the society for solid-state
and electrochemical
science and technology

Journal of The Electrochemical Society

Electrodeposition of Cu Nanoparticles on BDD Electrodes: Reactions and Nucleation Mechanism

J. T. Matsushima, L. C. D. Santos, A. B. Couto, M. R. Baldan and N. G. Ferreira

J. Electrochem. Soc. 2012, Volume 159, Issue 4, Pages D246-D252.
doi: 10.1149/2.093204jes

Email alerting service

Receive free email alerts when new articles cite this article - sign up
in the box at the top right corner of the article or [click here](#)

To subscribe to *Journal of The Electrochemical Society* go to:
<http://jes.ecsdl.org/subscriptions>

Electrodeposition of Cu Nanoparticles on BDD Electrodes: Reactions and Nucleation Mechanism

J. T. Matsushima,^z L. C. D. Santos, A. B. Couto, M. R. Baldan, and N. G. Ferreira

Instituto Nacional de Pesquisas Espaciais – INPE, São José dos Campos, Brazil

In this paper, the Cu electrodeposition on boron doped diamond (BDD) electrodes was studied. The reactions and the nucleation mechanism were evaluated by analyzing the influence of different electrolytes and Cu^{2+} ion concentrations in the solution. The cyclic voltammetry results showed that the Cu deposition and dissolution processes were affected by the solution pH. In acidic solutions (pH~2.0), the energy required to initiate the nucleation process was higher than that for the Na_2SO_4 solution (pH~5.0). The nucleation mechanisms were examined by fitting the experimental chronoamperometric data into appropriated nucleation models. Using the model developed by Scharifker-Hill, the Cu nucleation mechanism in $0.1 \text{ mol L}^{-1} \text{ Cu}^{2+}$ ions concentration was inconclusive – independent of the pH solution. However, the Cu nucleation mechanism was conclusive in $10^{-3} \text{ mol L}^{-1} \text{ CuSO}_4$ solutions containing Na_2SO_4 and H_2SO_4 as electrolyte. So, from $(i/i_{\text{max}})^2$ vs t/t_{max} profile, Cu instantaneous nucleation was verified. Other more complete models of nucleation like those developed by Sharifker-Mostany (SM) and Hermann-Tarallo (HT), also confirmed the Cu instantaneous nucleation, from the Cu nuclei density (N_0) determined by fitting the potentiostatic transients. © 2012 The Electrochemical Society. [DOI: 10.1149/2.093204jes] All rights reserved.

Manuscript submitted November 28, 2011; revised manuscript received January 12, 2012. Published February 7, 2012.

The deposition process of metallic nanoparticles on foreign substrates has attracted high attention due to the different properties of nanoparticles compared to those of bulk materials.¹ This process leads to an increase in the surface roughness, thereby providing an increase in the conductive area, with a corresponding sensitivity increase. Besides, the electrode surface modification with metallic nanoparticles may increase the electrocatalytic activity considering its application in electroanalysis. In particular, this condition may lead to an improvement at the ability to recognize and/or to amplify the current signal, which at the same time may make the analysis more selective due to the electrocatalytic effect, i.e., by decreasing in the overpotential of the electrode processes and leading to a better separation of the voltammetric peaks.

Among several deposition techniques, the electrodeposition is one of the most used to deposit metallic nanoparticles.^{2,3} However, the thermal decomposition⁴ and the microemulsion synthesis⁵ have also been used. The major advantages offered by the electrodeposition are their simplicity, compatibility of the processing at room temperature and the controllability of the thin film properties.

Particularly, the electrodeposition of the Cu nanoparticles on foreign substrates has been applied in order to increase the electrocatalytic activity for the electrochemical detection of the nitrate.^{6–11} In recent years, due to the excessive use of fertilizers in agriculture, the nitrate amount found in natural water increased significantly. Depending on its concentration, the nitrate may cause environment problems and affect human health.^{12,13} Therefore, the control of the nitrate amount in natural water is very important, especially by using the electrochemical process.

Taking into account the development of new materials for electrochemical applications, the boron doped diamond (BDD) films have been considered as one of the most effective electrodes.^{14,15} The BDD presents excellent physical-chemical properties, such as low background currents, a wide potential window for analyzing the chemical species without involving the water decomposition reaction, a high corrosion resistance, as well as mechanical stability. As far as we know, there are only some papers in the literature that deal with the Cu electrodeposition on BDD electrodes.^{9–11,16–19} However, a study regarding the initial stage of Cu electroformation, i.e., the Cu nucleation on BDD electrodes has not yet been developed and explained. The comprehension of the initial stage of the Cu electroformation becomes increasingly important because it may involve the most critical stage to define the final film properties, such as the general appearance and the deposit structure. The study of nucleation via electrochemical methods has an important advantage over other methods, since

the driving force of the nucleation may be varied simply by varying the applied potential.²⁰ The nucleation process is normally associated with two and three-dimensional growth where the number of nuclei formed on the surface electrode depends on the applied overpotential. In order to characterize the mechanism and kinetics of the nucleation in a quantitative way, conventional electrochemical techniques of potentiostatic current transient measurements are used. The obtained data have been interpreted by applying different and useful theoretical methods developed for this purpose.^{21–24} Considering the importance of the nucleation process, this paper proposes, for the first time, to evaluate Cu reactions and nucleation mechanisms on the BDD electrode as function of the different electrolyte types and the Cu^{2+} ion concentration in the solution.

