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Article

# The Effect of Concentration on the Electrocrystallization Mechanism for Copper on Platinum Ultramicroelectrodes

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O mecanismo de eletrocristalização de cobre sobre ultramicroeletrodos de Pt foi estudado por voltametria cíclica, cronoamperometria e microscopia de força atômica *ex situ* em soluções ácidas contendo diferentes concentrações de $Cu^{2+}$. Para análise dos transientes potenciostáticos utilizou-se um modelo desenvolvido em nossos laboratórios que leva em consideração a difusão esférica para ultramicroeletrodos na forma de disco. Uma mudança mecanística de nucleação progressiva para instantânea foi observada com o aumento da concentração de íons $Cu^{2+}$ de 0,01 para 0,1 mol $dm^{-3}$. A forma e a distribuição dos núcleos sobre a superfície do eletrodo foram investigados por microscopia de força atômica. A dependência da taxa de formação dos núcleos com o potencial de salto foi analisada em termos da teoria atomística da eletrocristalização e os resultados obtidos sugerem a presença de um único átomo de cobre no núcleo crítico.

The mechanism of copper electrocrystallization on Pt ultramicroelectrode surfaces has been studied by cyclic voltammetry, chronoamperometry and *ex situ* atomic force microscopy in acid solutions containing different $Cu^{2+}$ concentrations. To analyze the potentiostatic transients a new model developed in our laboratories that takes into account spherical diffusion towards a disc-shaped ultramicroelectrode was used. A mechanistic change from progressive to instantaneous nucleation was observed when the $Cu^{2+}$ concentration was increased from 0.01 to 0.1 mol $dm^{-3}$. The shape and distribution of the nuclei formed on the surface were investigated by AFM. The dependence of the nucleation rate with potential was analyzed in terms of the atomistic theory of electrocrystallization and the results suggest the presence of only one copper atom in the critical nucleus.

**Keywords:** electrocrystallization, copper, Pt ultramicroelectrodes, atomistic theory

## Introduction

One fundamental aspect in electrodeposition processes is the initial stage of phase formation, usually called electrocrystallization. This stage is normally associated with a two - or three - dimensional growth process where the number of nuclei formed on the electrode surface is strongly dependent on the overpotential. In these processes the rate determining step is the incorporation of atoms or molecules at the growth centers[1-4]. The nucleation mechanism has two limiting forms: (a) instantaneous nucleation, when all nuclei are formed immediately after the application of an appropriate overpotential, or (b) progressive nucleation, when the nuclei are formed in a continuous fashion following first order kinetics after the potential step.

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The electrocrystallization of copper on foreign substrates is a matter of great technological importance since that process has been used in industry for manufacturing printed-circuit boards as well as protective and decorative coatings. Besides, the initial stage of Cu deposition serve as a suitable model system for electrocrystallization studies[5-17].

On the other hand, ultramicroelectrodes (UME) have proved to be a convenient tool for electrodeposition studies because their small dimensions allow the formation and growth of a reduced number of nuclei, minimizing the interference between neighboring nucleus. However, one of the major problems in the utilization of disc-shaped UME for this type of studies was the lack of equations properly derived to describe the nucleation process controlled by spherical diffusion. The border of the disc acts as barrier, hindering the electroactive species to reach its center. This effect has been previously discussed[18,19] and imposes the need of developing equations to correctly interpret the current transients[20-22].

In a previous investigation from our laboratories[23], the electrocrystallization of copper from 0.1 mol dm$^{-3}$ $CuSO_4$ + 0.5 mol dm$^{-3}$ $H_2SO_4$ on a 40 µm Pt UME was studied by cyclic voltammetry and chronoamperometry. The final potentials for the potentiostatic transients were varied from -0.22 to -0.35 V (*vs* SCE). The analysis of these transients was carried out using the theoretical equations specially derived for studies of electrochemical nucleation on disc-shaped UME under diffusion control[24]. Those equations properly account for the blockage by the borders for the two limiting cases, namely, instantaneous or progressive nucleation, and their fitting with the experimental data allows a clear definition of the prevailing mechanism.

