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Electroless copper deposition using Co(II)–deiethylenetriamine complex as reducing agent

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The autocatalytic copper(II) reduction by cobalt(II) in deiethylenetriamine (dien) solutions (electroless copper plating) was studied by measuring the copper deposition rate, open-circuit potential and electrochemical parameters of partial reactions. The Cu(II) reduction process depended largely on solution pH and anions present in plating solution; the process rate changed in the sequence chloride >> tetrafluoroborate > nitrate ~ sulfate. The process in tetrafluoroborate, sulfate and nitrate solutions can be effectively accelerated by adding small amounts of bromide. EQCM measurements provided data on the instantaneous copper deposition rate and indicated the sensitivity of partial electrochemical reactions to ligand concentration.

Key words: electroless copper plating, cobalt(II)-diethylenetriamine complexes, EQCM

INTRODUCTION

The cobalt(II) complex with ethylenediamine was found [1] to be an effective reducing agent in the autocatalytic reduction of copper(II) to metal (electroless copper plating). Thermodynamic analysis and kinetic investigations were carried out for copper deposition in this system [2–6], and a rather high rate of reduction on the metal surface without any appreciable bulk reduction was observed at certain reactant concentrations and solution pH. This electroless copper deposition method may be of practical importance due to several specific features: a less-defective structure of the copper layers because of absence of hydrogen evolution and its inclusion into the deposits, the possibility to regenerate the reducing agent (cobalt(III) is reducible to the initial cobalt(II) complex electrochemically or chemically, in contrast to the conventional reducing agents).

Co(II) complexes with another diamine, propane-1,2-diamine (propylenediamine) was also shown to be a strong enough reducing agent to reduce copper(II) to metal and suitable to use in electroless copper plating solutions [7].

In the recent comparative studies of various amines in alkaline Co(II) solutions [8, 9], diethylenetriamine (dien) was shown to enhance effectively the anodic oxidation of cobalt(II); this effect was explained by the formation of easily oxidized and active Co(II) complexes with dien. The anodic oxidation of a reducing agent is one of the two partial electrochemical reactions of the autocatalytic (electroless) metal deposition process, and its rate is usually the main factor determining the overall electroless process rate. Therefore, the anodic oxidation data on cobalt(II)-dien complexes were used for constructing new electroless metal plating solutions.

According to data of [9], the reducing activity of Co(II)–dien complexes is similar or even higher than that of ethylenediamine ones. They are able to reduce autocatalytically copper(II) ions to metal. This reduction process was studied in this work by simple kinetic measurements and by electrochemical quartz crystal microgravimetry (EQCM). The EQCM method, alongside with the instantaneous copper deposition rate measurements, allowed to obtain the rates of both partial reactions of the electroless plating process *in situ*.

The earlier electrochemical investigation of the autocatalytic process of copper(II) reduction by a cobalt(II)–ethylenediamine complex [10, 11] showed that copper deposition resulted from coupling of partial electrochemical reactions of Cu(II)–ethylenediamine reduction and Co(II)–ethylenediamine oxidation occurring simultaneously on copper surface. Some deviations from partial reaction additivity were found and explained by differences in the ligand con-

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centration at the catalytic surface in separate Cu(II) and Co(II) solutions and the total electroless plating system; no great non-additivity effects typical of the classical electroles plating systems (Cu(II)–formaldehyde, Ni(II)–hypophosphite) were observed.

EXPERIMENTAL

A 2 cm² Cu sheet electrode was used as a substrate for electroless copper deposition. A closed cell was used, solutions were purged with Ar before introducing Co(II) to avoid its oxidation by atmospheric oxygen; the Ar atmosphere was maintained during measurements. The potential was measured with respect to the Ag|AgCl|KCl_{sat} reference electrode, and its values are given *vs.* this SHE.

