case of diethylenetriamine [9] or pentaethylenhexamine [10]).

No copper(II) reduction was observed in the Tetraen containing system at pH equal to 4.6 (Fig. 4b and 5b), the open-circuit potential being close to zero (Fig. 4a; Fig. 5a). Further pH increase up to 4.8 and 5.0 practically does not change the open-circuit potential (Fig. 4a; Fig. 5a), whereas the autocatalytic copper(II) reduction begins at pH 4.8 and rises up to pH 6, the maximum copper plating rate being ca. $3.3 \mu\text{g cm}^{-2}$ (Fig. 4b; 5b), i. e. about one and a half higher than that using Trien as a complexing agent (Fig. 2b; 3b).

Inconsiderable (about $-0.3 \mu\text{g cm}^{-2}$) dissolution of copper substrate was observed during the first 20 seconds in

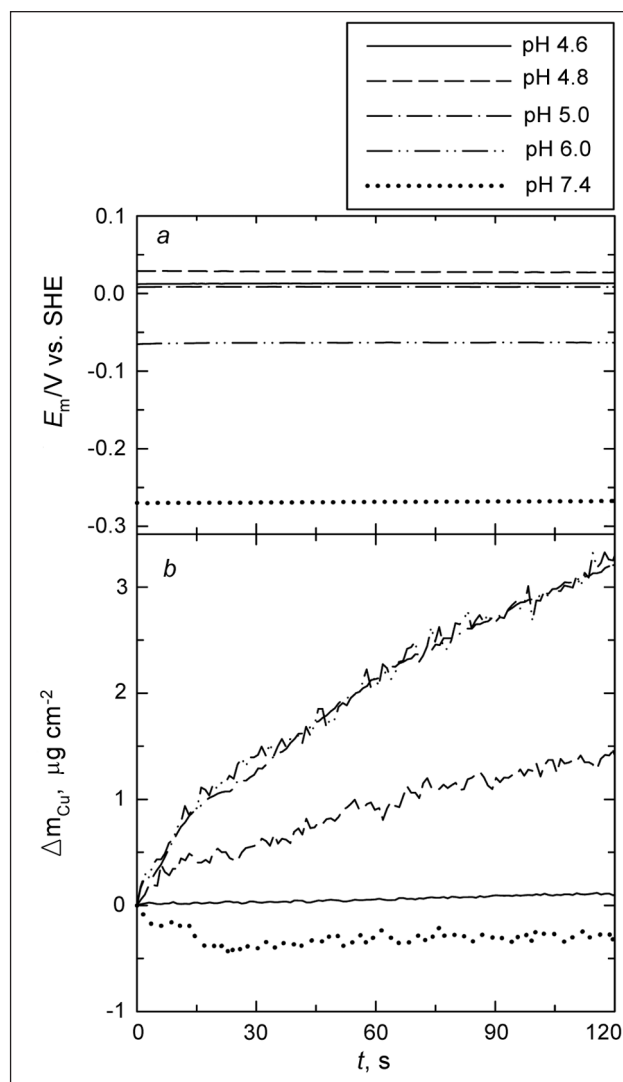


Fig. 4. Kinetics of electroless copper deposition (dissolution) at different solution pH: open-circuit potential (a), copper mass change (b). Solution composition (mol l^{-1}): $\text{CuCl}_2 - 0.05$, $\text{CoCl}_2 - 0.15$, tetraethylenepentamine (Tetraen) – 0.4. 20 °C

solutions with pH equal to 7.4 (Fig. 4b, 5b). It is worth noting that after 20 seconds the mass of electrode remains unchanged. This phenomenon could be explained by the presence of small amounts of Co(III) formed in the solution (by oxidation of Co(II) with residual oxygen or by reduction of Cu(II) with Co(II)). It is possible that the potential of the Co(III)/Co(II) redox couple becomes more positive than that of the Cu(II)/Cu redox couple (Fig. 1c) at higher pH values. Thus Co(III)-Tetraen complexes act as an oxidizing agent and dissolve metallic copper. Since the amount of the Co(III)-Tetraen complex formed is negligible, the dissolution of copper is also insignificant.

