

Copper–cobalt alloy electrodeposition from thiocyanate solutions

2. Initial stages of Cu electrocrystallisation onto polycrystalline Au electrode

Dijana Šimkūnaitė*,
Ignas Valsiūnas,
Emilija Ivaškevič and
Antanas Steponavičius

*Institute of Chemistry,
A. Goštauto 9,
LT-2600 Vilnius, Lithuania*

The characteristics of the initial stages of Cu electrocrystallisation onto a polycrystalline Au surface from a near-neutral 0.05 M Cu(I) + 3 M KSCN solution were estimated using cyclic voltammetry and chronoamperometry. It was confirmed that the initial stages of Cu electrocrystallisation onto polycrystalline Au proceeded through the progressive 3D nucleation and diffusion-controlled growth mechanism developed by Scharifker and Hills. From the atomistic theory of electrochemical nucleation and based on the chronoamperometric data, the stationary nucleation rate I_{st} of Cu onto polycrystalline Au at various Cu deposition potentials E_{dep} was determined. Depending on the value of E_{dep} , I_{st} was found to vary from $2.72 \cdot 10^4$ to $2.29 \cdot 10^6$ cm⁻² s⁻¹. Using the E_{dep} -dependence of I_{st} , the number of Cu atoms in the critical nucleus n_k was calculated and obtained to be equal to no less than 3.

Key words: polycrystalline Au, copper, thiocyanate solution, progressive nucleation, stationary nucleation rate, number of atoms in critical nucleus

INTRODUCTION

An understanding and control of the factors governing the structural and physicochemical properties of thin and even thick metal deposits is of significant importance. One of the factors determining these properties is the mode of nucleation and growth [1, 2].

Electrodeposited Cu thin films are widely used, for instance, in electronics and anticorrosion protection, for producing ductile intermediate layers, etc. A great deal of work has been carried out on the mechanism and kinetics of nucleation and growth of Cu layers onto various substrates from noncomplexing acidic Cu(II) solutions (see, e.g., the reviews [1, 2]). However, very few kinetic data are available concerning this problem in complexing media, which are highly advantageous for the deposition of Cu layers onto semiconductor surfaces, when the energetic position of acceptors state in a metal ion redox couple with respect to the bandedges of a semiconductor must be taken into account to a greater or lesser extent, and also for the electrodeposition of Cu alloys.

The initial stages of Cu electrodeposition onto foreign substrates have recently been investigated using Cu(II) pyrophosphate solutions [3, 4] and ammonia media [5, 6] and also Cu(I) thiocyanate solutions [7]. In particular, it has been shown that the Cu growth kinetics on a Si(100) substrate from pyrophosphate solution with a low Cu(II) concentration (c) is consistent with progressive nucleation followed by diffusion-limited growth, while for a higher c of Cu(II) there is a transition from progressive nucleation at more positive potentials (E) to instantaneous nucleation at more negative E [3]. In the case of a TiN substrate used as a diffusion barrier material, Cu electrochemical deposition from Cu(II) pyrophosphate solution has been shown to proceed through instantaneous nucleation followed by diffusion-controlled growth over a wide E range [4]. Cu electrocrystallisation from solutions of the copper ammonia complex onto a GC electrode has been suggested to follow the 3D progressive nucleation with the diffusion-limited growth mechanism [5]. When Cu electrodeposition is carried out using the TiN substrate, a strong influence of the deposition potential (E_{dep}) on the Cu electrocrystallisation mode is observed [6]. At lower overpotentials, the 3D nucleation is progressive and the growth of spheri-

* Corresponding author. E-mail address: nemezius@kchl.mii.lt

cal clusters is eventually limited due to coalescence. As the overpotential is increased to the second limiting current density, the 3D nucleation and growth mechanism has been proposed to become less favourable and the 2D nucleation and growth mechanism is preferred. The preliminary studies of the first stages of Cu electrocrystallisation from a near-neutral Cu(I) thiocyanate solution on a polycrystalline Au electrode [7] have shown for the first time that the chronoamperometric results obtained rather well fit the Scharifker and Hills model involving the progressive 3D nucleation and diffusion-controlled growth [8–10]. However, a more detailed examination of this process in the cited report has not been made.

