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The autocatalytic reduction of copper(II) by cobalt(II) in aqueous diethylenetriamine solutions studied by EQCM

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ABSTRACT

Calculations show that cobalt(II) complexes with diethylenetriamine (*dien*) are rather strong reducing agents and are capable to reduce copper(II) ions to the metallic state and, therefore, can be used in electroless plating systems for the deposition of copper coatings. A thermodynamic analysis of equilibria in system Cu–Cu(II)–Co(II)–Co(III)-diethylenetriamine was carried out and the conditions of Cu(II) reduction to metal by Co(II) were predicted. Copper(II) reduction is supposed to occur in pH region from ca. 5 to ca. 9.5 (20 °C). The reduction process is predicted to be strongly dependent on the solution pH and ligand (*dien*) concentration. The most negative difference of a redox potential (ΔE) between Cu(II)/Cu and Co(III)/Co(II) couples could reaches values of -200 mV. The autocatalytic copper(II) reduction by cobalt(II) in diethylenetriamine solutions (electroless copper plating) was studied by measuring the instantaneous copper deposition rate, open-circuit potential and electrochemical parameters of partial reactions. The Cu(II) reduction process depended largely on the solution's pH and the anions presenting in the plating solution. A comparison of copper deposition under the same conditions using chloride, tetrafluoroborate, sulfate, acetate salts and corresponding acids (to adjust solution pH) showed that the process rate decreased in the following sequence: chloride$\gg$tetrafluoroborate>sulfate>acetate. The process investigation by EQCM measurements provided data on the rate of partial electrochemical reactions both in the separate Cu(II) and Co(II), and the complete electroless plating solutions; these data indicated the sensitivity of the partial anodic reaction to solution pH, anion nature and to ligand concentration. Co(II)-*dien* complexes are very active in the copper(II) reduction and high process rates can be obtained.

1. Introduction

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. The electroless copper deposition process is consisting of anodic oxidation of the reducing agent and cathodic reduction of Cu(II) species occurring simultaneously on the same copper surface; the electrons appeared in anodic oxidation of the reducing agent are transferred through the metallic copper to Cu(II) ions, and the autocatalytic deposition of Cu takes place.

The cobalt(II) complex with ethylenediamine was found to be an effective reducing agent in the autocatalytic reduction of copper(II) to metal (electroless copper plating) [1]. Thermodynamical analysis and kinetical investigations were carried out for copper deposition in this system [2–6], and a rather high rate of reduction on the metal surface (up to 6 μm h^{-1} at 50–70 °C) 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 diamines, such propane-1,2-diamine (propylenediamine), were also shown to be sufficiently strong to reduce copper(II) to metallic state and suitable to use as reducing agent in electroless copper plating solutions [7].

In the recent, comparative studies of various amines in alkaline Co(II) solutions [8–10], diethylenetriamine (*dien*) $H_2N–CH_2–CH_2–NH–CH_2–CH_2–NH_2$ (2,2′-diaminodiethylamine) was shown to enhance effectively the anodic oxidation of cobalt(II). This effect was explained by the formation of easily oxidizable 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

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process rate. Therefore, the anodic oxidation data on cobalt(II)-*dien* complexes were used at constructing of new electroless metal plating solutions.

As it was described earlier [9,10], 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 Cu(II) reduction process by Co(II)-amine complexes was shown to be very sensitive to solution pH and anions present in solution [11–13]. The autocatalytic copper(II) reduction by cobalt(II)-*dien* complex occurs at solution pH over 4 in the most cases. The copper deposition rate reaches a maximum at pH 5–7, falls down at higher solution pH values and at pH 9–10 copper deposit formation practically stops. The decrease of copper deposition rate was explained by the enhancement of copper(II) reduction in all solution volume (solution instability) at a higher solution pH because of thermodynamical 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 previously published data indicate that the cobalt(II)-*dien* complex is the most active reducing agent among all cobalt(II)-amine complexes used for electroless copper deposition [11].

This work is aimed at a thermodynamic analysis of Cu–Cu(II)–Co(II)–Co(III)-diethylenetriamine system, i.e., prediction of conditions of Cu(II) reduction to metal by Co(II), and to the experimental study of Cu(II) reduction by using electrochemical quartz crystal microgravimetry (EQCM). This method allows the instantaneous copper deposition rate measurements.

2. Experimental

2.1. Calculations

The distribution of Co(II), Co(III), Cu(II) among the complexes with diethylenetriamine was calculated by solving the system of non-linear equations in terms of the Newton iteration method [14], using metal-ion complex stability and ligand protonization constants. The possibility of Co(II) and Co(III) hydroxide formation was considered, as well. The following values of the standard redox potentials were used:

$$E^0_{\mathrm{Co}^{3+}/\mathrm{Co}^{2+}} = 1.82\ \mathrm{V}\ \text{and}$$

$$E^0_{\mathrm{Cu}^{2+}/\mathrm{Cu}} = 0.345\ \mathrm{V}.$$

2.2. Electrochemical investigations

The details of the EQCM set-up employed are described elsewhere [12,13,15,16]. AT-cut quartz crystals of 6 MHz fundamental frequency (from Intellemetrics Ltd., UK) sputtered by gold from both sides were used. Their electrochemically and piezoelectrically active geometric areas were 0.636 and 0.283 cm^2, respectively.