Experimental

The Cu electrodeposition was studied on highly doped diamond films grown by hot filament assisted chemical vapor deposition (HFCVD) technique at 780°C and 7h. A gaseous mixture (99% vol. H_2 and 1% vol. CH_4) with a pressure of 50 Torr was used. The boron doping was obtained from H_2 forced to pass through a bubbler containing B_2O_3 dissolved in methanol. From the Mott Schottky plot, the doping level was estimated to approximately 10^{20} boron atoms cm^{-3} .²⁵

The electrochemical measurements were made using the Autolab PGSTAT 302 equipment with a three-electrode cell. The BDD films were used as a working electrode and the geometric area in contact with the electrolyte was 0.27 cm^2 . A platinum coil wire served as a counter electrode and the Ag/AgCl electrode was used as a reference electrode. The electrochemical behavior of the Cu on BDD electrodes was evaluated by cyclic voltammetry measurements using aqueous solutions of Cu^{2+} containing different supporting electrolytes. Two solutions containing $10^{-3} \text{ mol L}^{-1} \text{ CuSO}_4 + 1.0 \text{ mol L}^{-1} \text{ HClO}_4$ and $10^{-3} \text{ mol L}^{-1} \text{ CuSO}_4 + 1.0 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ (pH~2.0) were used to evaluate the influence of the anion type, while the solution containing $10^{-3} \text{ mol L}^{-1} \text{ CuSO}_4 + 0.5 \text{ mol L}^{-1} \text{ Na}_2\text{SO}_4$ (pH~5.0) was used to analyze the pH effect. The morphological characterization of the BDD electrode in different stages of the Cu deposition and dissolution processes was made by the Atomic Force Microscopy (AFM) analysis. In all experiments, the electrolytic solutions were prepared using reagents with analytical grade and water purified by the reverse osmosis system. Prior to the experiments, the solutions were deaerated with N_2 gas for 10 min.

The Cu nucleation mechanism was evaluated by using potentiostatic current transient measurements in solutions with different electrolyte types and Cu^{2+} concentrations. The nucleation potential was

^z E-mail: jtmatsushima@yahoo.com.br

determined by using the cyclic voltammogram. In order to understand the nucleation and growth of Cu on the BDD electrodes, adequate theoretical models were applied.

Results and Discussion

The Cu electrochemical reactions on BDD electrode were investigated by cyclic voltammetry. The reactions were accompanied by the electrode surface morphology examination from the AFM analysis to correlate the electrochemical data with the solid reaction products formed on the electrode surface. The cyclic voltammogram of the Cu on BDD electrode in $10^{-3} \text{ mol L}^{-1} \text{ CuSO}_4 + 0.1 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ solution ($\text{pH} \sim 2.0$) as well as the AFM images, obtained at different stages, during the occurrence of the Cu electrochemical reactions are shown in Fig. 1. The AFM image (A) presents the BDD surface condition at the beginning of the cyclic voltammogram showing the topography of the polycrystalline BDD surface. When the potential is shifted to more negative values, an increase in the cathodic current

at -0.2 V is associated with the onset of the Cu deposition due to the reduction reaction of the Cu^{2+} ions to metallic Cu. A current peak at -0.4 V followed by a current decrease is a characteristic of the diffusion controlled Cu deposition process. At -0.4 V , a new AFM image (B) was obtained and a change in the BDD topography may be associated with the increase in the density of small particles of Cu electrodeposited on grain faces of the BDD. An abrupt increase in the current at -0.6 V is attributed to the hydrogen evolution reaction due to the water decomposition on the BDD electrode surface. Reversing the potential at -0.7 V , the Cu deposition proceeds up to -0.07 V . This behavior is confirmed by the AFM image (C) where a higher amount of Cu small particles of Cu on grain faces of the BDD may be observed due to the massive deposition of Cu. In this potential range, two crossovers between cathodic current branches are visualized. According to Fletcher et al. the more cathodic crossover at -0.26 V corresponds to the nucleation overpotential (E_n) where the parameters of the nucleation and the growth mechanism are taken, while the second crossover at -0.07 V corresponds to the Cu/Cu^{+2} reversible

Figure 1. Cyclic voltammogram of the Cu on the BDD electrode obtained in a solution containing $10^{-3} \text{ mol L}^{-1} \text{ CuSO}_4 + 0.1 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ and AFM images (A-D) of the BDD surface at four stages during the Cu deposition and dissolution processes. Sweep rate of 20 mV s^{-1} .

Figure 2. Cyclic voltammograms of the Cu on the BDD electrode obtained at different solutions. Sweep rate of 20 mV s^{-1} . Inset: the cyclic voltammogram of the Cu on the BDD electrode in $10^{-3} \text{ mol L}^{-1} \text{ CuSO}_4 + 0.5 \text{ mol L}^{-1} \text{ Na}_2\text{SO}_4$ solution for a better visualization of the deposition and dissolution processes. (Observation: The Fig. 2 has already been published in a paper accepted by the *Quimica Nova*, prepared by the same authors of this manuscript).

potential (E_{rev}).^{26,27} As for potential scanning to more positive values two Cu dissolution processes are observed. A current peak at 0.12 V is associated to the Cu dissolution process corresponding to the oxidation of metallic Cu to Cu^{2+} ions, followed by a current shoulder at 0.2 V that may be attributed to the oxidation process of Cu^+ to Cu^{2+} ions. The details of these two Cu oxidation processes will be discussed later on. In order to complete the correlation between the electrochemical data and the solid reaction products, the AFM image (D) was obtained at the end of the cyclic voltammogram. The same topography (only the morphology of the BDD surface) was observed when compared to the AFM image (A), indicating the total dissolution of Cu on the BDD electrode surface.

The solution composition is an important experimental parameter to be considered in the electrodeposition process. As mentioned before, three electrolytes were used: H_2SO_4 and HClO_4 electrolytes (pH~2 solutions) and Na_2SO_4 electrolyte (pH~5.0 solution). The cyclic voltammetric curves of the Cu on the BDD electrode in these three electrolytic solutions are presented in Fig. 2. According to them, practically the same electrochemical behavior of the Cu at pH~2.0 solutions was observed. As a result, the Cu electrodeposition on the BDD electrode is not influenced by any type of anions in the solution, where the adsorption process of these anions did not interfere in the Cu electrodeposition process. Nonetheless, the highest cathodic current observed in the solution containing H_2SO_4 as a supporting electrolyte, due to the hydrogen evolution reaction, which is associated to the difference regarding the arrangement of the electrical double layer. On the other hand, the cyclic voltammetric behavior of the Cu in the pH~5.0 solution was quite different. In the negative potential sweep, the onset of the Cu reduction process occurred at a more positive potential without interference of the hydrogen evolution reaction when compared to the one in the pH~2.0 solutions. In this case, the energetically favorable discharge of the Cu^{+2} ions on the BDD/electrolyte in the pH~5.0 solution may be explained by the highest ionic strength of this solution. The presence of the Cu reduction processes (Ic and IIc) in the pH~5.0 solution, which is better visualized in the inset of Fig. 2, is attributed to the reduction of the Cu^{2+} to Cu^+ ions (Ic process) and to the reduction of the Cu^{2+} ions to metallic Cu (IIc process). The occurrence of the Ic process involving a small cathodic current in the pH~5.0 solution may be associated to the hydrolysis reaction of the CuSO_4 , where the $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ species may be reduced to the $\text{Cu}_x(\text{OH})^{(2x-y)+}$ leading to the appearance of the Ic process that is not visualized in the pH~2.0 solutions.²⁸ The

Ic and IIc processes attributed to this mechanism were also observed by Grujicic and Pesic for the Cu electrodeposition on vitreous carbon electrodes.²⁹ The initial cathodic current corresponding to the Ic process is assigned to the reduction of Cu^{2+} to Cu^+ ions according to the following reaction:

Based on Eq. 1, it may be deduced that there may be a disproportionation of the produced Cu^+ ions into metallic Cu and Cu^{2+} ions, as it is shown in Eq. 2.

The Ic process is immediately accompanied by the IIc process as a consequence of the direct reduction of the Cu^{2+} ions (from the Cu^{2+} ions of the bulk solution and those from Eq. 2) to metallic Cu according to the Eq. 3.

As it can be seen at the cyclic voltammograms of the Cu in the pH~2.0 solutions, only the cathodic current involved in the IIc process is observed. In this pH condition, the Ic process is not observed, but the appearance of an anodic current shoulder (labeled Ia process), during the potential sweep to more positive values, may be an evidence of the occurrence of the reduction reaction associated to the Ic process, which will be discussed below.

In the reverse potential sweep, the appearance of two crossovers between the cathodic current branches in the three solutions defines the Cu nucleation overpotential (E_n) and the Cu/ Cu^{+2} reversible potential (E_{rev}).^{26,27} Both potentials were previously defined in Fig. 1. In the three solutions studied, the E_{rev} presented the same value. However, the more positive of the E_n verified in the pH~5.0 solution indicates that the nucleation work required to form Cu nuclei is lower when compared to the one in the pH~2.0 solutions, due to the discharge of the Cu^{2+} ions on the BDD/electrolyte interface. At a more positive potential, two regions of the anodic current in the three solutions are observed. The first anodic process, labeled IIa, corresponds to the oxidation of the metallic Cu to the Cu^{2+} ions presented in Eq. 4:

The appearance of the anodic current shoulder, due to the Ia process, may be associated to the oxidation of the Cu^+ to Cu^{2+} ions (Eq. 6) produced by the disproportionation reaction (Eq. 5) where a better definition of the Ia process in the pH~5.0 solution may be justified by the oxidation reaction of the Cu^+ ions favored by the pH condition and the ionic strength, as previously discussed. After the Ia process, the current falls to zero, indicating that all the metallic Cu deposited on the BDD was extinguished from the BDD surface and that the Cu^+ ions were oxidized to Cu^{2+} ions.

From the results previously presented, it was verified that the Eqs. 1 and 6, were particularly influenced by the pH solution, where the Ic and Ia processes were not well defined in the pH~2.0 solutions.

Hung et al. also verified the presence of an anodic current shoulder, but they associated this behavior to a possible occurrence of ad-ions desorption of Cu on the pyrolytic graphite.³⁰ According to them, this process may be attributed to the specific adsorption of Cu^{2+} ions occurred during the negative potential sweep, and depending on the intrinsic difference of the substrate, the underpotential process may occur. In this case, the underpotential deposition was not attributed to the Ic process because the main evidence, which refers to the occurrence of this same process in a more positive potential regarding the E_{rev} of Cu^{2+}/Cu (Fig. 1) was not observed.

Besides the study of Cu electrochemical reactions, the nucleation mechanism was also evaluated. With this purpose, chronoamperometric measurements were carried out using different electrolytes as well as different Cu^{2+} ion concentrations. The potential was stepped from

Figure 3. Potentiostatic transients recorded in $0.1 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ solution in different Cu^{2+} ions concentrations. Inset: the potentiostatic transient recorded in $10^{-3} \text{ mol L}^{-1} \text{ Cu}^{2+}$ ions + $0.1 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ solution.

an initial value, where the Cu is not deposited on the electrode surface, to a defined potential range in the Cu deposition region characterized by cyclic voltammetry.

Fig. 3 shows the potentiostatic transients in the H_2SO_4 solution obtained at three different Cu^{2+} ion concentrations. The transients exhibited the typical shape for a nucleation process with three-dimensional growth of nuclei limited by the diffusion of the electroactive species,²¹ except for the solution containing $0.1 \text{ mol L}^{-1} \text{ Cu}^{2+}$ ions. A better visualization of the potentiostatic transient regarding the three-dimensional growth of Cu nuclei can be seen in the inset of Fig. 3, which shows the nucleation process of Cu in solution containing $0.001 \text{ mol L}^{-1} \text{ Cu}^{2+}$ ions. According to Hyde and Compton, the nucleus growth at low ionic concentrations and at high overpotentials is limited by

the rate at which the material is transported from the solution to the electrode surface.²⁰ In this concept, the Cu^{2+} species diffusion from the solution bulk to the electrode/solution interface is the slow step of the process. In this case, the potentiostatic transient is characterized by the appearance of a maximum current, which is associated to the overlap of the diffusion zones and the development of the nucleation exclusion zones around the nuclei already established. The same behavior was not assigned to the Cu nucleation process in $0.1 \text{ mol L}^{-1} \text{ Cu}^{2+}$ concentration, since in this condition is probably controlled by the charge transfer, i.e., the nucleus growth rate is limited by the velocity at which the Cu^{2+} ions can be incorporated into the new phase, where the overlap of the diffusion zones was not possible to occur.

The typical shape of these transients is well defined in Fig. 4, where the current response as a function of the time at different electrolytes containing $10^{-3} \text{ mol L}^{-1} \text{ Cu}^{2+}$ ions was obtained. In the $\text{pH} \sim 5.0$ solution (Na_2SO_4 electrolyte), a lower amount of energy was required to initiate the Cu nucleation process compared to that discussed in Fig. 2. In this case, an applied potential range between -0.35 V to -0.61 V was necessary. In a very short time, an abrupt increase in the current density was observed, which is associated to the growth of a new metallic phase and/or to the increase in the number and size of Cu nucleus. At later stages, the diffusion zones of adjacent nuclei are overlapped, and the current reached a maximum level followed by a decrease in the current transient. After longer periods of time elapsed, the current reached a plateau corresponding to the current limited by the Cu^{2+} species diffusion, which obeys the Cottrell equation.

