Kinetic Mechanism of Copper UPD Nucleation and Growth on Mono and Polycrystaline Gold

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The copper electrodeposition process was studied onto different gold substrates, single crystal (111) and polycrystalline, using chronoamperometry. The potentiostatic current transients were analysed; it was found that, in both cases, different electrodeposition processes take place. In the underpotential region, the transients involve three types of processes, one of adsorption and two nucleation ones limited by the incorporation of ad-atoms, thus giving bidimensional growth for both electrodes.

Introduction

Underpotential deposition (UPD) of the first metal monolayer onto substrates with a different nature has attracted considerable attention during the last few years (1-5). Therefore, a fairly large amount of structural information of the formed deposit is now available under UPD conditions. However, the influence of the substrate's structure on the mechanism and kinetics to form a monolayer, which involves formation of a new 2D phase, onto the electrode surface has been relatively less studied. The structure of the substrate surface by itself plays quite a significant role to determine subsequent growth of the deposit, particularly during the initial stages of the process. Polycrystalline metal electrodes display a complex character in view of the variety of crystallographic surface orientations, defects and grain boundaries. The studies related to formation of monolayers on such surfaces are somewhat limited, in as much as the mechanism and kinetics are concerned. Conventional electrochemical methods generally involve a macroscopic measure, such as the current, which makes slightly difficult to differentiate the individual contributions to an overall process arising from the crystallographic orientations and other structural features alike. The use of single crystals has indeed facilitated systematic study of the said UPD initial stages to investigate the influence of substrate's surface morphological features on the electrocrystallization process.

Chronoamperometry, as an electrochemical technique in which the potential of the working electrode is stepped, and the resulting current from capacitive and faradaic processes occurring at the electrode (caused by the potential step) is monitored as a function of time; the technique is known to facilitate the experimental measurements of ensuing interfacial phenomena. The potentiostatic current transients thus recorded are usually interpreted by means of various theoretical formalisms, first through their deconvolution by means of non-linear fitting of a given model to the experimental data,

which permits to identify diverse contributions to the overall current that certainly represent either, rate limiting steps, the deposit dimensionality, or to determine kinetic parameters closely associated to physicochemical features of the electrodeposited material (6-11).

Cyclic voltammetry gives the possibility to detect, with quite a high degree of certainty, the initiation of the UPD process such as formation of the first monolayer. It provides enough information during the cathodic potential scan (dE/dt) within the range chosen. It is a fact that when the potential is more positive than that necessary for the massive deposit the first electrodeposited layer forms, whereby the metal ad-atom is strongly bonded to a substrate with a different nature. Therefore, in view of the aforementioned, this work aims at studying the initial stages of copper nuclei formation and growth onto gold single crystal (111) and polycrystalline electrodes from a 1 mM $CuSO_4$ solution in H_2SO_4 1M.

Experimental

All experiments were performed within a typical three-electrode electrochemical cell, and a nitrogen atmosphere circulating over the electrolyte to prevent oxygen dissolution. The working electrode was a single crystal Au(111), 200 nm gold layer supported on a heat-resistant glass substrate from Berlin Glass, or a polycrystalline gold tip from BAS, having an 0.0707 cm^2 exposed working area. The Au(111) was annealed under a hydrogen flame prior to each experiment. The results were obtained at pH 1 under UPD conditions, with the potential steps starting at -50 mV vs. a Hg/Hg_2SO_4 reference electrode, using a BAS CV-50W BioAnalytical System. All reagents were suprapure grade supplied by Merck, dissolved in high resistivity deionised water Type I with 18MΩ Millipore, free from organic matter. The counter electrode was a Pt wire.

Results and Discussion

Potentiostatic study

Figure 1 shows two experimental potentiostatic current transients obtained during copper UPD onto Au(111) single crystal and polycrystalline, starting with a gold surface free from copper ad-atoms (E_{ar} = -0.05 V). The values of the applied potential steps (E) correspond to values closely located to the equilibrium values. In both cases, the overall charge density involved, estimated by integration of the -J vs. t plot, was very close to the theoretical value found for a Cu onto gold Au (111) pseudomorphic monolayer (1x1) (13).
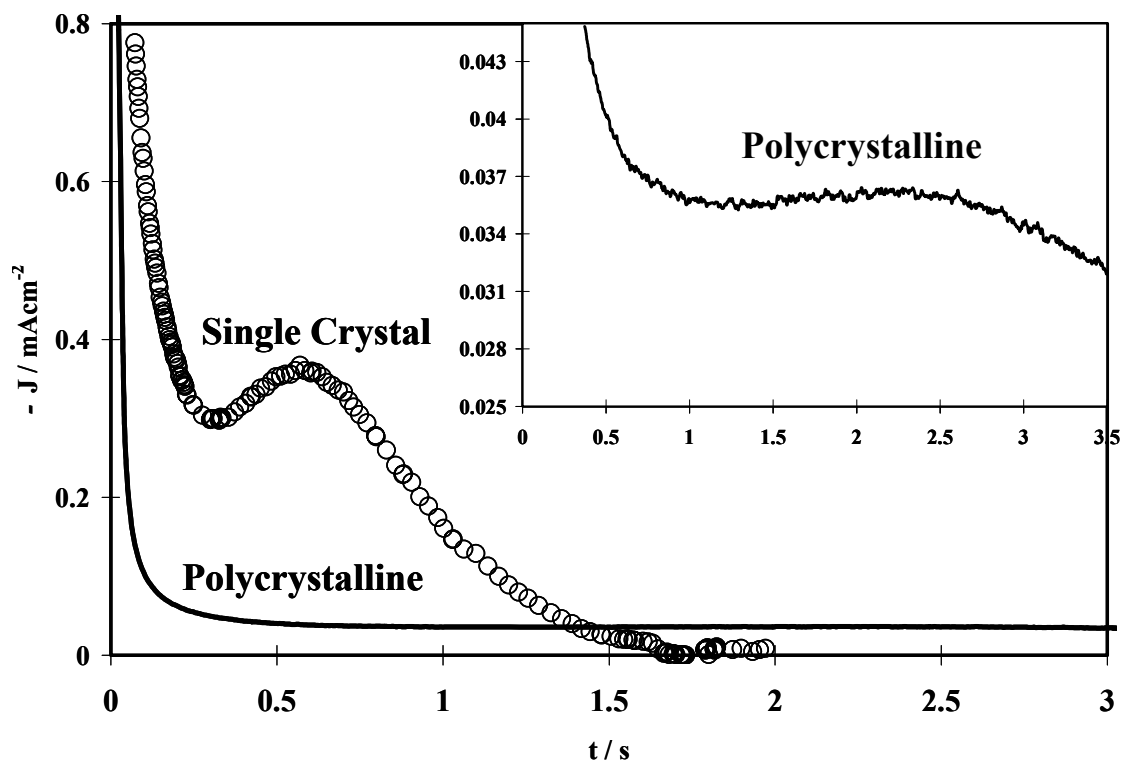
Figure 1. Typical potentiostatic current transients obtained during copper UPD onto different gold substrates from a 10 mM CuSO$_4$ solution in 1M de H$_2$SO$_4$ the potential step was started at a -50 mV and ended at -445mV vs. SSE. See inset for a zoom of the transient with the polycrystalline electrode.

The differences shown in Figure 1 are quite obvious for both substrates not only in terms of the currents densities involved, but mainly in the shape of the transients generated under the same experimental conditions. In order to discuss these results further, the following section will focus on the single crystal substrate.

Monolayer formation onto Au(111). The transient obtained for the single crystal Au(111) as shown in Figure 1 indicates that for t > 0.4 s the shape of the transient is indeed similar to those predicted for the formation and growth of 2D nuclei, limited by ad-atom incorporation. In these cases, the maxima indicate that the said growing centers have grown to such an extent that there is nuclei coalescence. However, for t < 0.4 s the current density falls abruptly in such a way that there is no nucleation model giving a clear description of the transient shape. Furthermore, if a Langmuir-type adsorption process is invoked to attempt a fitting of the transient, there is a good agreement (14). In order to describe fully the shape of the transients, we referred to the model used by Hölzle et al. (2), where the overall current density for the electrodeposition process j_{total} is the linear sum of a Langmuir-type adsorption term and a 2D nucleation process (j_{2D}) as shown in the following equation [1].