A comparison of copper deposition under the same conditions using as ligands different amines, namely, pentaethylenhexamine (Penta) [10], tetraethylenepentamine (Tetraen) [this work] and triethylenetetramine (Trien) [this work], showed that the process rate decreased in the mentioned sequence.

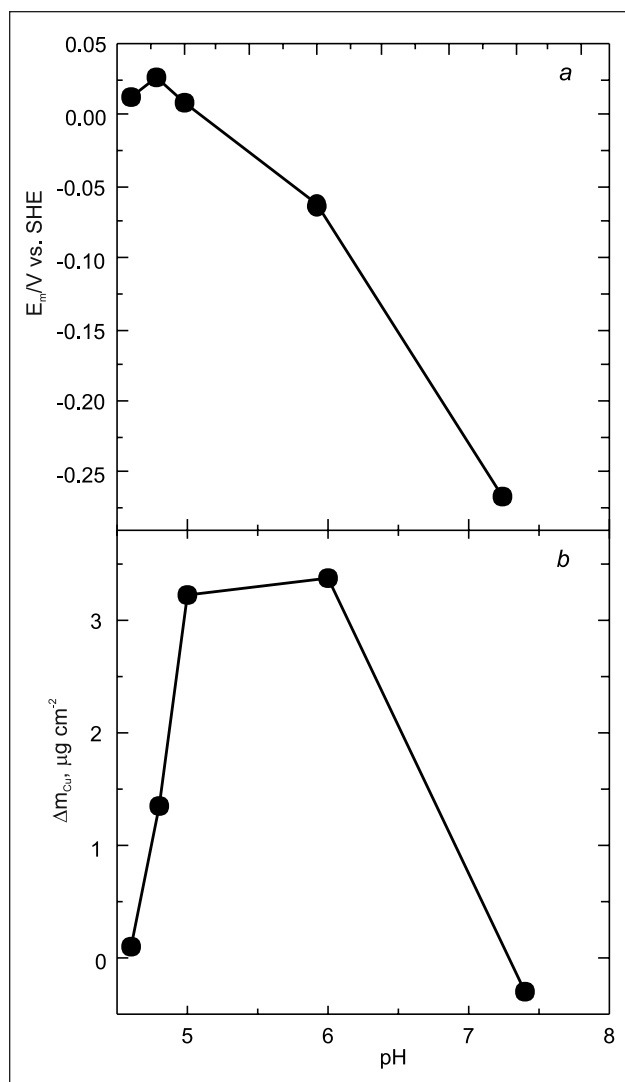


Fig. 5. Kinetics of electroless copper deposition (dissolution) at different solution pH: open-circuit potential (a), copper mass change (b). Solution composition (mol l^{-1}): $\text{CuCl}_2 - 0.05$, $\text{CoCl}_2 - 0.15$, tetraethylenepentamine (Tetraen) - 0.4. Deposition time - 120 s, 20 °C

Generally, copper deposition rates from the solutions containing the above mentioned amines as Cu(II) and Cu(II) ligands are markedly lower than those obtained from the solutions containing ethylenediamine, propylenediamine or diethylenetriamine as ligands. Therefore, pentaethylenehexamine (Penta), tetraethylenepentamine (Tetraen) and triethylenetetramine (Trien) could be presumably used as stabilizing agents or plating rate adjusters in electroless copper plating solutions containing ethylenediamine, propylenediamine or diethylenetriamine as ligands.

Fig. 6 shows different influence of the above mentioned amines on the process of electroless copper deposition from diethylenetriamine (Dien) containing solutions (Fig. 6). At lower concentrations (mmol range), pentaethylenehexamine (Penta) has a retarding effect and diminishes the plating rate at its concentration 10 mmol l^{-1} up to twice (Fig. 6). On the contrary, the same amount of tetraethylenepentamine

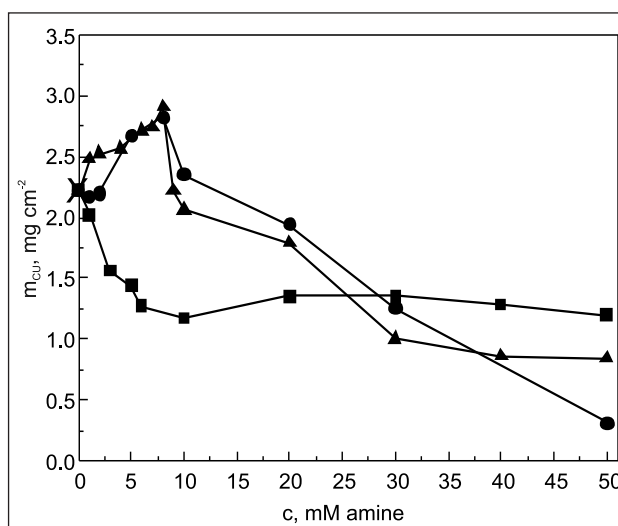


Fig. 6. Dependence of the copper deposition rate on the concentration of amines added. Solution composition (mol l^{-1}): $\text{CuCl}_2 - 0.05$, $\text{CoCl}_2 - 0.15$, diethylenetriamine (Dien) - 0.6. X - initial solution; ▲ - triethylenetetramine (Trien), ● - tetraethylenepentamine (Tetraen), ■ - pentaethylenehexamine (Penta). Solution pH - 6.3, deposition time - 15 minutes, 20 °C

(Tetraen) or triethylenetetramine (Trien) has an accelerating effect and increases the plating rate from 2.25 to about 3 mg cm^{-2} (Fig. 6). Further increase in the concentration of the amines mentioned results in decrease of the copper plating rate (Fig. 6). Thus, small amounts of tetraethylenepentamine (Tetraen) or triethylenetetramine (Trien) (up to 10 mmol l^{-1}) have an accelerating effect, which merges into retardation at higher investigated amine concentrations, whereas pentaethylenehexamine (Penta) exhibits a retarding effect in all concentration range investigated (Fig. 7). It can be noted that

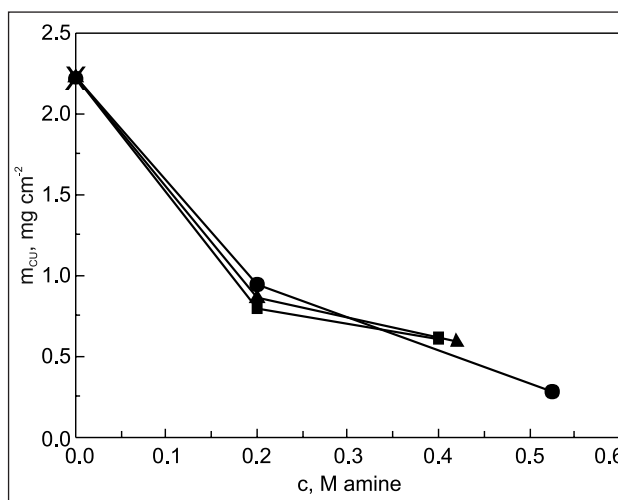


Fig. 7. Dependence of the copper deposition rate on the concentration of amines added. Solution composition (mol l^{-1}): $\text{CuCl}_2 - 0.05$, $\text{CoCl}_2 - 0.15$, diethylenetriamine (Dien) - 0.6. X - initial solution; ▲ - triethylenetetramine (Trien), ● - tetraethylenepentamine (Tetraen), ■ - pentaethylenehexamine (Penta). Solution pH - 6.3, deposition time - 15 minutes, 20 °C

higher concentrations (0.2–0.5 mol l⁻¹) of pentaethylenhexamine (Penta), tetraethylenepentamine (Tetraen) and triethylenetetramine (Trien) have a more expressed retarding effect (comparing with lower concentrations). In the last case, the retarding behavior of all three amines is practically the same or very similar.

CONCLUSIONS

1. Tetraethylenepentamine (Tetraen) and triethylenetetramine (Trien) are suitable ligands for electroless copper plating systems using Co(II)-amine complexes as reducing agents. The highest copper deposition rate (during 2 minutes) determined for the tetraethylenepentamine (Tetraen) system was ca. 3.3 μg cm⁻², whereas this rate for the triethylenetetramine (Trien) system was lower being ca. 2 μg cm⁻².