Prior 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 mol l^{-1} $CuSO_4$ and 0.5 mol l^{-1} H_2SO_4 at a current 10 mA for 1 min.

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, the joints for the electrolyte inlet and the Luggin capillaries, and the electrolyte outlet tube. EQCM measurements were carried out in unstirred solutions.

All EQCM measurements were performed with a precision frequency counter CH3-64 and two digital voltmeters B7-46/1 connected to a PC through the IEEE 488 interface. A programming potentiostat PI-50-1 and a sweep generator PR-8 (Izmeritel, Russia) were used. The potential scan rate was 5 mV s^{-1}. The potential was measured with respect to $Ag/AgCl/KCl_{sat}$ reference electrode and is given below versus a standard hydrogen electrode (SHE). The measured electrode potential, the current and the frequency (the stability ± 0.5 Hz) were transferred to the PC every 1.3 s. Differential EQCM data (the quartz crystal frequency change rate d*f*/d*t*) were found as the difference between two frequency measurements per 1 s, and were used in this work for calculation of Cu deposition and dissolution current.

A theoretical calibration constant, –41 Hz s^{-1} mA^{-1}, calculated from the Sauerbrey's equation for 6 MHz quartz crystal [17], was used for converting the counted frequency change to current units at copper deposition. Partial currents of Co(II) oxidation and Co(III) reduction were calculated as the difference between the measured net current and that found from the EQCM data.

The mass of deposited copper was calculated converting the frequence changes to mass units using the 6 MHz quartz crystal sensitivity constant equal to 12.26 ng cm^{-2} Hz^{-1} (or 7.8 ng Hz^{-1} with respect to the electrochemically active geometrical area (0.636 cm^2) of the electrode used).

2.3. Chemicals and solutions

Analytical grade chemicals and triply distilled water were used to prepare the solutions. The solutions contained (mol l^{-1}): Cu(II) – 0.05, Co(II) – 0.15, diethylenetriamine (*dien*) – 0.6. Four types of solutions containing different anions – chloride, sulfate, tetrafluoroborate and acetate were used. Solution pH was adjusted by adding the acid with the necessary anion. Ar purged the electroless copper plating and cobalt(II) solutions constantly. All experiments were carried out at 20 ± 1 °C.

3. Results and discussion

3.1. The thermodynamical analysis of the Cu(II) reduction process

Initially the distribution of *dien* forms in wide pH range was calculated using ligand protonation constants given in [18,19]:

$$dien + \mathrm{H}^+ \overset{K_{a1}}{\rightleftarrows} dienH^+ \quad 20\,^\circ\mathrm{C} \quad \log K_{a1} = 9.94, \tag{1}$$

$$dien\mathrm{H}^+ + \mathrm{H}^+ \overset{K_{a2}}{\rightleftarrows} dien\mathrm{H}_2^{2+} \quad 20\,^\circ\mathrm{C} \quad \log K_{a2} = 9.13, \tag{2}$$

$$dien\mathrm{H}_2^{2+} + H^+ \overset{K_{a3}}{\rightleftarrows} dien\mathrm{H}_3^{3+} \quad 20\,^\circ\mathrm{C} \quad \log K_{a3} = 4.34. \tag{3}$$

Diethylenetriamine molecules are protonated in an acid medium and the triply protonated form of $dien\mathrm{H}_3^{3+}$ is the predominant form *of dien* when pH is lower than 4. Increasing pH of the solution, one proton splits of from $dien\mathrm{H}_3^{3+}$ and when pH is about 6, the deprotonated form of $dien\mathrm{H}_2^{2+}$ predominates. After the pH value of the solution reaches 9.5, the monoprotonated form of $dien\mathrm{H}^+$ prevails. Further increase of the pH leads to the full deprotonation of the *dien* (Fig. 1).

In the next step the distribution of Co(III), Co(II) and Cu(II) among the complexes with *dien* was calculated using metal-ion stability constants as well as ligand protonation constants given in [18–20].

Co(III) composes very stable complexes with amines. Co(III) complex with *dien* can be characterized by the following equilibrium constant of diligand complex formation [20]:

$$\mathrm{Co}^{3+} + 2dien \overset{\beta_2}{\rightleftarrows} \mathrm{Co}dien_2^{3+} \quad 20\,^\circ\mathrm{C} \quad \log\beta 2 = 48. \tag{4}$$

Due to the high stability of the complex, it predominates over the whole range of the solution pH studied by us. Hence, in our system Co(III) is always in the form of $\mathrm{Co}dien_2^{3+}$ ions.

Co(II) forms two complexes with *dien*: $\mathrm{Co}dien^{2+}$ and $\mathrm{Co}dien_2^{2+}$. The stability of the complexes is characterized by the following equilibrium constants: