Influence of the substrate's surface structure on the mechanism and kinetics of the electrochemical UPD formation of a copper monolayer on gold

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ABSTRACT

The copper electrodeposition process was studied onto different gold substrates, single crystal (1 1 1) and polycrystalline, using electrochemical techniques. It was found, from the analysis of the experimental current density transients, that the potentiostatic formation of a full copper monolayer onto the gold electrode under UPD conditions follows the same mechanism, regardless of the crystallinity of the substrate. The mechanism involved the simultaneous presence of an adsorption process and of two 2D nucleation processes, progressive and instantaneous, respectively.

1. Introduction

In the last two and a half decades, the electrochemical scientific international community has devoted a great deal of attention to few fundamental aspects of the electrodeposition of metals [1], namely the mechanism and kinetics associated to the initial stages of formation of the first metallic nuclei. The main reason underlying such study preference, is that both aspects involve the significant occurrence of surface phenomena: for example, ordered adsorption, nucleation and growth, short-range phase transformations, cluster formation (including that of nanoparticles), and several others, which can be studied in depth. In view of the amount of information, particularly structural, that has been made increasingly available on the subject of underpotential deposition, UPD, it is only natural to expect the publication of authoritative works correlating the aforementioned with other aspects of UPD phenomena of the first metal monolayer, over a foreign substrate [2–9]. Consequently, such efforts have contributed to a significant increase of the fundamental understanding of electrochemical phase formation. However, the influence of the substrate's structure on the mechanism and kinetics of the monolayer formation, which entails formation of a new 2D phase growing on the surface of the substrate, has been relatively less studied [9]. The structure of the substrate surface plays an important role in its own right, as it determines specific features of the growing deposit, particularly during the first stages of the deposition process. The polycrystalline metal electrodes [10–15] do display a complex crystallographic character, bearing quite a large variety of surface orientations, separated by a network of grain boundaries, also with other emerging structural faults inherited from the mechano-thermal history of the substrate. Thus, diverse studies have attempted to relate the formation of monolayers onto such surfaces, being rather limited, insofar as the mechanism and the kinetics of formation concerned. The conventional electrochemical methods generally involve one macroscopic measurement, namely that of the current passing through the system, which makes it sufficiently difficult to differentiate among the diverse contributions to the overall current, likely to arise in association with those of the crystallographic variety. This is, the grain boundaries and other defects of the polycrystalline system must be considered an inherent part of the working electrode, because they may influence the measurement of relevant parameters like the density number of nucleating sites. The utilization of single crystal electrodes has helped us to study in a more systematic manner the influence of the surface morphology of the substrate upon the electrocrystallization process [2–9]. The formal study of interfacial phenomena is particularly well suited when basic data emerges from the analysis of the temporal response of the current passing through an electrode which is under potentiostatic control [16–32]. For this matter, the framework of several theoretical formalisms associated with metal electrodeposition, allow discernment of the dimensionality of the deposit, the rate limiting step for

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the overall process, as well as the determination of a reduced variety of kinetic parameters that have physical meaning. In view of the aforementioned, this research work deals with the application of chronoamperometry to study the initial stages of the formation and growth of copper nuclei onto gold electrodes like, Au(1 1 1), and Au polycrystalline from an aqueous 1 mM $CuSO_4$ solution in 1 M H_2SO_4.

2. Experimental

All experiments were performed within a typical three-electrode electrochemical cell, where a nitrogen atmosphere was circulated over the electrolyte to prevent oxygen dissolution. The working electrode was a 200 nm gold layer, supported on a heat-resistant glass substrate (Berlin Glass). The surface of the vacuum-deposited gold layer is (1 1 1), and could be safely annealed under a hydrogen flame. Other experiments were performed with a BAS polycrystalline gold tip of a rotating disc electrode, having 0.0707 cm^2 exposed working area. Cyclic voltammograms were obtained at pH 1 under UPD conditions, with the potential scans starting at 0.8 V vs. Cu^{2+}/Cu toward the negative direction at 15 mV s^{-1} scan rate. The gold electrode surface area was observed with a Scanning Tunneling Microscope, Digital Instruments NanoScope IIIa, in the case of the single crystal Au(1 1 1) and for the polycrystalline electrode an Olympus PMG3 metallographic microscope was used.

3. Results and discussion

3.1. Theoretical considerations

When a metal (Me) is in contact with a solution containing its ions (Me^{z+}), it can adopt its equilibrium potential E_{eq} generally referred to as the reversible Nernst potential given by the following equation:

$$Me_{sol}^{z+} + ze^- \underset{b}{\overset{a}{\longrightarrow}} Me \qquad (1)$$

which is described through the well known Nernst equation below

$$E_{eq} = E^0 + \frac{RT}{zF} \ln \frac{(Me_{sol}^{z+})}{(Me)} \qquad (2)$$

where z is the electron's number, F is Faraday's constant and E^0 is the standard potential for reaction (2) and E^0 gives the metal ions' activity. However, in concentration terms of the species involved, E_{eq} is described by Eq. (3):

$$E_{eq} = E^0 + \frac{RT}{zF} \ln \frac{\gamma_{Me_{sol}^{z+}}[Me_{sol}^{z+}]}{\gamma_{Me}[Me]} \qquad (3)$$