The analysis of the other two electrolytes followed the same procedure, but different potential were applied. The nucleation kinetic presents two limiting cases: instantaneous and progressive nucleation. In the first case, all the active sites available on the electrode surface will be occupied in a very short period of time after applying overpotentials and, as a consequence, the nuclei start to grow. Therefore, instantaneous nucleation occurs when the nucleation rate is very high. If the nucleation rate has a low value, the nucleation process will be progressive. Thus, the nuclei are continuously formed during the whole time at which the overpotential is applied.

Figure 4. Potentiostatic transients recorded at different nucleation potential in $10^{-3} \text{ mol L}^{-1} \text{ CuSO}_4$ solution containing (A) $0.5 \text{ mol L}^{-1} \text{ Na}_2\text{SO}_4$, (B) $0.1 \text{ mol L}^{-1} \text{ HClO}_4$ and (C) $0.1 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$.

Figure 5. Dimensionless curves, $(i/i_{\max})^2$ vs $t/t_{\max}$ experimental and theoretical for instantaneous and progressive for the Cu nucleation mechanism on BDD electrode in solution containing (A) $0.1 \text{ mol L}^{-1} \text{ CuSO}_4 + 0.5 \text{ mol L}^{-1} \text{ Na}_2\text{SO}_4$ and (B) $0.1 \text{ mol L}^{-1} \text{ CuSO}_4 + 0.1 \text{ mol L}^{-1} \text{ HClO}_4$.

In order to evaluate the kinetic parameters for Cu nucleation, the characterization of the nucleation process as instantaneous or progressive is necessary. A comparison between the experimental curves and theoretical data, obtained from the appropriate models, allow us to understand the nucleation and the growth type. In the literature, there are several methods that utilize the coordinates of chronoamperometric curves to the determinate nucleation mechanisms and also the parameters related to the nucleation process. According to the model developed by Scharifker and Hills (SH),²¹ the nucleation could occur either instantaneously or progressively. The kinetic may be evaluated from the criteria that distinguish between these two extreme forms. The experimental potentiostatic transients were normalized to dimensionless form $(i/i_{\max})^2$ vs $t/t_{\max}$ and then compared with theoretical $(i/i_{\max})^2$ vs $t/t_{\max}$ curves derived for the instantaneous and progressive three-dimensional nucleation models presented by the Eqs. 7 and 8, respectively:

$$\left(\frac{I}{I_{\max}}\right)^2 = \frac{1.9542}{t/t_{\max}} \left\{ 1 - \exp \left[-1.2564 \left(\frac{t}{t_{\max}} \right) \right] \right\}^2 \quad [7]$$

$$\left(\frac{I}{I_{\max}}\right)^2 = \frac{1.2254}{t/t_{\max}} \left\{ 1 - \exp \left[-2.3367 \left(\frac{t}{t_{\max}} \right)^2 \right] \right\}^2 \quad [8]$$

Fig. 5 presents the $(i/i_{\max})^2$ vs $t/t_{\max}$ profile in solutions containing $0.1 \text{ mol L}^{-1} \text{ Cu}^{2+}$ ions. In all electrolytic composition, the nucleation mechanism was inconclusive. The use of the SH model was not adequate because the $i_{\max}$ and $t_{\max}$ were not observed in the potentiostatic transient (Fig. 3), making it impossible to analyze the nucleation mechanism from the normalized potentiostatic curves. The $(i/i_{\max})^2$ vs $t/t_{\max}$ profiles for more dilute Cu^{2+} ions solutions (10^{-2} up to $10^{-3} \text{ mol L}^{-1}$) is shown in Fig. 6. According to the profiles in Figs. 6C–6D, the Cu nucleation mechanism evaluated in Cu^{2+} ions solution containing HClO_4 as supporting electrolyte was not conclusive in the limit of very short time. However, in the limit of very long time, the Cu nucleation was defined as instantaneous. On the other hand, the Cu nucleation evaluated in Cu^{2+} ions solutions containing Na_2SO_4 and H_2SO_4 as electrolyte was conclusive in the time period analyzed, as presented in Figs. 6A–6B and 6E–6F. For both conditions, the nucleation mechanism was well defined in $10^{-3} \text{ mol L}^{-1} \text{ CuSO}_4$ solution and the instantaneous nucleation was verified from $(i/i_{\max})^2$ vs $t/t_{\max}$ profiles, as presented in Fig. 6B and 6F.