The aim of the present work, which is a continuation of our previous work [7], is the characterisation of the initial stages of Cu electrodeposition onto polycrystalline Au from a near-neutral Cu(I) thiocyanate solution in more detail by means of cyclic voltammetry and potentiostatic step techniques.

EXPERIMENTAL

Solution. The working solution 0.05 M Cu(I) + 3 M KSCN was prepared as described elsewhere [7]. The solution pH was 5.8 ± 0.1 . Prior to each experiment, the working solution was deaerated with purified Ar gas for 0.5 h.

It has been known that Cu^+ ions, like other metal ions of a d^{10} -system, form complexes with SCN^- through a metal– SCN^- bond [11]. The complex species have been shown to be $\text{Cu}(\text{SCN})_n^{1-n}$, where $n = 2, 3, 4, 5$ and 6 [12, 13]. The distribution of the species was calculated using the values of cumulative stability constants as follows: $\log \beta_2 = 12.11$, $\log \beta_3 = 9.9$, $\log \beta_4 = 10.09$, $\log \beta_5 = 9.59$ and $\log \beta_6 = 9.27$ [12, 13] by the procedure described in [14]. The calculation showed that the equilibrium concentrations in the solution 3 M KSCN + 0.05 M Cu(I) used in our experiments were as follows: $\text{Cu}(\text{SCN})_2$ $3.97 \cdot 10^{-2}$, $\text{Cu}(\text{SCN})_3$ $7.03 \cdot 10^{-4}$, $\text{Cu}(\text{SCN})_4$ $2.85 \cdot 10^{-3}$, $\text{Cu}(\text{SCN})_5$ $2.83 \cdot 10^{-3}$, $\text{Cu}(\text{SCN})_6$ $3.89 \cdot 10^{-3}$, SCN^- (free) 2.87, Cu^+ $3.75 \cdot 10^{-15}$ M. One can see that the particle $\text{Cu}(\text{SCN})_2$ is the predominant complex species.

As regards the possibility of the formation of Cu_2O , the calculation of the maximum value of the equilibrium concentration of Cu^+ when the formation of bulk Cu_2O does not yet occur ($[\text{Cu}^+]_{\text{max}}$) according to the known equation

$$\log [\text{Cu}^+]_{\text{max}} = -0.84 - \text{pH} \quad (1)$$

gave a value of $ca. 2.3 \cdot 10^{-7}$ mol l^{-1} . A comparison of this quantity with the calculated equilibrium con-

centration of Cu^+ ions as one of the particles existing in the Cu(I) thiocyanate solution (see above) allows to conclude that low-soluble Cu_2O is not expected to be formed as a bulk phase.

Electrochemical measurements. All experiments were performed at 20 ± 0.1 °C in a conventional three-electrode cell. The working electrode was a vertical disc made from polycrystalline Au (99.95% purity) with a Teflon sheath (an exposed area was 0.5 cm^2). The determination of the real surface area of the Au electrode was given elsewhere [7]. The roughness factor (f) was found to be equal to 2.5 ± 0.05 . The counter-electrode was a Cu sheet of $ca. 4 \text{ cm}^2$ in the area. The reference electrode was an Ag/AgCl/KCl(sat.) electrode. In the text, all potentials were recalculated with respect to the standard hydrogen electrode (SHE).

The details of the preparation of the polycrystalline Au electrode for electrochemical measurements and those of the electrochemical experiments are given elsewhere [7].

In the potentiodynamic experiments, the potential was swept singly or repetitively starting with E_{start} to the negative direction. In chronoamperometric measurements, I/t traces were recorded starting with E_{start} to various deposition potentials E_{dep} situated in the Cu overpotential deposition (OPD) region. In all cases, before electrolysis the working Au electrode was allowed to stand at E_{start} for 1 min.

The reversible potential (E_r) for a couple Cu/Cu^+ , SCN^- was evaluated: (i) by measuring the open-circuit potential (OCP) of Cu in the working solution; OCP was found to be equal to $ca. -0.36$ V; and (ii) by equating E_r to the value of the crossover potential (E_c) recorded at a scan rate of 0.5 mV s^{-1} ; the E_c value was found to be about -0.38 V.