The results obtained using the model mentioned above demonstrated that, under those experimental conditions, the electrocrystallization of copper on platinum starts with an instantaneous nucleation followed by a diffusion controlled growth of the nuclei. The actual number of nuclei formed on the UME was calculated and found to be strongly dependent on the applied potential, with values varying from 11 to 67 in the interval under investigation. However, several other authors have shown that copper electrocrystallization occurs either instantaneously or progressively depending on different plating parameters, such as electrode potential or current density, the presence of organic additives, such as surfactants, and/or the pH of the solution.

Following that approach, Rynders and Alkire[6] studied copper electrocrystallization on Pt(100) and Pt(111) surfaces from 0.25 mol dm$^{-3}$ $CuSO_4$ + 0.5 mol dm$^{-3}$ $H_2SO_4$ by potentiostatic transients and *in situ* atomic force microscopy (AFM). The authors claim that with increasing overpotentials, the data from the current transients shifted from the progressive to the instantaneous behavior. At high overpotentials, AFM images recorded during the deposition experiments indicated that nucleation was three-dimensional leading eventually to the overlap of the nuclei. At low overpotentials, the current transients were not consistent with existing theories and the AFM images confirmed that nuclei did not overlap.

Fabricius et al.[7] reported the influence of thiourea (TU) on copper nucleation and growth onto glassy carbon from 0.07 mol dm$^{-3}$ $CuSO_4$ + 1.8 mol dm$^{-3}$ $H_2SO_4$ solutions containing either 0, 1, 10 or 1000 mg L$^{-1}$ TU. The final potentials were varied from -0.15 to -0.30V (*vs* SCE). With increasing concentration of the organic additive the mechanism changes from instantaneous nucleation to the purely progressive one. Thiourea is used to promote smooth and bright metallic deposits and it has been found that this effect is due to a change in the initial nucleation process.

Hölzle et al.[9] studied the influence of TU on the initial stages of Cu deposition on a Au(111) electrode by potential step experiments and *in situ* scanning tunneling microscopy. The electrolyte for the electrochemical measurements was 1 mmol dm$^{-3}$ $CuSO_4$ + 50 mmol dm$^{-3}$ $K_2SO_4$ and the final potential varied from -0.052 to -0.064 V (*vs* SCE). They observed that additions of small amounts of TU (1x10$^{-7}$ mol dm$^{-3}$) drastically change the results obtained for copper electrocrystallization. Initially, the current maximum shifts to shorter times. Further increases in the additive concentration accelerate the deposition process. For TU concentrations higher than 1x10$^{-6}$ mol dm$^{-3}$, the deposition occurs so fast that the rising part of the transients merges with the falling portion. In addition to the results obtained with TU on copper electrocrystallization, they also investigated the effect of varying the pH on this process. With increasing pH, the maximum of the transients moves to shorter times and higher current densities. A change from instantaneous to progressive nucleation with increasing pH was observed and explained by an increase in the number of nucleation sites at the surface as the pH changed from 1.5 to 4.

In the meantime, Mostany et al.[25] studied the effect of $Pb^{2+}$ concentration on lead electrocrystallization onto vitreous carbon. The transition from a progressive nucleation regime in dilute (1 mmol dm$^{-3}$) solutions to an instantaneous one at higher (20 mmol dm$^{-3}$) concentrations indicates that the nucleation rate increases with the concentration of the metal ion and that the deposition mechanism strongly depends on that parameter.

Although many studies involving copper electrocrystallization have been reported in the literature, the influence of $Cu^{2+}$ concentration on that process has not yet been reported. Therefore, the purpose of the present study is to verify the effect of $Cu^{2+}$ concentration on the electrocrystallization mechanism for copper on Pt UME from sulfuric acid solutions using cyclic voltammetry, potentiostatic transients and *ex situ* atomic force microscopy.

## Experimental

The electrolytes used were 0.5 mol dm$^{-3}$ $H_2SO_4$ solutions containing 0.01 or 0.1 mol dm$^{-3}$ $CuSO_4$, respectively. These solutions were prepared from Millipore quality water and analytical grade reagents. Oxygen in the solution was removed by a nitrogen flux. All measurements were carried out at room temperature.

The electrochemical measurements were performed using a two-electrode Pyrex® cell with a saturated calomel electrode (SCE) as the combined reference/auxiliary. The working electrode was a disc-shaped 50 µm Pt UME. The UME was constructed by sealing a 50 µm Pt wire into a Pyrex glass tube with subsequent polishing of the tip to obtain a flat

surface[26]. Before each electrochemical measurement, the UME surface was again polished with emery paper 1200 (3M) to remove any residues from previous experiments.

An EG&G PARC potentiostat-galvanostat model 273 linked to a microcomputer controlled by the M270 software from EG&G PARC was used in all electrochemical experiments. The Atomic Force Microscopy (AFM) images were acquired in the constant force mode, using a Topometrix® Explorer TMX 1010. The AFM parameters used were: plane image with linearized height, high Z gain, image size of 6.5 x 6.5 µm, resolution of 300 x 300 pixels and a scan rate of 6.5 µm $s^{-1}$.

## Results and Discussion

### *Voltammetric Studies*

The voltammetric responses of the Pt UME in 0.5 mol $dm^{-3}$ $H_2SO_4$ + (0.01 or 0.1 mol $dm^{-3}$) $CuSO_4$ at 5 mV $s^{-1}$ are displayed in Figure 1. The curves show the typical crossover of the cathodic and anodic branches that are associated with the increase of the electroactive area of the surface during the deposition process. This crossover is indicative of a nucleation and growth mechanism.

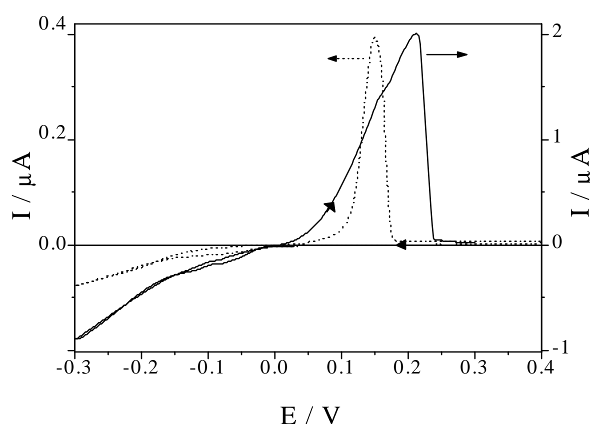


**Figure 1**. Cyclic voltammograms (first cycle) for copper deposition/dissolution on a disc-shaped Pt UME (ϕ = 50µm) in 0.01 mol $dm^{-3}$ (dotted line) and 0.1 mol $dm^{-3}$ (full line) $CuSO_4$ + 0.5 mol $dm^{-3}$ $H_2SO_4$, $v$ = 5 mV $s^{-1}$.

In accordance to previously reported studies[23], the anodic scans reveal one main dissolution process at potentials more positive than 0.15 V. The observed peak corresponds to the dissolution of metallic copper previously deposited. As expected, both the peak potential and the associated charge vary considerably with the $Cu^{2+}$ concentration. The potentials used in the potentiostatic transients (see below) were selected from the cathodic sweep in these voltammograms.

### *Electrocrystallization Studies*

In order to verify the influence of $Cu^{2+}$ concentration on the electrocrystallization of copper, potentiostatic current transients were recorded using the same solutions as before. In all cases, the electrode potential was stepped from -0.10V to a final value in the range -0.25 to -0.32 V, as indicated in the legend of Figure 2 where the experimental results are presented.