Based on the established instantaneous nucleation mechanism, the Cu nuclei density was calculated using the Scharifker-Hills model considering the peak coordinates on a current transient,²¹ according to Eq. 9:

$$N_0 = \left(\frac{1}{8\pi C_0 V_m} \right)^{\frac{1}{2}} \left(\frac{nFC_0}{i_{\max} t_{\max}} \right)^2 \quad [9]$$

where n is the number of electrons involved, F is the Faraday constant, C_0 is the concentration of species in the bulk, V_m is the molar volume,

$t_{\max}$ is the peak time and, $i_{\max}$ is the peak current. The Cu nuclei density was calculated using the conclusive Cu nucleation mechanism on the BDD electrode. Table I presents the calculated values of Cu nuclei density for the Cu instantaneous nucleation on the BDD electrode. It was verified that the applied overpotential influenced the Cu nuclei density. In the nucleation process in $0.1 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ solution the Cu nuclei density increased about five times, when compared to that in $0.1 \text{ mol L}^{-1} \text{ HClO}_4$ solution.

Although the SH model is widely used to define the characteristic shape for instantaneous and progressive nucleation, it is difficult to extract useful parameters from it, as indicated by Hyde and Compton.²⁰ In this model the instantaneous and progressive character of the reactions has to be treated separately and the estimation of the nucleation parameters is based only on a single point ($t_{\max}$ and $i_{\max}$). Thus to estimate the kinetic parameters, other models were used to simulate more adequately the Cu nucleation mechanism on BDD electrodes. The Sharifker and Mostany (SM) model introduces a considerable improvement in the potentiostatic current transient simulation and it is not necessary to classify the nucleation process as instantaneous or progressive in order to obtain the kinetic parameters.²² The nucleation rate constant, A , and the active sites density on the substrate surface, N_0 , can be estimated separately from the current density recorded during an experimental potentiostatic transient employing the Eq. 10:

$$i(t) = \left(\frac{zFD^{1/2}c}{\pi^{1/2}t^{1/2}} \right) \left\{ 1 - \exp \left[-N_0 \pi k^* D \left(t - \frac{1 - e^{-At}}{A} \right) \right] \right\} \quad [10]$$

where $k^* = (8\pi cM/\rho)^{1/2}$, zF is the molar charge transferred during electrodeposition, c is the species concentration in the bulk, M is the mass molar of the deposit, D is the diffusion coefficient and ρ is the density of the deposited material.

The N_0 values obtained from potentiostatic transients fitted using the Eq. 10 (SM model) as seen in Table I corroborate with the

Table I. Calculated values of the N_0 for the instantaneous nucleation according to Eqs. 9–11.

Solutions containing $10^{-3} \text{ mol L}^{-1} \text{ Cu}^{2+}$	Overpotential (mV)	$N_0 \text{ (cm}^{-2}\text{)}$		
		SH model	SM model	HT model
$0.5 \text{ mol L}^{-1} \text{ Na}_2\text{SO}_4$	0.49	8.61	8.19	7.93
	0.51	9.91	8.60	8.98
	0.55	13.4	11.4	11.4
$0.1 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$	0.49	23.2	24.7	29.5
	0.51	26.8	28.3	31.2
	0.55	44.2	34.8	31.4
$0.1 \text{ mol L}^{-1} \text{ HClO}_4$	0.49	5.61	9.00	8.54
	0.51	4.98	9.14	9.41
	0.55	7.97	9.20	8.40

Figure 6. Dimensionless curves, $(i/i_{\max})^2$ vs $t/t_{\max}$ experimental and theoretical for instantaneous and progressive for the Cu nucleation mechanism on BDD electrode in different Cu concentrations containing as electrolyte (A-B) $0.5 \text{ mol L}^{-1} \text{ Na}_2\text{SO}_4$, (C-D) $0.1 \text{ mol L}^{-1} \text{ HClO}_4$ and (E-F) $0.1 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$.

nucleation type already defined by SH model in the Na_2SO_4 and H_2SO_4 solutions, but N_0 values adjusted in HClO_4 solution were observed. In this case, this adjustment may be considered, since the N_0 values were estimated by fitting the entire potentiostatic transients.

According to Sluters-Rehbach et al.²³ the SM model predicts the correct value of the current density in the limit of longer time (Cottrell decayment) but does not simulate the current transient correctly in the limit of very short time. Hermann and Tarallo²⁴ developed another model that combines the approach of the Sharifker-Mostany and Sluters-Rehbach models. According to them, such suggested adjustments must be discouraged because their utility to get qualitative conclusions is not definitive in all cases.²⁴ However, an additional efficacy of these adjustments is that, if the experimental data fall within range of validity of the theory proposed, the full equation may be used to predict the overall behavior. Hermann and Tarallo have proposed a correction to the model initially proposed by SM, where the deviation may be adjusted by using the Eq. 11²⁴

$$i(t) = zFDc \frac{1}{(\pi Dt)^{1/2}} \frac{\Phi}{\Theta} \{1 - \exp[-\alpha N_0 (\pi Dt)^{1/2} t^{1/2} \Theta]\} \quad [11]$$

where

$$\Phi = 1 - \frac{\exp(-At)}{(At)^{1/2}} \int_0^{(At)^{1/2}} \exp(\lambda^2) d\lambda$$

and

$$\Theta = 1 - \frac{(1 - e^{-At})}{At}$$

with $\alpha = 2\pi(2MDc/\rho)^{1/2}$. The function Φ is directly related to the Dawson's integral³⁰ and reflects the retardation of the current by slow nucleation, and Θ reflects the retardation of the growth of the coverage due to the slow nucleation.

The N_0 values obtained by fitting the potentiostatic transients using the HT model are included in Table I. It is clearly observed that the SM and HT models could be applied with sufficient accuracy, since N_0 presented the same values in the analyzed solutions, within the potential range investigated. Moreover, both theories were important to evaluate the nucleation process occurring at very short times, where the SH model was not accurate to predict the Cu instantaneous mechanism in HClO_4 solution.

Figure 7. AFM images of the (A) BDD and (B) Cu nuclei on the BDD electrode obtained in 10^{-3} mol L $^{-1}$ CuSO $_4$ + 0.1 mol L $^{-1}$ Na $_2$ SO $_4$ solution. $E_{\text{deposition}}$: -0.4 V; t : 0.6 s.

The D values were also obtained by fitting the potentiostatic transients using the SM and HT models and their respective values in 0.1 mol L $^{-1}$ H $_2$ SO $_4$ solution of 1.61×10^{-6} cm 2 s $^{-1}$ and 1.65×10^{-6} cm 2 s $^{-1}$ are in good agreement with those calculated from Cottrell equation 31 by linearization of the falling part of the transients for long times, which presented a value of 1.26×10^{-6} cm 2 s $^{-1}$ in 0.1 mol L $^{-1}$ H $_2$ SO $_4$.

To confirm the Cu instantaneous nucleation process on the BDD electrode, we analyze the morphology of Cu nuclei from AFM analyzes. Fig. 7 shows the AFM image for the Cu deposit obtained from 10^{-3} mol L $^{-1}$ CuSO $_4$ + 0.5 mol L $^{-1}$ Na $_2$ SO $_4$ solution. Despite the polycrystalline structure of the BDD films, which may be observed in Fig. 7A, the Cu instantaneous growth was possible, where the homogeneous distribution of the Cu nuclei presenting practically the same size may be visualized over the entire surface of the BDD, as shown in Fig. 7B. Similar morphology showing the Cu instantaneous growth in Na $_2$ SO $_4$ and HClO $_4$ solutions (not shown) was also observed.

Conclusions

In the Cu electrodeposition process, the reactions and the nucleation mechanism on BDD electrode were reported. The Cu deposition and dissolution processes were influenced by the solution pH. At pH $\sim$ 5.0 solution (Na $_2$ SO $_4$ electrolyte), the onset of the Cu deposition was verified to occur in more positive potentials and the energy required to initiate the nucleation process was lower when compared to that at pH $\sim$ 2.0 solutions. The amount of intermediary Cu $^+$ ions related to the disproportionation reaction was also influenced by pH solution, where the Ic and Ia processes were not well defined at pH $\sim$ 2.0 solutions. The potentiostatic transients confirmed the occurrence of the Cu nucleation process on BDD electrode, with three-dimensional growth of nuclei limited by diffusion of the electroactive species, except for

solution containing 0.1 mol L $^{-1}$ Cu $^{2+}$ ions. Based on the Scharifker – Hills models, the nucleation mechanisms were examined by fitting the experimental chronoamperometric data. It was found that the nucleation mechanism in 0.1 mol L $^{-1}$ Cu $^{2+}$ ions solution, independent of the pH solution, was inconclusive. However, the nucleation mechanism was conclusive in 10^{-3} mol L $^{-1}$ Cu $^{2+}$ ions solutions containing Na $_2$ SO $_4$ and H $_2$ SO $_4$ as electrolyte, where from $(i/i_{\text{max}})^2$ vs t/t_{max} profile, Cu instantaneous nucleation was verified. The same nucleation mechanism was also confirmed from the Cu nuclei population density (N_0) determined by fitting the potentiostatic transients applying the more complete models, such as those described by Sharifker and Mostany (SM) and Hermann-Tarallo (HT). In spite of the polycrystalline structure of BDD films, the instantaneous growth of Cu nuclei was possible to be characterized by AFM analysis.

Acknowledgments

We are grateful to the Brazilian Agencies CNPq (Processes 554148/2008-0 and 202126/2009-0) and Fapesp (Processes and 07/00013-4) by the financial support. Also, we are grateful to the E. Fumachi by the fitting the potentiostatic curves in the characterization of the Cu nucleation mechanism and to the Professor Dr. Ernesto C. Pereira and Dr. Roberto de Matos (LIEC-UFSCar) by the AFM analysis.