RESULTS AND DISCUSSION

Cyclic voltammetry. CV applied to polycrystalline Au in a blank solution of 3 M KSCN showed that the currents slightly decreased with the repetitive sweeps (not shown here), especially at the cathodic-going scans in the E region from about -0.4 to -0.8 V being of main interest in this study, and, for the essentially stabilized voltammetric curves, the background current did not exceed $ca. 1 \cdot 10^{-4}$ A in the cathodic half-cycle and $5 \cdot 10^{-5}$ A in the anodic one.

In addition, it can be mentioned that the SCN^- species has been estimated to bond strongly to Au, showing an E -dependent reorientation on this surface [15–18]. In particular, it has been found by *in situ* SNIPTIRS and SERS techniques that, in almost neutral unbuffered solutions, the adsorption of thiocyanate at polycrystalline Au in the region of

a more positive E (+0.230 to -0.170 V) occurs only via a S atom, whereas at a more negative E (e.g., at $E \leq -0.370$ V) the S- and N-bound thiocyanate co-exist [15, 16]. No evidence, however, for the N-bound thiocyanate from sum-frequency (SF) spectra of polycrystalline Au at negative E has been reported by other authors [18]. At the same time, the absence of any SF signal for $E < -0.250$ V has been thought to be consistent with a SCN^- species adsorbed flat on the surface in this E region. It has also been pointed out that a near-monolayer coverage of thiocyanate on polycrystalline Au exists throughout a double layer region [18]. There is a difference in the calculated binding energies for the adsorbed SCN^- particles at Au, namely, 1.42 and 1.51 eV for the S- and N-down adsorbed SCN^- species, respectively [15].

Bearing in mind the considerations on the E -dependent SCN^- orientation at the Au electrode surface, it can be concluded that the initial Cu electro-deposition occurs at the Au surface covered by the irreversibly adsorbed SCN^- species. It can also be expected that the coverage should be close to a monolayer. Relating the orientation of the adsorbed SCN^- species, the preference was given to the co-existence of S- and N-bound SCN^- on the Au surface, as stated in [15, 16].

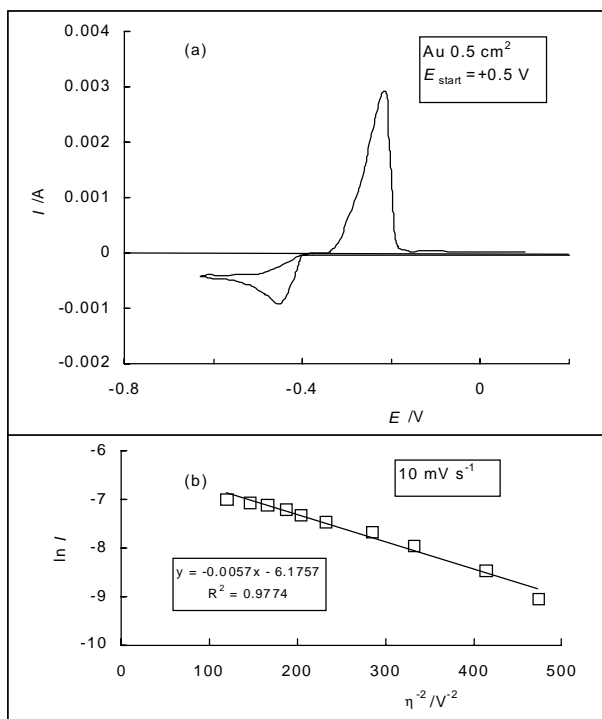


Fig. 1. (a) Cyclic voltammogram for Cu deposition and stripping onto polycrystalline Au electrode from 0.05 M Cu(I) + 3 M KSCN solution at 10 mV s^{-1} ; (b) $\ln I$ vs. η_c^2 plot obtained from I vs E curve (from Fig. 1a); E_r was taken to be equal to -0.36 V

The voltammetric response (the 1st scan) recorded with the polycrystalline Au electrode from 3 M KSCN + 0.05 M Cu(I) solution at 10 mV s^{-1} is presented in Fig. 1a. One can see that the cyclic voltammogram exhibits a single cathodic current peak and a single anodic one. The cathodic current peak at the peak potential (E_{pc}) of ca. -0.45 V is assigned to Cu overpotential deposition (OPD). The Cu OPD commences at about -0.40 V. Then, the anodic current peak is correspondingly assigned to the Cu stripping process. These results are assumed to indicate that, in the potential range -0.10 V to ca. -0.45 V in which the initial stages of Cu electrocrystallisation will be studied here (see below), the contribution of electrochemical reactions of SCN^- and that of surface oxide formation/reduction appear to be insignificant.