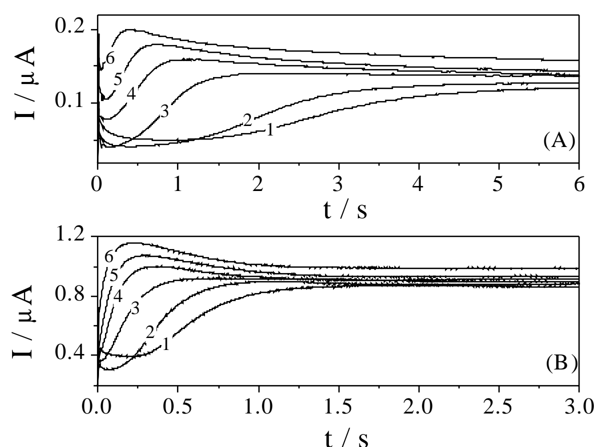


**Figure 2**. Potentiostatic transients for Cu electrocrystallization on a 50µm Pt UME in 0.01 mol $dm^{-3}$ (A) and 0.1 mol $dm^{-3}$ (B) $CuSO_4$ + 0.5 mol $dm^{-3}$ $H_2SO_4$. The initial potential for both concentrations is -0.10 V. The final potentials for (A) are: -0.25 (1), -0.26 (2), -0.28 (3), -0.29 (4), -0.31 (5) and -0.32 V (6); and for (B) are: -0.27 (1), -0.28 (2), -0.29 (3), -0.30 (4), -0.31 (5) and -0.32 V (6).

In both cases, typical current transients with a single maximum were recorded for the nucleation process under diffusion control. After a very short initial spike followed by an exponential decay that are due to double-layer charging, the current rises to a maximum. The final portion of the transients reflects the diffusion limitation described by Cottrell's equation. The characteristic parameters obtained from those current transients are presented in Table 1.

**Table 1**. Parameters extracted from the current transients for copper electrocrystallization on a 50µm Pt UME from solutions with different $Cu^{2+}$ concentration.

| E / V (SCE) | $t_{max}$ / s | $I_{max}$ / µA |
|---|---|---|
| $[Cu^{2+}]$ = 0.01 mol $dm^{-3}$ | | |
| -0.25 | 6.00 | 0.12 |
| -0.26 | 5.47 | 0.13 |
| -0.28 | 1.89 | 0.14 |
| -0.29 | 1.17 | 0.16 |
| -0.31 | 0.72 | 0.18 |
| -0.32 | 0.40 | 0.20 |
| $[Cu^{2+}]$ = 0.1 mol $dm^{-3}$ | | |
| -0.27 | 2.18 | 0.89 |
| -0.28 | 1.10 | 0.90 |
| -0.29 | 0.76 | 0.93 |
| -0.30 | 0.37 | 1.00 |
| -0.31 | 0.30 | 1.08 |
| -0.32 | 0.21 | 1.16 |

The variations of $t_{max}$ and $I_{max}$ with concentration and with the final potential showed an expected behavior. The maximum of the transients moves to shorter times and therefore higher currents for larger overpotentials and also with the increase in $Cu^{2+}$ concentration. The analysis of the transients was carried out using the equations of the theoretical model previously developed in our laboratories[24] for the progressive and instantaneous processes.

For a system having a high nucleation rate, all nuclei will be formed immediately after the potential step is applied and their number will remain constant during the growth process. This is the so-called instantaneous nucleation and the dependence of the current with time can be described by:

$$I = (4nFDc^{\infty}r+8nFc^{\infty}r^2D^{1/2}\pi^{-3/2}t^{-1/2})[1-\exp(-N\pi kDt)] \quad (1)$$

with

$$k = \left(\frac{8\pi c^{\infty}M}{\rho}\right)^{1/2} \quad (2)$$

where n is the number of electrons, F the Faraday's constant, D the diffusion coefficient, $c^{\infty}$ the bulk concentration of the species in solution, M the molecular weight of the metal ion, ρ the metal density, r the UME radius, t the time and N the total number of nuclei formed.