$$j_{total} = j_{AD} + j_{2D-LI} \qquad [1]$$

where the adsorption process is defined as:

$$j_{AD} = K_1 \, exp(-K_2 t) \qquad [2]$$

with $$K_1 = \frac{E}{R_s}, \qquad K_2 = \frac{1}{R_s C}$$

and the 2D nucleation process can be given by an instantaneous or a progressive nucleation process, equations [3] and [4]:

$$j_{2Di-LI}(t) = P_1 t \, exp(-P_2 t^2) \qquad\qquad [3]$$

with $$P_1 = \frac{2\pi z F M h N_0 K_g^2}{\rho} \quad \text{and} \quad P_2 = \frac{\pi M^2 N_0 K_g^2}{\rho^2} \;.$$

$$j_{2Dp-LI}(t) = P_3 t^2 \, exp(-P_4 t^3) \qquad\qquad [4]$$

with $$P_3 = \frac{\pi z F M h A N_0 K_g^2}{\rho} \quad \text{y} \quad P_4 = \frac{\pi M^2 A N_0 K_g^2}{3\rho^2} \;.$$

In the equations above, t is the perturbation time, E is the applied potential, R_s is the solution's resistance, C is the double layer capacitance, K_g represents the nuclei growth rate constant (mol cm^{-2} s^{-1}), M and ρ are the molecular mass and the deposit's density, respectively, h is the thickness of the layer and N_0 is the number density of active sites for the nucleation process occurring on the substrate's surface and A represents nucleation rate constant.

Previous results have shown that nucleation can not be classified as instantaneous or progressive for the whole of the time period considered, which involves a discussion to be presented next (12). Even when the doubt persists as to which of the equations is to be used in the general equation [1], instantaneous or progressive, first we have to fit the experimental transients data with the model proposed by Hölzle et al., using instantaneous nucleation, as stated by the following equation.

$$j_{total} = j_{AD} + j_{2Di-LI} \qquad\qquad [5]$$

where j_{2Di-LI} is represented by equation [3]. Figure 2 shows a comparison between the experimental data obtained and the result of the non linear fitting of equation [5] to the data. It becomes straightforward that the fitting procedure was adequate for the initial and final parts of the curve, though the description of the maximum was indeed poor.
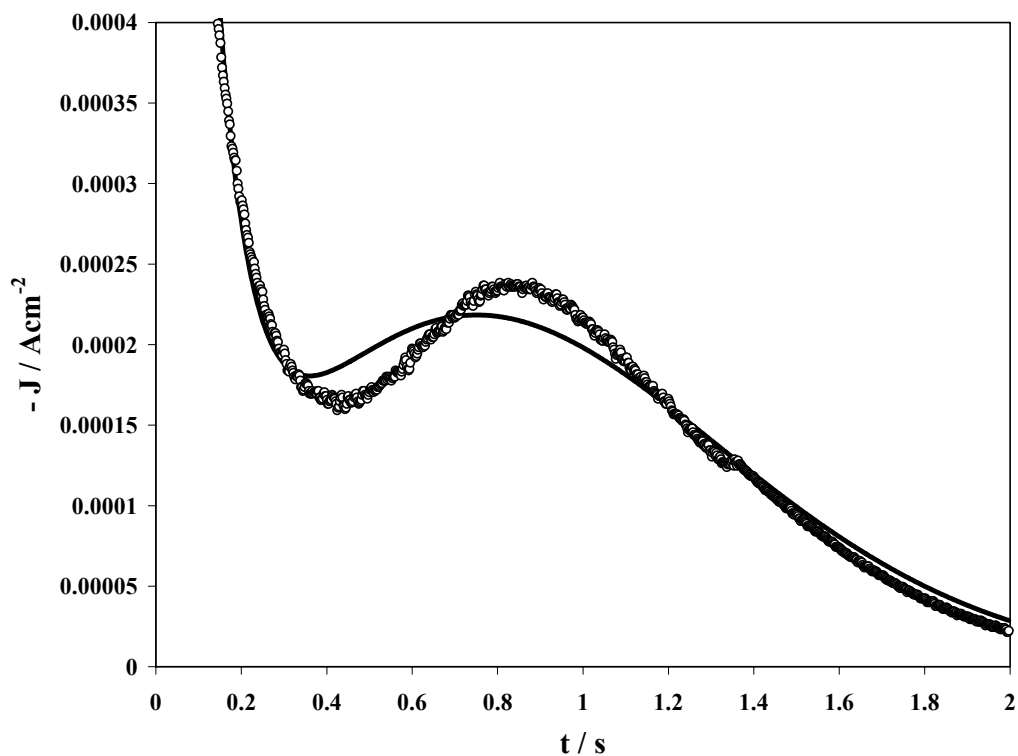
Figure 2. Comparison between the experimental (○○○) obtained during a copper monolayer formation onto Au(111), and a theoretical transient (▬▬▬) obtained through non-linear fitting of equation [5] to the experimental data. The system was the same as shown in Figure 1.