From the analysis of voltammetric data displayed in Fig. 1a, a question also arises whether the initial stages of Cu electrocrystallisation onto the polycrystalline Au surface include a limiting step of the formation of 3D nuclei. To make an estimate of the occurrence of 3D nucleation we can follow the considerations on the nature of a I vs E relationship relating to this problem [19]. In this Ref., it has been assumed that if the rate of the formation of nuclei is proportional to the probability of their occurrence, the current I , i.e. the rate of the limiting step of nucleation, varies directly with $1/\eta^2$:

$$\ln I = \text{const} - k_1/\eta^2, \quad (2)$$

where $k_1 = 16\pi\sigma^3v_m^2/3z^2F^2RT$, v_m is the molar volume of the depositing new phase, σ is surface tension. Hence, the voltammetric curve I vs. E corresponding to the limiting step of the formation of 3D nuclei of a new phase has been claimed to present a straight line in coordinates $\ln I$ vs. η^2 .

The rising part of the cathodic I vs. E curve (Fig. 1a) re-plotted in the coordinates $\ln I$ vs. η_c^2 (Fig. 1b) gives a straight line and therefore clearly indicates that, within a certain range of overpotentials, such limiting step is highly expected, in accordance with the qualitative criterion in [19].

Chronoamperometric results. The nucleation and growth during Cu OPD on the polycrystalline Au electrode from the nearly neutral Cu(I) thiocyanate solution were further studied by the conventional potential step technique. Figure 2 shows a set of cathodic current transients recorded starting from $E_{\text{start}} = -0.30$ V to various values of E_{dep} . Most of these transients are typical of a metal 3D nucleation and diffusion-controlled growth process onto a foreign substrate [8–10]. The capacitive part of the transient is followed by a rise in the value of the current due to an increase in the effective electrode surface area as the nuclei form

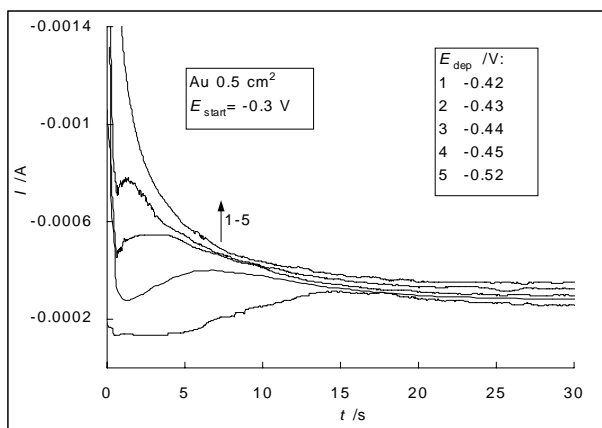


Fig. 2. Potentiostatic current transients for Cu deposition onto a polycrystalline Au electrode in 0.05 M Cu(I) + 3 M KSCN solution, recorded after a potential pulse from -0.30 V to various values of Cu deposition potential E_{dep}

and grow in size [8, 9]. The current reaches the maximum (I_{max}) at a corresponding time (t_{max}), as the hemispherical diffusion zones radiating from each growing nucleus begin to overlap and the hemispherical mass transfer becomes a semi-infinite linear diffusion to a planar surface of the electrode. Finally, at $t > t_{\text{max}}$, a rather slow decrease in the current should be typical of an electrode reaction limited by a semi-infinite linear diffusion of discharging ions, and the current–time relation should follow the Cottrell relationship [8–10].

Several models have been developed for the 3D nucleation and growth processes taking place during bulk metal deposition on a foreign substrate [1, 2, 20, 21]. Up to now, the models involving two limiting cases of 3D nucleation, instantaneous or progressive, in conjunction with the hemispherical diffusion-controlled growth of the formed nuclei, developed by Scharifker and Hills (SH) [8–10], are widespread and adopted for analysing the initial stages of metal electrocrystallisation onto a foreign surface [20].