The electroless copper plating solutions contained (M): Cu(II) – 0.05, Co(II) – 0.15, diethylenetriamine (dien) – 0.6. In some cases small KBr additions were used. Four types of plating solutions containing different anions (chloride, sulfate, nitrate and tetrafluoroborate) were investigated. Solution pH was adjusted by adding an acid with a necessary anion. All experiments were carried out at 20 ± 1 °C. Analytical grade chemicals and distilled water were used to prepare the solutions.

The electroless copper deposition rate was determined by two experimental techniques, gravimetry and electrochemical quartz crystal microgravimetry. In the first case the average rate value for 15 min was found from the data of weighing the amount of copper deposited on the Cu electrode in 15 min. In the second case the instantaneous copper deposition rate was found from quartz oscillator frequency change.

EQCM measurements were carried out using AT-cut quartz crystals of 6 MHz fundamental frequency (from Intelemetrics Ltd., UK) sputtered by gold (geometric area 0.636 cm²). Prior to the experiments, copper was electrodeposited onto the gold sublayer on quartz crystal. The measurement procedure was as described in [12]. Quartz crystals were installed at the bottom of a cell with a working volume of *ca.* 2 ml. The upper part of the cell contained a Pt-wire CE, joints for the electrolyte inlet and the Luggin capillaries, and an electrolyte outlet tube. EQCM me-

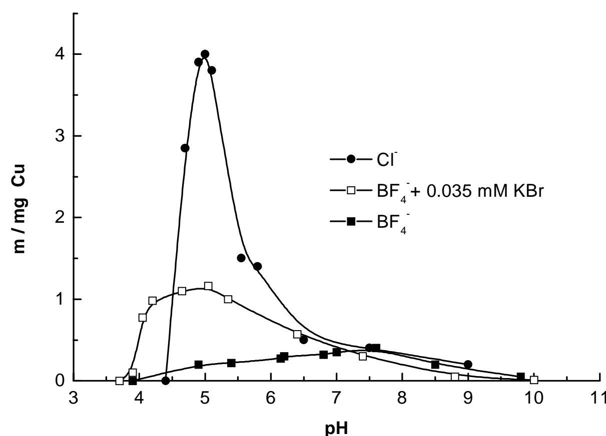

Fig. 1. Dependence of copper amount deposited on electroless plating solution pH. Solution contained (mol l⁻¹): Cu(II) – 0.05; Co(II) – 0.15; dien – 0.6

Table 1. **Electroless cupper deposition characteristics in chloride solution**

Cl^-		
pH	m, mg/2 cm² 15 min	E_m, V
4.4	0	0.05
4.7	2.85	0.02–0.01
4.9	3.9	0.01
5	4	–0.02 – –0.03
5.1	3.8	–0.05 – –0.07
5.55	1.5	0.01
5.8	1.4	–0.02 – –0.07
6.5	0.5	–0.22 – –0.23
7.5	0.4	–0.23
9	0.2	–0.23 – –0.24
10	0	–0.24

Table 2. **Electroless cupper deposition characteristics in tetrafluoroborate solution**

BF_4^-			BF_4^- + 0.035 mM KBr		
pH	m, mg/2 cm² 15 min	E_m, V	pH	m, mg/2 cm² 15 min	E_m, V
3.9	0	0.09–0.10	3.7	0	–0.10
4.9	0.2	0.01 – –0.03	3.9	0.1	–0.07
5.4	0.22	–0.06 – –0.10	4.05	0.775	0.02–0.0
6.15	0.27	–0.12 – –0.15	4.2	0.98	0.03; 0.02
6.2	0.3	–0.18 – –0.19	4.65	1.1	0.03 – 0.01
6.8	0.32	–0.18	5.05	1.16	0.00 – –0.02
7	0.35	–0.20 – –0.21	5.35	1	–0.04
7.6	0.4	–0.20 – –0.23	6.4	0.57	–0.17 – –0.18
8.5	0.2	–0.25 – –0.30	7.4	0.3	–0.24 – –0.25
9.8	0.05	–0.34 – –0.35	8.8	0.05	–0.26 – –0.27
			10	0.01	–0.28