Next, the progressive 2D nucleation mechanism is tried. This way equation [1] becomes equation [6]

$$j_{total} = j_{AD} + j_{2Dp-LI}$$ [6]

Figure 3 shows the results obtained. In this case the description of the overall transient turned out to be even less precise than the previous one, except for the initial stages.
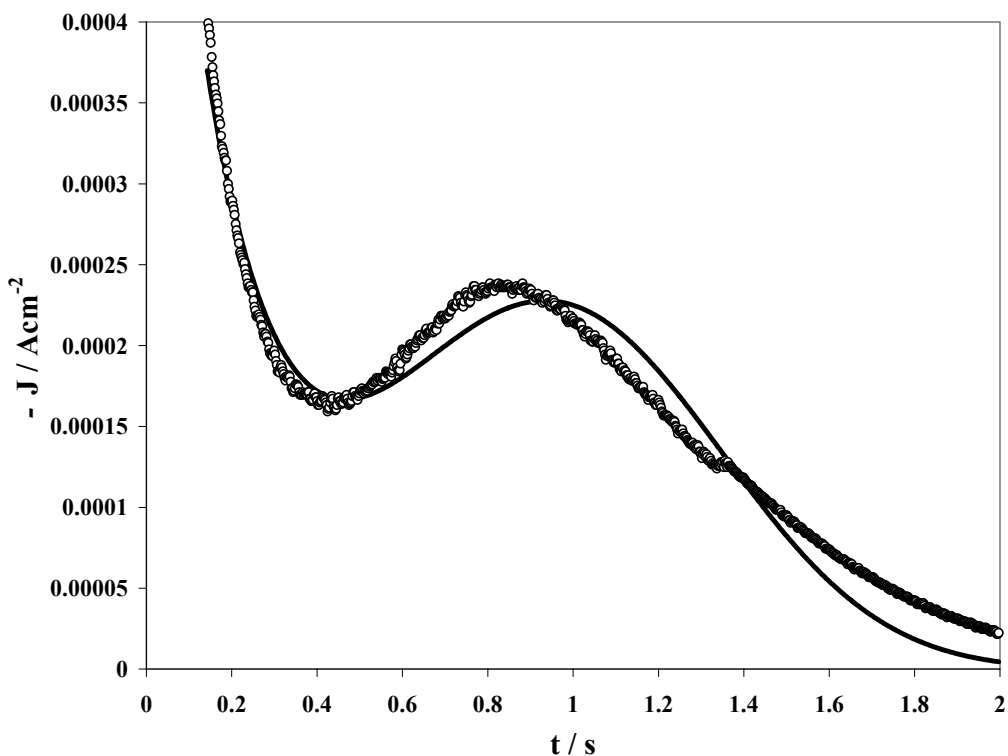
Figure 3. Comparison between the experimental current transient (○○○) obtained during formation of a copper monolayer onto Au(111), and a theoretical transient (▬▬▬) obtained through non-linear fitting of equation [6] to the experimental data.