The second case is progressive nucleation, were the nuclei are continuously formed during the whole growth process. In this case, the current is then given by:

$$I = (4nFDc^{\infty}r+8nFc^{\infty}r^2D^{1/2}\pi^{-3/2}t^{-1/2})[1-\exp(-0.5AN_{\infty}\pi k'Dt^2)] \quad (3)$$

where

$$k' = \frac{4}{3}\left(\frac{8\pi c^{\infty}M}{\rho}\right)^{1/2} \quad (4)$$

In Eq. (3), $AN_{\infty}$ is the nucleation rate while the others parameters have their usual or their previously defined meaning.

Adjusting equations (1) and (3) to the experimental data using the Microcal Origin's non-linear fitting procedure, the mathematical reproduction of the experimental transients was achieved. The variables used for the fitting were D, N and $AN_{\infty}$ for each type of nucleation. Figures 3 and 4 illustrate some of the results obtained from those calculations for solutions with $Cu^{2+}$ 0.01 and 0.1 mol $dm^{-3}$, respectively. For all final potentials investigated here, a very good agreement between the experimental transients and one of the adjusted curves was observed. In all cases, the transients recorded using 0.01 mol $dm^{-3}$ $Cu^{2+}$ solutions could be reproduced by the progressive nucleation curves while for the 0.1 mol $dm^{-3}$ $Cu^{2+}$ solutions, the best fittings correspond to an instantaneous nucleation process. Small differences observed between the curves for $t > t_{max}$ could be attributed to the influence of parameters not included in the model such as the variation in electrode area. Nevertheless, the calculations are mainly based on the ascendant part of the transient where the fitting is very satisfactory.

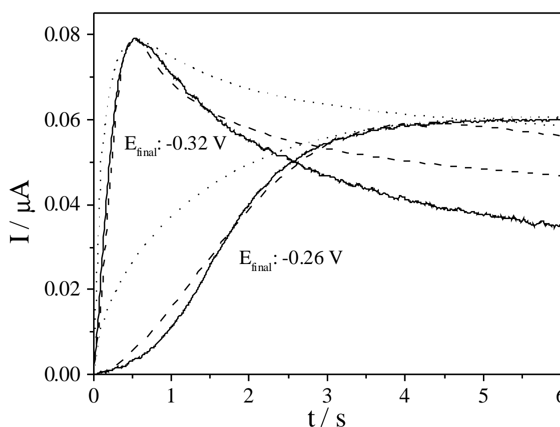


**Figure 3**. Comparison between the experimental transients (full lines) in 0.01 mol $dm^{-3}$ $CuSO_4$ + 0.5 mol $dm^{-3}$ $H_2SO_4$ and the best fittings obtained for instantaneous (dotted lines) and progressive (dashed lines) nucleation processes at selected potentials, as indicated on the curves.

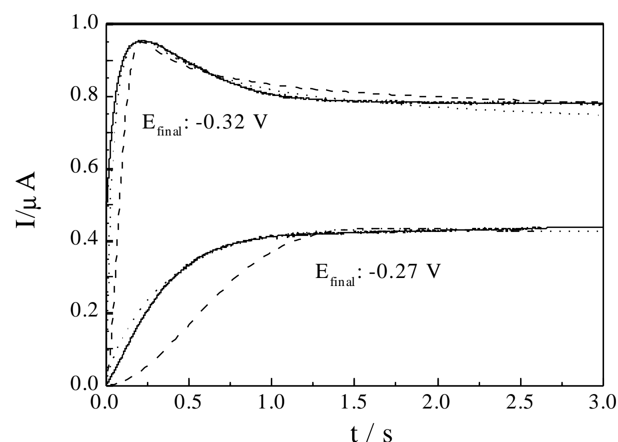


**Figure 4**. Comparison between the experimental transients (full lines) in 0.1 mol $dm^{-3}$ $CuSO_4$ + 0.5 mol $dm^{-3}$ $H_2SO_4$ and the best fittings obtained for instantaneous (dotted lines) and progressive (dashed lines) nucleation processes at selected potentials, as indicated on the curves.