The most appropriate method for differentiating the two SH 3D nucleation models is to compare the experimental dimensionless current–time transients to the theoretical ones for each nucleation mechanism [8–10]. The following theoretical equations have been proposed [9] for instantaneous (3) and progressive (4) nucleation:

$$(I/I_{\text{max}})^2 = 1.9542(t/t_{\text{max}})^{-1}\{1 - \exp[-1.2564(t/t_{\text{max}})]\}^2, \quad (3)$$

$$(I/I_{\text{max}})^2 = 1.2254(t/t_{\text{max}})^{-1}\{1 - \exp[-2.3367(t/t_{\text{max}})^2]\}^2. \quad (4)$$

The experimental $(I/I_{\text{max}})^2$ vs. (t/t_{max}) plots obtained for the selected values of E_{dep} along with the theo-

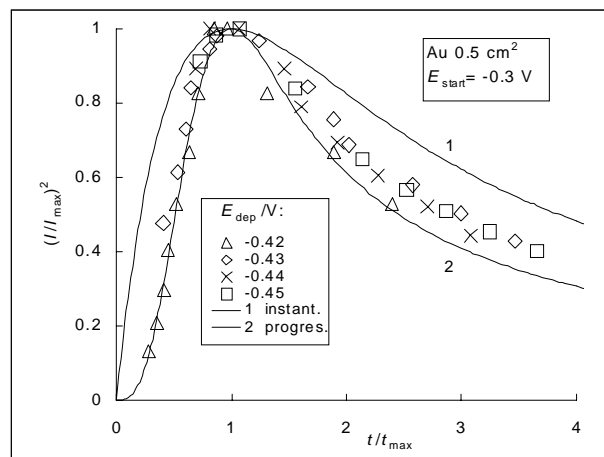


Fig. 3. Comparison of experimental reduced current–time dependences for Cu nucleation onto polycrystalline Au electrode from 0.05 M Cu(I) + 3 M KSCN solution (from Fig. 2) to the calculated reduced current–time dependences for the 3D nucleation models developed by Scharifker and Hills [8–10]

retical plots resulting from Eqs. (3) and (4) are shown in Fig. 3. These plots suggest that the initial stages of Cu deposition onto the polycrystalline Au electrode from the near-neutral Cu(I) thiocyanate solution in the E_{dep} range -0.42 to -0.45 V agrees rather well with the limiting SH model of progressive 3D nucleation.

Once it has been established that the 3D nucleation is progressive, it is possible to get an information about the diffusion coefficient (D) of the electroactive species from the maximum in the transients through the equation [9]:

$$I_{\text{max}}^2 \cdot t_{\text{max}} = 0.2598(zFc)^2D. \quad (5)$$

Taking the valence $z = 1$ and the concentration of Cu(I) $c = 5 \cdot 10^{-5}$ mol cm^{-3} and also using the current density maximum to the whole Au electrode surface (0.5 cm^2) instead of the current maximum, from a single experimental point ($I_{\text{max}}, t_{\text{max}}$) at the selected value of the E_{dep} , e.g., at -0.42 V, it was obtained that the calculated average diffusion coefficient D of the predominant Cu(I) thiocyanate complex was about $1.3 \cdot 10^{-6}$ $\text{cm}^2 \text{s}^{-1}$.

According to Ref [22], a single experimental point ($I_{\text{max}}, t_{\text{max}}$), also allows us to evaluate the stationary nucleation rate (I_{st}) from the atomistic theory of electrochemical nucleation [23]. The procedure to calculate this parameter is given in Appendix.

Figure 4 shows $-\ln M$ vs. t^2 plots (see, Appendix) obtained from the I/t transients at different values of E_{dep} (Fig. 2) taking $z = 1$, $c = 5 \cdot 10^{-5}$ mol cm^{-3} , $S = 0.5$ cm^2 and $v_m = 7.1$ $\text{cm}^3 \text{mol}^{-1}$. The values of the stationary nucleation rate I_{st} calcula-