References

1. K. H. Meiwes-Broer, *Metal cluster at surface – structure, quantum properties, Physical Chemistry*, Springer-Verlag, Berlin (2000).
2. J. W. Dini, in *Modern Electroplating*, 4th ed., M. Schlesinger and M. Paunovic Editors, p. 61, Wiley-Interscience, New York (2000).
3. P. C. Andriacos, C. Uzoh, J. O. Dukovic, J. Horkans, and D. Deligianni, *IBM J. Res. Dev.*, **42**, 567 (1998).
4. B. El. Roustom, G. Foti, and C. Comninellis, *Electrochem. Commun.*, **7**, 398 (2005).
5. G. Sine and C. Comninellis, *Electrochim. Acta*, **50**, 2249 (2005).
6. N. G. Carpenter and D. Pletcher, *Anal. Chim. Acta*, **317**, 287 (1995).
7. J. Davis, M. J. Moocroft, S. J. Wilkins, R. G. Compton, and M. F. Cardosi, *Analyst*, **125**, 737 (2000).
8. A. O. Solak, P. Gulser, E. Gokmese, and F. Gokmese, *Mikrochim. Acta*, **134**, 77 (2000).
9. S. Ward-Jones, C. E. Banks, A. O. Simm, L. Jiang, and R. G. Compton, *Electroanalysis*, **17**, 1806 (2005).
10. A. O. Simm, C. E. Banks, S. Ward-Jones, T. J. Davies, N. S. Lawrence, T. G. J. Jones, L. Jiang, and R. G. Compton, *Analyst*, **130**, 1303 (2005).
11. C. M. Welch, M. E. Hyde, C. E. Banks, and R. G. Compton, *Anal. Sci.*, **21**, 1421 (2005).
12. S. W. Boese, V. S. Archer, and J. W. O’Laughlin, *Anal. Chem.*, **49**, 479 (1977).
13. T. Le Gooff, J. Braven, L. Ebdon, N. P. Chilcott, D. Schofield, and J. W. Wood, *Analyst*, **127**, 507 (2002).
14. M. C. Granger, M. Witek, J. Xu, J. Wang, M. Hupert, A. Hanks, M. D. Koppang, J. E. Butler, G. Lucazeau, M. Mermoux, J. W. Strojek, and G. M. Swain, *Anal. Chem.*, **72**, 3793 (2000).
15. J. A. Bennet, J. Wang, Y. Show, and G. Swain, *J. Electrochem. Soc.*, **151**, E306 (2004).
16. F. Bouamrane, A. Tadjeddine, R. Tenne, J. E. Butler, R. Kalish, and C. Levy-Clement, *J. Phys. Chem. B*, **102**, 134 (1998).
17. S. Yoshihara, K. Shinozaki, T. Shirakashi, K. Hashimoto, D. A. Tryk, and A. Fujishima, *Electrochim. Acta*, **44**, 2711 (1999).
18. J. Zak and M. Kolodziej-Sadlok, *Electrochim. Acta*, **45**, 2803 (2000).
19. S. Nakabayashi, D. A. Tryk, A. Fujishima, and N. Ohta, *Chem. Phys. Lett.*, **300**, 409 (1999).
20. M. E. Hyde and R. G. Compton, *J. Electroanal. Chem.*, **549**, 1 (2003).
21. B. R. Scharifker and G. Hills, *Electrochim. Acta*, **28**, 879 (1983).
22. B. Scharifker and J. Mostany, *J. Electroanal. Chem.*, **177**, 13 (1984).
23. M. Sluyters-Rehbach, J. H. O. J. Wijenberg, E. Bosco, and J. H. Sluyters, *J. Electroanal. Chem.*, **236**, 1 (1987).
24. L. Heerman and A. Tarallo, *J. Electroanal. Chem.*, **470**, 70 (1999).
25. N. G. Ferreira, L. L. G. Silva, E. J. Corat, V. J. Trava Airoldi, and K. Iha, *Braz. J. Phys.*, **29**, 760 (1999).
26. S. Fletcher, *Electrochim. Acta*, **28**, 917 (1983).
27. S. Fletcher, C. S. Halliday, D. Gates, M. Westcott, T. Lwin, and G. J. Nelson, *J. Electroanal. Chem.*, **159**, 267 (1993).
28. M. R. Schock, D. A. Lytle, and J. A. Clement, *Effect of pH, DIC, Ortho-phosphate and Sulfate on Drinking Water Cuprosolvency*, p. 11, EPA, Cincinnati (1995).
29. D. Grujicic and B. Pesic, *Electrochim. Acta*, **50**, 4426 (2005).
30. L. Huang, E. Lee, and K. Kim, *Colloids Surf. A*, **262**, 125 (2005).
31. J. H. Lindsay and T. J. O’Keefe, in *Modern Aspects of Electrochemistry*, vol. 26, B. E. Conway, J. O’M. Bockris and R. E. White Editors, p. 165, Plenum Press, New York (1994).