The fitting procedure furnishes the values of $AN_{\infty}$, corresponding to the rate of nuclei formation (for progressive nucleation) or the number of nuclei, N, instantly formed in the potential step (for instantaneous nucleation). It also gives the value of the diffusion coefficient. The $AN_{\infty}$, N and D values extracted from the fittings are listed in Table 2.

**Table 2**. Electrochemical parameters resulting from the non-linear regression fitting for copper electrocrystallization on 50µm Pt UME at different $Cu^{+2}$ concentrations.

| $[Cu^{2+}] = 0.01$ mol dm$^{-3}$ | | |
|---|---|---|
| E / V (SCE) | $10^6$ D / cm$^2$ s$^{-1}$ | $10^{-5}$ $AN_\infty$ / cm$^{-2}$ s$^{-1}$ |
| -0.25 | | 3.20 |
| -0.26 | | 7.40 |
| -0.28 | | 37.0 |
| -0.29 | 2.3 | 79.9 |
| -0.31 | | 235 |
| -0.32 | | 640 |
| $[Cu^{2+}] = 0.1$ mol dm$^{-3}$ | | |
| E / V (SCE) | $10^6$ D / cm$^2$ s$^{-1}$ | $10^{-5}$ N/ cm$^{-2}$ s$^{-1}$ |
| -0.27 | | 8.50 |
| -0.28 | | 14.0 |
| -0.29 | 6.0 | 19.5 |
| -0.30 | | 34.0 |
| -0.31 | | 41.0 |
| -0.32 | | 55.0 |

*Atomistic Theory*

The investigation of the first stage of an electrochemical phase formation (birth and growth of the first nuclei) is an important subject that can contribute to the understanding of several characteristics of massive electrodeposits. During those early moments of deposition, the determination of the minimum number of atoms or molecules necessary to generate a stable cluster (formation of the critical nucleus) furnishes important information on the system at a molecular level. In particular, this information is related to the energy requirement for stable clusters generation and can be obtained from measurements of the dependence of $AN_\infty$ with potential for processes exhibiting a progressive nucleation mechanism.

In order to account for the observed relationship between $AN_\infty$ and the final potential, it is necessary to consider the atomistic theory of electrocrystallization[27,28]. According to that theory, the partial derivative of the nucleation rate with respect to the final potential in the potentiostatic step can be expressed by[28]:

$$\left(\frac{\partial \ln AN_\infty}{\partial E_{final}}\right) = \left(n^* + \alpha\right)\frac{zF}{RT} \quad (5)$$

where n* is the number of atoms or molecules in the critical nucleus, α is the electrochemical transfer coefficient and the other constants retain theirs usual meanings.

Considering Eq. (5) and the slope of 70.38 V$^{-1}$ of the line shown in Figure 5 for the variation of $AN_\infty$ with $E_{final}$, it is possible to find the $n^*$ value for copper deposition from dilute solutions (progressive nucleation). Assuming α as 0.5 a value of ~1.4 was obtained for n*. This value suggests that there will be only one atom in the critical nucleus for copper electrocrystallization under the present experimental conditions. A unitary value for the critical nucleus has been frequently reported[29,30] and suggests an irreversible nuclei formation process. This is a rough approach with regard to the boundary conditions of the atomistic theory and must be carefully interpreted. In fact, the theory was developed for highly reversible depositions operating at very small overpotentials and such boundary conditions are not completely fulfilled in this work.