2. A comparison of copper deposition under the same conditions using different amines as ligands, namely, earlier investigated pentaethylenhexamine (Penta), tetraethylenepentamine (Tetraen) and triethylenetetramine (Trien), showed that the process rate decreased in the mentioned sequence, the highest plating rate being considerably soaring for pentaethylenhexamine (Penta) – ca. 57 μg cm⁻² during 2 minutes.

3. When investigating the electroless copper deposition process from diethylenetriamine (Dien) containing solutions, it was found that small amounts of tetraethylenepentamine (Tetraen) or triethylenetetramine (Trien) (up to 10 mmol l⁻¹) have an accelerating effect, which merges into retardation at higher investigated amine concentrations, whereas pentaethylenhexamine (Penta) exhibits a retarding effect in all concentration range investigated. The amines under investigation can be applied as stabilizing agents or plating rate adjusters in electroless copper plating solutions containing other amines as ligands, e. g. ethylenediamine, propylenediamine or diethylenetriamine.

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References

1. A. Vaškelis, J. Jačiauskienė, E. Norkus, *Chemija*, N 3, 16 (1995).
2. A. Vaškelis, E. Norkus, G. Rozovskis, J. Vinkevičius, *Trans. Inst. Metal Finish.*, 75, 1 (1997).
3. A. Vaškelis, E. Norkus, J. Reklaitis, J. Jačiauskienė, *Chemija*, 9(3), 199 (1998).
4. E. Norkus, A. Vaškelis, J. Jačiauskienė, *Chemija*, 9(4), 284 (1998).
5. A. Vaškelis, E. Norkus, *Electrochim. Acta*, 44, 3667 (1999).
6. A. Vaškelis, E. Norkus, J. Jačiauskienė, J. Reklaitis, *Galvanotechnik*, 90, 1556 (1999).
7. A. Vaškelis, J. Jačiauskienė, A. Jagminienė, E. Norkus, *Solid State Sci.*, 4, 1299 (2002).
8. I. Stankevičienė, A. Vaškelis, A. Jagminienė, L. Tamašauskaitė Tamašiūnaitė, E. Norkus, *Chemija*, 18(1), 8 (2007).
9. A. Vaškelis, I. Stankevičienė, A. Jagminienė, L. Tamašauskaitė Tamašiūnaitė, E. Norkus, *J. Electroanal. Chem.*, 622, 136 (2008).
10. I. Stankevičienė, E. Norkus, L. Tamašauskaitė Tamašiūnaitė, A. Jagminienė, K. Prušinskas, *Electrochimica Acta*, submitted.
11. J. Jačiauskienė, E. Norkus, A. Vaškelis, *Chemija*, 10(4), 264 (1999).
12. A. Vaškelis, G. Stalnionis, Z. Jusys, *J. Electroanal. Chem.*, 465, 142 (1999).

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BESROVIO (CHEMINIO) VARIO NUSODINIMO PROCESO, REDUKTORIUMI NAUDOJANT ĮVAIRIUS CO(II)-AMINŲ KOMPLEKSINIUS JUNGINIUS, PALYGINAMASIS TYRIMAS

Santrauka

Pirmą kartą tetraetilenpentaminas (Tetraen) ir trietilentetraminas (Trien) buvo panaudoti ligandais besrovio (cheminio) vario nusodinimo sistemose, kur reduktoriumi naudojami Co(II)-aminų kompleksai. Didžiausias vario nusėdimo greitis (nustatytas po 2 min. dengimosi) tetraetilenpentamino (Tetraen) sistemoje buvo 3,3 μg cm⁻², o trietilentetramino (Trien) sistemoje jis buvo žemesnis ir apytikriai lygus 2 μg cm⁻². Darbe aptariamas vario pagrindo tirpimas minėtųjų aminų tirpaluose esant tam tikroms pH vertėms. Pasiūlyta tirtuosius aminus naudoti stabilizuojančiais priedais ar vario nusėdimo greičio reguliatoriais cheminio variavimo tirpaluose, kuriuose ligandais naudojami kiti aminai, pvz., etilendiaminas, propilendiaminas, dietilentriaminas.