In view of the aforementioned analyses, we are proposing a new mechanism as represented by equation [7] to describe the copper underpotential deposition process onto Au(111), which involves complete formation of a monolayer on a copper-free substrate surface:

$$ j_{total} = j_{AD} + j_{2Dp-LI} + j_{2Di-LI} \qquad [7] $$

Equation [7] gives the possibility to apply a deconvolution process to describe the overall current density of the experimental transients, as compounded by three different contributions that occur simultaneously on the Au(111) electrode's surface, namely, and adsorption process and two 2D nucleation processes, as indicated by Figure 4, which shows the comparison between the customary results of the non-linear fitting procedure of equation [7] to the experimental data. As can be clearly seen, the fitting procedure describes closely the whole of the experimental transients. The individual contributions to the overall current density are shown separately. Note that the nucleation processes fully overlap and that the final stages of the transient are due exclusively to a j_{2Di-LI} nucleation process.
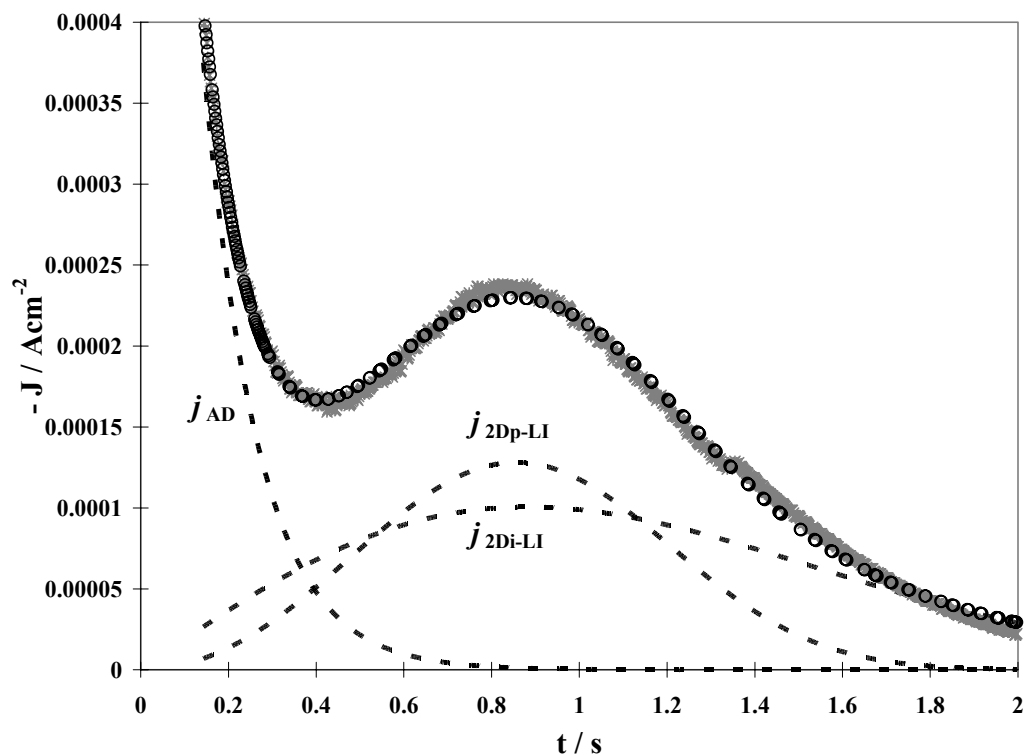
Figure 4. Comparison between the experimental current transient (grey) obtained during formation of a copper monolayer onto Au(111), and a theoretical transient (○○○) obtained through non-linear fitting of equation [7] to the experimental data under the same conditions as stated in Figure 1. The individual contributions to the overall current density are also shown: a Langmuir-type adsorption process (j_{AD}), a 2D progressive nucleation process limited by ad-atom incorporation (j_{2Dp-LI}) and a 2D instantaneous nucleation process also limited by ad-atom incorporation.

<u>Copper monolayer formation onto a Au polycrystalline substrate.</u> From the previous analysis it becomes clear that, regardless of the crystalline nature of the Au substrate, a copper monolayer is formed during the UPD regime, see Figure 1, even if, at first, it appeared that there is a difference in the corresponding current transients. It would seem that different mechanisms should be involved during formation of the monolayer in each case. However, a more detailed analysis of the results presented indicates otherwise, as the transient for the polycrystalline Au displays more similarities than actual differences with respect to the single crystal substrate.