Table 3. **Electroless cupper deposition characteristics in nitrate solution**

NO_3^-			NO_3^- + 0.035 mM KBr		
pH	m,mg/2 cm² 15 min	E_m, V	pH	m, mg/2 cm² 15 min	E_m, V
3.9	0	0.13–0.07	3	0	0.17
4.3	0.225	0.03–0.00	3.2	0.05	0.15–0.14
4.6	0.375	–0.04	3.5	0.1	0.07–0.06
5.1	0.3	–0.06 – –0.10	3.8	0.4	0.05–0.04
5.4	0.225	–0.10	4.6	0.9	0.04–0.03
6	0.2	–0.10 – –0.12	4.75	1	–0.03–0.02
7.1	0.15	–0.15	5.4	0.9	–0.13–0.05
8.5	0.05	–0.26 – –0.28	8.2	0.6	–0.20 – –0.22
10.7	0.01	–0.30 – –0.32	8.7	0.2	–0.23 – –0.26
			10.9	0.05	–0.30 – –0.32

Table 4. **Electroless cupper deposition characteristics in sulfate solution**

SO_4^{2-}			SO_4^{2-} + 0.035 mM KBr		
pH	m, mg/2 cm² 15 min	E	pH	m, mg/2 cm² 15 min	E
6.3	0	–0.04 – –0.05	5.5	0	0.03–0.03
6.5	0.2	–0.05 – –0.06	5.7	0.12	0.03–0.02
6.6	0.25	–0.06 – –0.10	5.9	0.7	–0.01
6.9	0.35	–0.12 – –0.15	6.1	0.8	–0.04 – –0.02
7.3	0.4	–0.17 – –0.21	6.15	0.9	–0.05
8.2	0.35	–0.25 – –0.27	6.2	0.9	–0.06
9.5	0.25	–0.26 – –0.27	6.45	1	–0.08 – –0.09
11.5	0.1	–0.28 – –0.34	7.5	0.9	–0.17 – –0.24
12	0	–0.34	7.6	0.9	–0.22 – –0.25
			9.1	0.7	–0.22 – –0.27
			10	0.3	–0.30
			11.5	0.1	–0.32 – –0.34
			12	0	–0.34

asurements were carried out under stopped-flow and wall-jet conditions. The electrolyte flow in wall-jet experiments was ensured by the hydrostatic pressure in a bottle connected to the inlet capillary through a PVC tube; Ar purged the electrolyte constantly.

EQCM measurements were carried out using a precision frequency counter (43–64) and two digital voltmeters (B7-46/1) connected to a PC through an IEEE 488 interface. A programming potentiostat (PI-50-1) and a sweep generator (PR-8) were used. The potential sweep rate was 2 mV s^{-1}. The measured electrode potential, the faradaic current and the frequency (the stability ± 0.5 Hz) were transferred to the PC every 1.3 s. Differential EQCM data (the frequency change rate df / dt) were found as the difference between two frequency measurements per 1 s and were used in this work for calculating the copper deposition rate and the cathodic copper deposition current.

RESULTS AND DISCUSSION

The copper plating process was shown to be very sensitive to solution pH (Figs. 1 and 2, Tables 1–4). The lower solution pH limit of copper(II) reduction by cobalt(II)–dien complex is approx. 4 for chloride, tetrafluoroborate and nitrate solutions, and over 6 for sulfate ones. The copper deposition rate dependences on solution pH go through a maximum which is reached at pH approx. 5 for the first three anions and over 7 for a sulfate bath.