As it is somewhat inconvenient to deal numerically with activities, because the activity coefficients are mostly unknown, thus it is customary to use the potential known as formal potential $E^{0'}$, which brings in the standard potential and some of activity coefficients, such that:

$$E^{0'} = E^0 + \frac{RT}{zF} \ln \frac{\gamma_{Me_{sol}^{z+}}}{\gamma_{Me}} \qquad (4)$$

Then, the definition of $E^{0'}$ using also Eq. (2), can be written as:

$$E_{eq} = E^{0'} + \frac{RT}{zF} \ln \frac{[Me_{sol}^{z+}]}{[Me]} \qquad (5)$$

Eq. (5) allows relating E_{eq} to the concentrations of the species involved. However, as the ionic strength influences the activity, the $E^{0'}$ for the same reaction will vary from one medium to the next,

even in the case when, due to change in the study medium, there were no stable complexes formed between the metal ions and any of the components of the new medium, Y_{sol}^{j-}. For the case when different species of the metal ions are formed, $[Me(Y)_i]_{sol}^{z-(i \times j)}$, then $E^{0'}$ will also comprise terms involving the equilibrium constants and concentrations of some of the species involved during the complexation equilibrium. This is, particularly, the case of complexation reaction (6), where the metal ion Me^{z+} is involved, as follows:

$$Me_{sol}^{z+} + iY_{sol}^{j-} \underset{b}{\overset{a}{\longrightarrow}} [Me(Y)_i]_{sol}^{z-(i \times j)} \qquad (6)$$

with an equilibrium constant given as:

$$K(T) = \frac{[[Me(Y)_i]_{sol}^{z-(i \times j)}]]}{[Me_{sol}^{z+}] \times [Y_{sol}^{j-}]^i} \qquad (7)$$

Then, E_{eq} must be estimated to produce Eq. (8) instead of Eq. (1):

$$[Me(Y)_i]_{sol}^{z-(i \times j)} + ze^- \underset{b}{\overset{a}{\longrightarrow}} Me + iY_{sol}^{j-} \qquad (8)$$
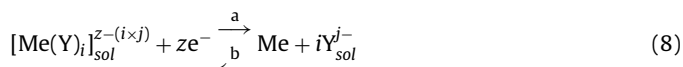
This is done using (4), (5) and (7), which gives (9)

$$E_{eq} = E^0 + \frac{RT}{zF} \ln \frac{\gamma_{Me_{sol}^{z+}}}{\gamma_{Me}} + \frac{RT}{zF} \ln \frac{[[Me(Y)_i]_{sol}^{z-(i \times j)}]}{[Me] \times K(T) \times [Y_{sol}^{j-}]^i} \qquad (9)$$

Now, defining $E^{0'}$ as (10), as follows:

$$E^{0'} = E^0 + \frac{RT}{zF} \ln \frac{\gamma_{Me_{sol}^{z+}}}{\gamma_{Me}} - \frac{RT}{zF} \ln K(T) - i \frac{RT}{zF} \ln[Y_{sol}^{j-}] \qquad (10)$$

The corresponding Nernst equation is now obtained:

$$E^0 = E^{0'} + \frac{RT}{zF} \ln \frac{[[Me(Y)_i]_{sol}^{z-(i \times j)}]}{Me} \qquad (11)$$

It follows from the treatment above, that quantitative thermodynamic data on E_{eq} of the solution studied is necessary.

The application of an electrode potential (E) more positive than E_{eq}, brings about the dissolution of the metal (refer to direction b in Eq. (1)), while for a potential more negative than the E_{eq} ($E < E_{eq}$), the metal ions will be reduced over the surface of the electrode, until a new equilibrium is reached. However, when a metal is deposited on a different metallic substrate, namely Cu on Au, rather than Cu on Cu, an apparent violation of the Nernst's Law becomes evident: the first monolayer is deposited at potentials more positive than the respective Nernst potential (E_{eq}). Such behavior has been termed underpotential deposition, UPD, which contrasts with the deposition processes taking place at overpotential, OPD. However, it must be remembered that in spite of the symmetry of the technical terms UPD and OPD, the physical origin of both effects is quite different. It becomes apparent that the reason for the OPD is only due to the kinetics of the deposition process, while that of the UPD is related to the energetics of the adatom-substrate bond.

The UPD deposit of metals has been extensively described in an authoritative revision [1,2]. The effect of the deposit at underpotential conditions is more conveniently demonstrated with cyclic voltammetry experiments, where the current observed is due to the electrochemical reaction taking place as the potential is continuously changed, with dE/dt constant within a selected range. The formation (dissolution) of the first monolayer is easily detected because pronounced current peaks at $E \geq E_{eq}$ become clearly apparent during the cathodic (anodic) potential scan, whereas the massive deposit (overpotential deposition, opd) or multilayers takes place only when $E < E_{eq}$. The fact that the first layer forms at much more positive potentials than those necessary for the massive deposit, simply means that the metal ad-atoms develop a stronger