Given the aforementioned argument, we intend to use equation [7] to describe the copper monolayer formation process onto polycrystalline Au. Figure 5 shows a comparison between an experimental transient and the corresponding theoretical one as generated by non-linear fitting of equation [7] to the experimental data. Also, the individual contributions to the overall current density are shown. Therefore, the mechanism proposed is adequate to describe the copper monolayer formation process onto the polycrystalline substrate. However, it should be underlined that the kinetics for the process exhibited differences, which in the present case indicated that the nucleation process was mostly due to the j_{2Di-LI} contribution.
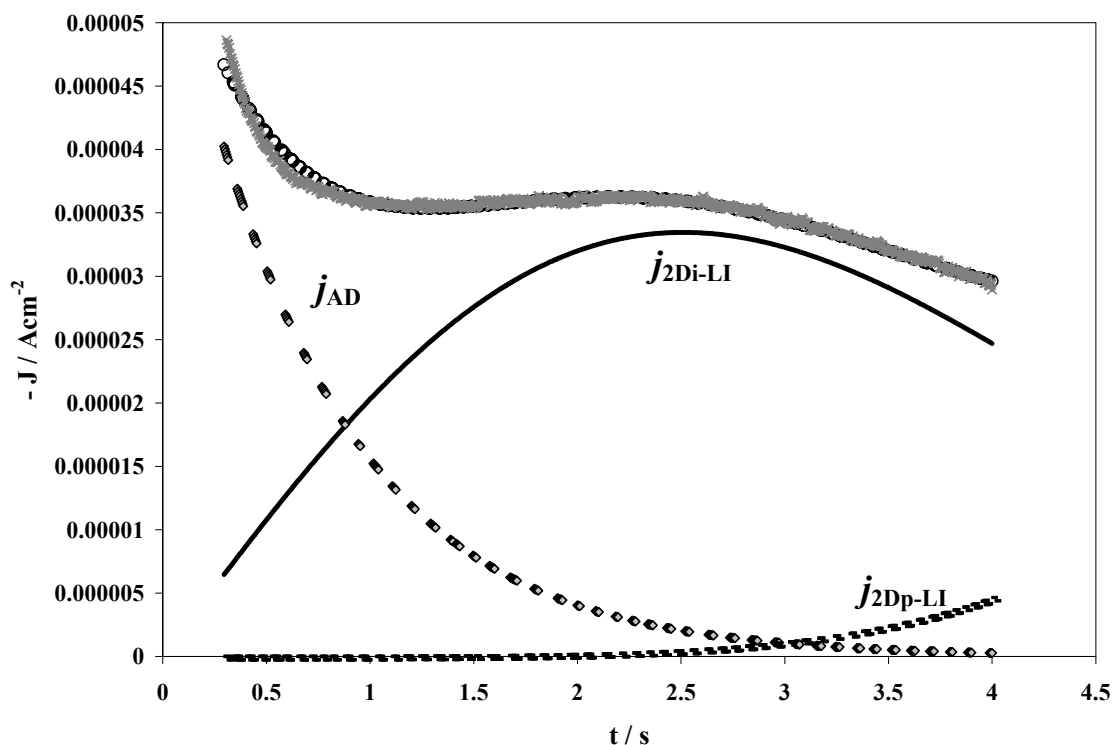
Figure 5. Comparison between the experimental potentiostatic current transient (○○○) obtained during formation of a copper monolayer onto the polycrystalline gold substrate, also under the same experimental conditions as stated in Figure 1, and a theoretical current transient (grey) obtained through non-linear fitting of equation [7] to the experimental data. Also, the individual contributions are shown to the overall current density due to and adsorption process (j_{AD}), a 2D progressive nucleation process limited by ad-atom incorporation (j_{2Dp-LI}) and a 2D instantaneous nucleation process, also limited by ad-atom incorporation (j_{2Di-LI}).

Conclusion

In the present study, it was found out that during the copper UPD electrodeposition onto two different gold substrates, there appeared three different contributions to the overall electrodeposition processes. All these transients involve three types of processes, one due to adsorption and two associated with 2D nucleation and growth stages, one instantaneous and the other progressive, both limited by the incorporation of ad-atoms. However the kinetics was different depending on the substrate crystallinity. In the single crystal Au(111) the processes it was faster than in the polycrystalline gold.

Acknowledgements

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