The copper deposition rate at higher solution pH values falls down and copper deposit formation stops practically at pH 9–10, except for sulfate-based solutions where the pH region pf copper deposition is shifted to higher values and extends to approx. 12 (Fig. 2 and Table 4). The decrease of copper deposition rate is caused mainly by the enhancement of copper(II) reduction in all solution volume (solution instability) at a higher solution pH because of thermodynamic reasons – a higher degree of cobalt(II) complexation and a shift of the Co(III) / Co(II) couple redox potential to more negative values. The solutions studied remains stable for the plating period only at solution pH up to the rate maximum, and over this pH value the formation of copper film on the cell walls and of copper powder on the cell bottom is observed. The overall rate if copper(II) re-

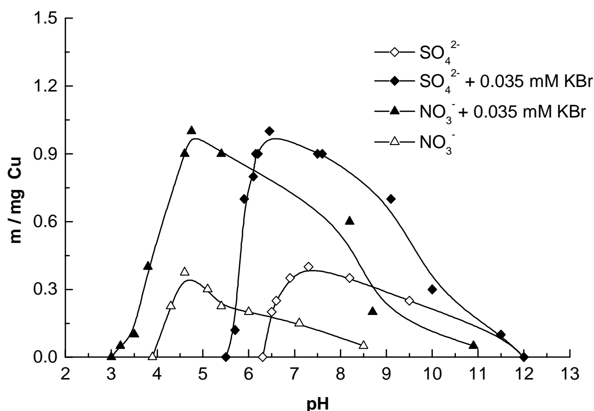

Fig. 2. Dependence of copper amount deposited on electroless plating solution pH. Solution contained (mol l^{-1}): Cu(II) – 0.05; Co(II) – 0.15; dien – 0.6

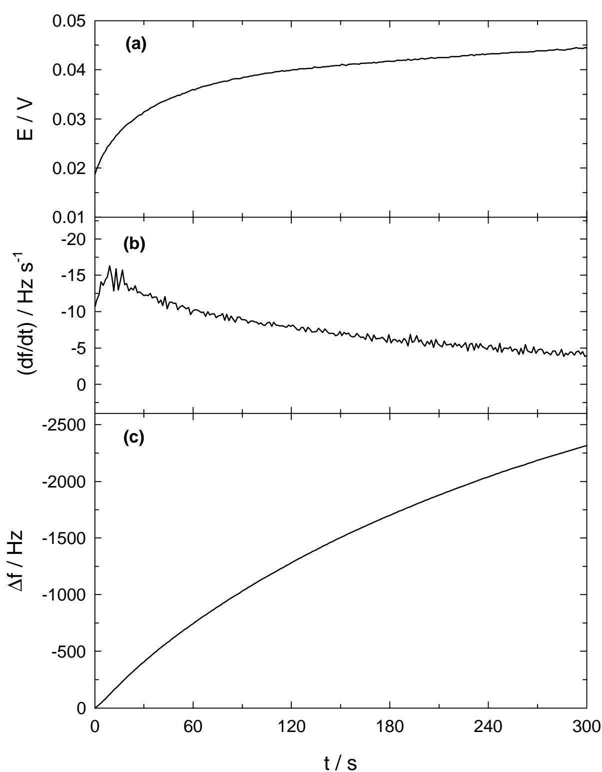

Fig. 3. Kinetics of electroless copper plating in unstirred solution (a, open-circuit potential; b, frequency change rate; c, change in frequency;). Solution contained (mol l^{-1}): $CuCl_2$ – 0.05; $CoCl_2$ – 0.15; dien – 0.6; pH 5.5; 20 °C