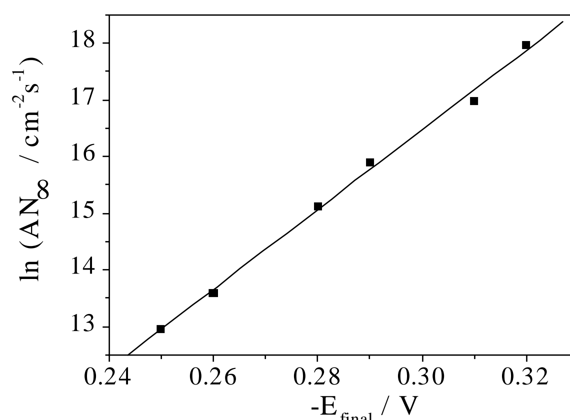


**Figure 5**. Dependence of the nucleation rate ($AN_\infty$) with the final potential for copper electrocrystallization from 0.01 mol dm$^{-3}$ $Cu^{2+}$ solutions.

*Morphologic studies*

Deposition processes have been investigated by electrochemical measurements coupled with observations of the deposit morphology. In the present work, *ex situ* atomic force microscopy (AFM) has been employed for the study of the initial growth morphology in the electrodeposition of copper. The high stability of the deposited metal allows the use of *ex situ* measurements without any loss in quality.

The use of this technique shows as advantages: a) higher resolution imaging (sub-micron scale is easily attainable; atomic-scale is possible under optimal conditions); b) ability to image under environmentally appropriate conditions (in air or fluid); c) non-destructive characterization with minimal sample preparation; d) three-dimensional measurement capability, including profile tracing of the surface; e) sensitivity to certain physico-chemical properties; f) ability to determine surface and interfacial forces.

In this case, the samples for morphologic studies were prepared by the deposition of Cu onto Pt ultramicroelectrodes from two different $Cu^{2+}$ concentrations, i.e., 0.01 and 0.1 mol dm$^{-3}$. The deposition times in the potentiostatic step were carefully chosen in an attempt to minimize the coalescence of nuclei. In this way, electrolysis times of 1.17 s for the dilute and 0.76 s for the concen-

trated $Cu^{2+}$ solutions were selected, for a common -0.29 V deposition potential. The total charge involved in the depositions was 4.67 x $10^{-3}$ and 17.7 x $10^{-3}$ C $cm^{-2}$ for the 0.01 and the 0.1 mol $dm^{-3}$ solutions, respectively. Next, the electrodes were removed from the electrolytic bath, washed in pure water, dried in the air and held in an appropriate home-made Teflon® support for the AFM measurements.

Figure 6 shows the AFM images (6.5 x 6.5µm) of the copper electrocrystallization for each of the concentrations used. The polycrystalline platinum used in these studies does not allow a better resolution due to its great superficial irregularity which, in turn, induces a preferential location for deposition. Nevertheless, it is possible to observe in Figure 6(a) the presence of hemispherical nuclei with different diameters, thus confirming the progressive mechanism obtained from the non-linear fitting. On the other hand, Figure 6(b) shows several nuclei uniformly covering the platinum surface. The profiles of the surfaces, included in the same figure, further confirm the conclusions above.

## Conclusions

The results of the present investigation have demonstrated that the mechanism of copper electrocrystallization on platinum is a function of the concentration of $Cu^{2+}$ ions in the plating solution. The initial nucleation changes completely from progressive in dilute solutions to instantaneous when the $Cu^{2+}$ concentration is increased to 0.1 mol $dm^{-3}$. In the former case, the application of the atomistic theory of electrocrystallization suggests the presence of only one copper atom in the critical nucleus. However, this result cannot be taken as conclusive due to the lack of total fulfillment of the boundary conditions of the theory in the present experiments.