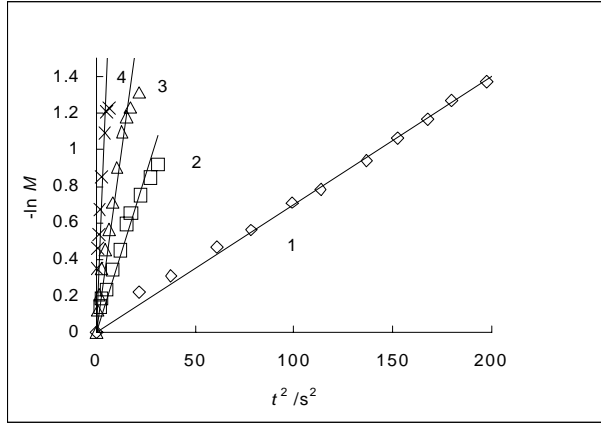


Fig. 4. $-\ln M$ vs. t^2 plots at the Cu deposition potentials E_{dep} : 1 -0.42 , 2 -0.43 , 3 -0.44 , 4 -0.45 V (according to the procedure described in Appendix)

Table. Data for I_{max} , t_{max} and I_{st} derived from chronoamperometric measurements

E_{dep} /V	$10^4 \cdot I_{\text{max}}$ /A	t_{max} /s	I_{st} /cm ⁻² s ⁻¹
-0.42	3.36	17.45	$2.72 \cdot 10^4$
-0.43	4.00	6.43	$2.56 \cdot 10^5$
-0.44	5.49	3.70	$5.32 \cdot 10^5$
-0.45	7.77	1.45	$2.29 \cdot 10^6$

ted from the slopes of these straight lines by means of Eq. (A. 7) are given in Table.

Then, using the E_{dep} -dependence of I_{st} it is possible to calculate the number of atoms in the critical nucleus (n_k) according to [22]:

$$n_k = (RT/zF)[d \ln I_{\text{st}}/d (-E_{\text{dep}})] - \alpha, \quad (6)$$

where α is the cathodic transfer coefficient, which is taken here to equal 0.5, the value of $d \ln I_{\text{st}}/d (-E_{\text{dep}})$ was estimated directly from the plot in coordinates $\ln I_{\text{st}}$ vs. $(-E_{\text{dep}})$ (Fig. 5). Thus, it was found

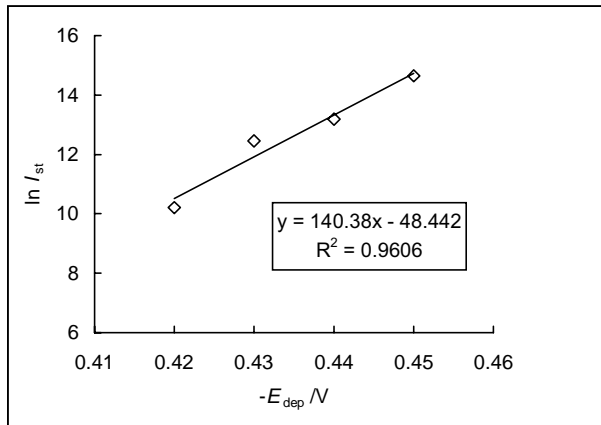


Fig. 5. Variation of I_{st} with E_{dep} during Cu deposition on Au

that $n_k \approx 3$. If the coefficient α is much less than 0.5 as revealed usually for the complexing media, say $\alpha = 0.2$, it becomes apparent that the parameter n_k is *ca.* 3.3, *i.e.* sufficiently close to the quantity of 3.0. So, it can be concluded that, in a more general way, n_k is no less than 3.

CONCLUSIONS

It was confirmed that the initial stages of electrocrystallisation of Cu onto a polycrystalline Au substrate can be described by the Scharifker and Hills model involving the progressive 3D nucleation and diffusion-controlled growth of the formed nuclei. From the atomistic theory of electrochemical nucleation and the chronoamperometric data obtained, the value of stationary nucleation rate I_{st} of Cu onto polycrystalline Au was calculated at various deposition potentials E_{dep} . In the E_{dep} region from -0.42 to -0.45 V, the calculated values of I_{st} varied from $2.72 \cdot 10^4$ to $2.29 \cdot 10^6$ cm⁻² s⁻¹. On the basis of E_{dep} -dependence of I_{st} , the number of Cu atoms in the critical nucleus n_k was estimated and obtained to be no less than 3.