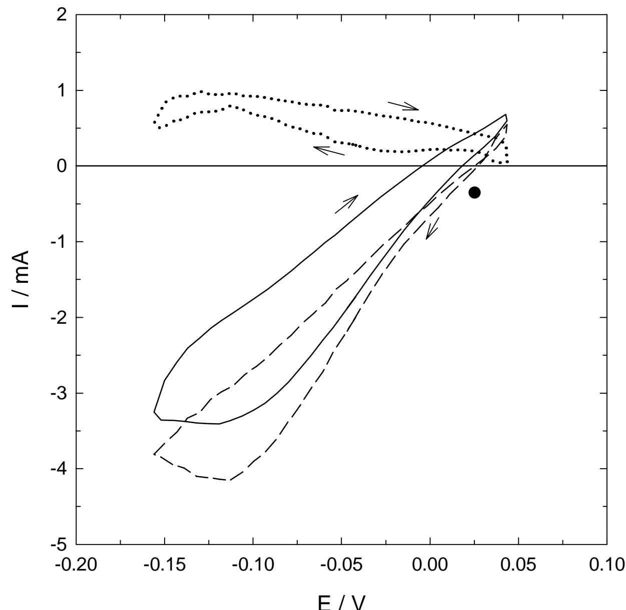

Fig. 4. Cyclic voltammograms of Cu electrode (0.636 cm^2) in electroless copper plating solution (mol l^{-1}): $CuCl_2$ – 0.05; $CoCl_2$ – 0.15; dien – 0.6; pH 5.5. Current: (–––) measured directly, (- - -) calculated from EQCM data, and (××××××) their difference (Co(II) oxidation rate). Potential scan rate 5 mV s^{-1}; 20 °C. • – copper deposition rate under open-circuit conditions

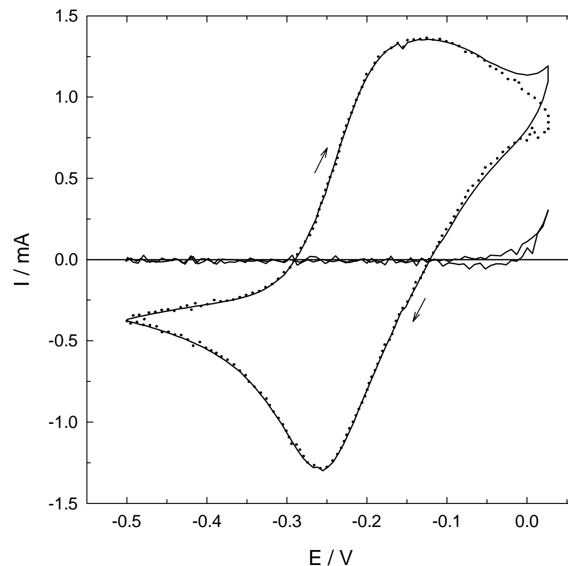

Fig. 5. Cyclic voltammograms of Cu electrode (0.636 cm^2) in Co(II)–*dien* solution (mol l^{-1}): $CoCl_2$ – 0.15; dien – 0.6; pH 5.5. Current (–––) measured directly, (- - -) calculated from EQCM data, and (××××××) their difference (Co(II) oxidation rate). Potential scan rate 5 mV s^{-1}; 20 °C

duction by cobalt(II) seems to rise with a rise in solution pH.

According to the copper deposition rate the study solutions form two groups: 1) chloride-based and 2) nitrate-, sulfate-, and tetrafluoroborate-based solutions. Using the chloride salt formulation, a very high copper deposition rate can be obtained – up to 8 mm/h, while the plating rate in solutions of the second group at best is 4-fold lower. The process rate dependence on the anions present in plating solution is expressed by the sequence: chloride $>>$ tetrafluoroborate $>$ nitrate ~ sulfate. This sequence is similar to that found earlier for ethylenediamine solutions [13].

The anion effect on copper (II) reduction rate is apparently related to the kinetic reasons such as the influence of anions on kinetic activity of cobalt(II) complexes and an especially high enhancing effect

of halides. This view is in agreement with the effect of bromide ions. The reduction process in tetrafluoroborate, nitrate and sulfate solutions can be accelerated effectively by adding rather small amounts of KBr (Figs. 1 and 2, Tables 2–4).

Bromide additions increase the maximum copper plating rate up to 3-fold and widen the solution pH range of electroless plating. Worth noting is the unusually low pH values at which the plating process may be carried out, approx. 3.5 (see data for nitrate and tetrafluoroborate solutions containing bromide).