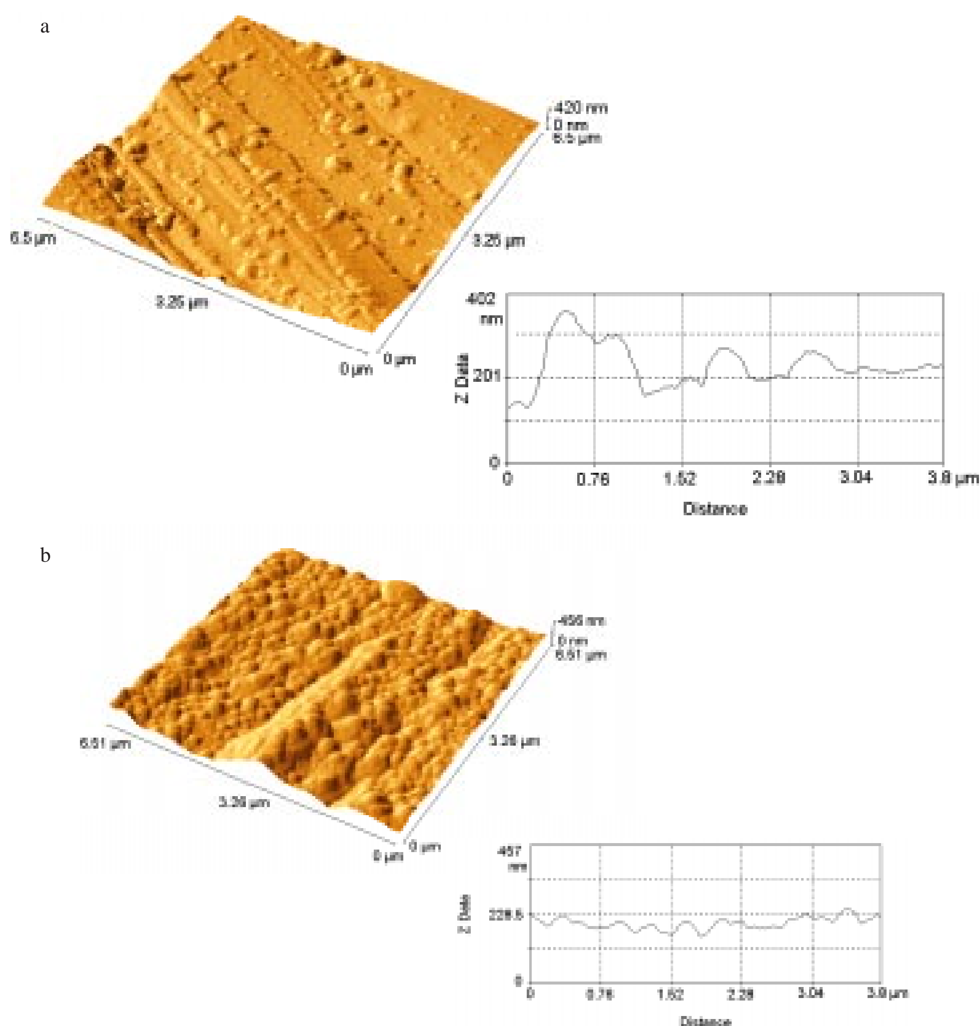


**Figure 6**. AFM images of copper electrodeposited on a 50µm Pt UME at -0.29 V for 1.17 s from a 0.01 mol $dm^{-3}$ (a) and for 0.765 s from a 0.1 mol $dm^{-3}$ $Cu^{2+}$ solution (b). The surface profiles taken for each image are also included.

Finally, the use of *ex situ* atomic force microscopy in this type of studies has revealed that this technique is a powerful tool for the definite assessment of nucleation processes due to its capability of three-dimensional resolution of the surface morphology. Therefore, the distinction between progressive and instantaneous nucleation initially revealed by the non-linear fitting procedure was fully confirmed through the analysis of the surface profiles obtained by AFM.

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