APPENDIX

According to [8], the cathodic current vs. time relationship and the coordinates (I_{max} , t_{max}) of the maximum of the potentiostatic current transient corresponding to the case of the progressive 3D nucleation are given, respectively, by:

$$-I(t) = (zFcD^{1/2}/(\pi t)^{1/2}) \cdot [1 - \exp(-0.5I_{\text{st}}\pi k'Dt^2)], \quad (\text{A. 1})$$

$$-I_{\text{max}} = 0.46 zFSc(D^3k')^{1/4} I_{\text{st}}^{-1/2}, \quad (\text{A. 2})$$

$$t_{\text{max}} = 2.16(\pi k'D)^{-1/2} I_{\text{st}}^{-1/2}, \quad (\text{A. 3})$$

where $I_{\text{st}} = AN_{\infty}$, N_{∞} is the maximum number of nuclei obtainable under the prevailing conditions, *i.e.* it may be thought as the total number of available sites (however, the final number of nuclei observed experimentally is more usually controlled by other factors [8]), A is the steady state nucleation rate constant per site, $k' = (4/3)(8\pi c v_m)^{1/2}$, v_m is the molar volume of the depositing metal, S is the surface area of working electrode. Then, the product $I_{\text{max}} \cdot t_{\text{max}}^{1/2}$ can be given by [22]:

$$-I_{\text{max}} \cdot t_{\text{max}}^{1/2} = 0.9032S\pi^{-1/2} zFcD^{1/2}. \quad (\text{A. 4})$$

From Eqs. (A. 1) and (A. 4) one can obtain:

$$-\ln M = Qt^2, \quad (\text{A. 5})$$

where

$$M = 1 - 0.9032 I t^{1/2} / I_{\max} \cdot t_{\max}^{1/2}, \quad (\text{A. 6})$$

$$Q = 0.613 \pi^2 k' t_{\text{mzx}} I_{\max}^2 I_{\text{st}} / (z F S c)^2. \quad (\text{A. 7})$$

So, it follows from Eq. (A. 5) that the potentiostatic I/t transient at a selected value of E_{dep} is transformed into a straight line passing through the origin, and the stationary nucleation rate I_{st} could be determined from the slope Q of this straight line.

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D. Šimkūnaitė, I. Valsiūnas, E. Ivaškevič ir
A. Steponavičius

VARIO-KOBALTO LYDINIO ELEKTROLITINIS NUSODINIMAS IŠ TIOCIANATINIŲ TIRPALŲ 2. Cu ELEKTROCHEMINĖS KRISTALIZACIJOS ANT POLIKRISTALINIO Au ELEKTRODO PIRMOSIOS STADIJOS

S a n t r a u k a

Linijinio potencialo skleidimo ir potencialo įjungimo metodais buvo nustatyti Cu elektrocheminės kristalizacijos ant polikristalinio Au elektrodo pirmųjų stadijų parametrai beveik neutraliame 0,05 M Cu(I) + 3 M KSCN tirpale, esant 20°C temperatūrai. Patvirtinta anksčiau šio straipsnio autorių padaryta išvada, kad Cu elektrocheminės kristalizacijos ant Au pirmosios stadijos pakankamai gerai aprašomos progresuojančiu 3D kristalų užuomazgų susidarymo ir difuzijos kontroliuojamo tolesnio jų augimo modeliu (pasiūlė Scharifker ir Hills). Remiantis atomistine metalų elektrocheminės kristalizacijos teorija, taip pat šiame darbe gautais chronoamperometriniais duomenimis, nustatytos pastoviojo Cu kristalizacijos ant Au elektrodo greičio I_{st} reikšmės. Parodyta, kad Cu nusodinimo potencialų intervale nuo -0,42 iki -0,45 V I_{st} kinta nuo $2,72 \cdot 10^4$ iki $2,29 \cdot 10^6 \text{ cm}^{-2} \text{ s}^{-1}$. Pritaikius I_{st} priklausomybę nuo Cu nusodinimo potencialo ir Milchevo su bendradarbiais pasiūlytą metodą, apskaičiuotas Cu atomų skaičius kritinėje kristalinėje užuomazgoje n_k . Gauta, kad šis parametras yra ne mažesnis kaip 3.