The open-circuit potential of copper in the course of electroless deposition (the mixed potential determined by coupling of two partial electrochemical reactions) shifts to more negative values with a rise of solution pH (Tables 1–4). This shift is not continuous and occurs in some cases under larger potential changes. Bromide additions, as a rule, shift the mixed potential in negative direction, indicating enhancement of the anodic oxidation reaction of cobalt(II).

EQCM measurements provide information on an instantaneous copper deposition rate (Fig. 3b), mixed potential (Fig. 3a) and copper film build-up kinetics (Fig. 3c). The instantaneous rate data seem to be especially valuable in this case due to difficulties in obtaining such information for this system by other experimental methods; for the classical electroless metal deposition processes hydrogen evolution gives a possibility to control the process rate continuously.

The copper deposition rate changes considerably in time (Fig. 3b).

After a short rise in the first 10 s (it could be assumed to be an induction period), the plating rate slowly decreases. The open-circuit (mixed) potential shifts continuously to more positive values (Fig. 3a), indicating a diminishing reducing activity of Co(II) species due to a cobalt(II) concentration decrease or/and cobalt(III) retarding effects.

Using cyclic voltammetry in combination with EQCM, the rate of partial electrochemical reactions, anodic Co(II) oxidation and Cu(II) reduction, both in separate systems and in the whole electroless solution are obtained.

Data for the whole eelctroless deposition system (Fig. 4) demonstrate a comparatively high degree of Cu / Cu(II) couple reversibility in dien solutions: the copper complex reduction to metal is replaced by copper dissolution at a small change in the electrode potential. The mixed potential is not far from the equilibrium potential of Cu/Cu(II), and the copper ions reduction process occurs at a rather low overpotential (less than 10 mV).

The cobalt(II) anodic oxidation curve measured in Co(II)–dien solution (Fig. 5) is typical of the cobalt(II)–amine complex oxidation on a copper electrode in unstirred solution (stopped-flow conditions) [10, 11]. The cathodic current at the reverse potential scan represents the reduction process of Co(III) species formed at the previous anodic potential scan and held at the electrode surface by some adsorption forces.

A comparison of Co(II) oxidation rate in a separate solution (Fig. 5) and in the electroless plating solution (calculated as a difference between the overall current an the current of copper deposition reaction found from quartz oscillator data, Fig. 4) shows a lower cobalt(II) oxidation current in the whole plating solution; one of the causes of this nonadditivity effect is the different concentration of the ligand, dien, in the systems under comparison: at the same total dien concentration (0.6 M) in electroless plating solution part of it is bounded with Cu(II) and the resulting complexation of Co(II) is lower; it should lead to a less active Co(II) oxidation. Similar non-additivity effects caused by changes in ligand concentration have been described earlier [10].

Electroless copper plating solutions containing Co(II)–dien complexes are similar in their behaviour to those containing ethylenediamine, but the dien system is more active in the copper(II) reduction process and thus a higher copper plating rate can be obtained.

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CHEMINIS VARIO NUSODINIMAS REDUKTORIUMI NAUDOJANT Co(II)- DIETILENTRIAMINO KOMPLEKSÀ

S a n t r a u k a
Tirta autokatalizinë vario(II) redukcija kobaltu(II) dietilentriamino (dien) tirpaluose: matuotas vario nusëdimo greitis, miðrus potencialas ir elektrocheminiai parcialiniø proceso reakcijø parametrai. Cu(II) redukcijos procesas labai priklauso nuo tirpalo pH ir tirpale esanèiø anijonø; proceso greitis kinta pagal sekà: chloridai >> tetrafluoroboratai > nitratai ~ sulfatai. Variavimà tetrafluoroboratø, sulfatø ir nitratø tirpaluose galima efektyviai pagreitinti pridëjus ðiek tiek bromido. Elektrocheminës kvarco kristalo mikrogravimetrijos metodu iðmatuoti momentiniai vario nusëdimo greièiai ir nustatyta, kad parcialinës reakcijos yra jautrios ligando koncentracijai.