Theoretical Considerations of Electrochemical Phase Formation in a Frank-van der Merwe System

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Abstract

Static calculation and preliminary kinetic Monte Carlo simulation studies are undertaken for the nucleation and growth on a model system which follows a Frank-van der Merwe mechanism. In the present case, we consider the deposition of Ag on Au(100) and Au(111) surfaces. The interactions were calculated using the embedded atom model. The process of formation and growth of 2D Ag structures on Au(100) and Au(111) is investigated and the influence of surface steps on this phenomenon is studied. Very different time scales are predicted for Ag diffusion on Au(100) and Au(111), thus rendering very different regimes for the nucleation and growth of the related 2D phases. These observations are drawn from application of a model free of any adjustable parameter.

Keywords: underpotential deposition, embedded atom method, dynamic Monte Carlo simulation, nucleation and growth, 2D phase formation.


1 Introduction

The electrodeposition of a metal (Me) onto a foreign solid surface (S) is one of the most extensively studied subjects in surface electrochemistry. This electrochemical phase formation phenomenon is a key aspect in important technological processes such as electroplating and electrocatalysis. In the last years, the application of in-situ local probe microscopy (SPM) techniques such as scanning tunneling microscopy (STM) and atomic force microscopy (AFM) provided a powerful tool to observe the initial stages of these processes on an atomic level. In a number of cases, metal overlayers can be electrodeposited onto a foreign metal substrate at a potential that is less negative than the Nernst equilibrium potential of the 3D metal phase. This so-called underpotential deposition process (UPD) occurs in the undersaturation or underpotential range, given by convention as:

\[ \Delta E = E - E_{3DMe} > 0 \]  

where \( E \) is the actual electrode potential, \( E_{3DMe} \) represents the equilibrium potential of the 3D metal phase, and \( \Delta E \) is the underpotential shift.

The UPD process has been well characterized for many systems with the SPM techniques and the preceding formation of metal phases of low dimensionality (0D, 1D, 2D) have been analyzed [1, 2, 3, 4, 5, 6]. The stability ranges of these \( iD \) Me phases \( (i = 0, 1, 2, 3) \) can be formally described by Nernst-type equations:

\[ E_{iDMe} = E_{iDMe}^0 + \frac{RT}{zF} \log \frac{a_{Me^{z+}}}{a_{iDMe}} \]  

where \( a_{Me^{z+}} \) denotes the activity of \( Me^{z+} \) ions within the electrolyte, \( a_{iDMe} \) is the activity of the \( iD \) Me phase, which is a constant for a condensed Me phase, and \( E_{iDMe}^0 \) represents the corresponding equilibrium potential. Usually, the electrochemical formation of the low dimensional condensed phases occurs under supersaturation conditions, whereas their dissolution takes place under undersaturation conditions. For an \( iD \) Me phase, the corresponding overpotential deposition (OPD) or supersaturation range, is given by:

\[ \eta_{iDMe} = E - E_{iDMe} < 0 \]  

where \( \eta_{iDMe} \) is the overpotential corresponding to the \( iD \) Me phase. The formation of these \( iD \) Me phases is strongly influenced by surface defects.
like kinks, vacancies, chemical impurities, monatomic steps, stacking faults, etc. The crystal surface can also be considered as a 2D crystal imperfection and plays an important role in the UPD phenomena. Thus, the stepwise formation of low-dimensional Me phases on a substrate in the underpotential range are generally characterized by the formation of 0D and 1D phases at relatively high underpotentials, followed by the formation of expanded and condensed 2D phases on atomically flat terraces at lower underpotentials.

In a previous work [7], we considered a theoretical model suitable to analyze the existence of these different phases when a metal is deposited on a foreign substrate with defects. We employed a lattice model along with a grand Canonical Monte Carlo simulation to study the thermodynamic features of the deposition process. One of the novel features of this model consisted in the realistic modelling of the interactions between the particles of the system, which was made using the embedded atom method (EAM). In this way, we introduced in a simple lattice model the many body features of the metallic binding which are indispensable for a reliable description of the metal-metal interactions. In agreement with the expectation drawn from the experience with experimental systems, we observed the correct sequence of appearance of 0D, 1D, and 2D phases when changing the chemical potential of the system in a direction corresponding to polarization of the surface towards negative potentials. Furthermore, the different regions of existence of the phases were separated by chemical potentials of a few hundreds of meV, whose values are of the order of magnitude of those observed experimentally.

In some cases, the 2D Me phase formation is not reached after sequence of appearance of 0D and 1D phases, but proceeds by the formation of 2D expanded commensurate Me adlayers which are transformed at lower undersaturation into condensed metal monolayers via a first order phase transition. Such phase transitions are observed, for example, during the Ag UPD on both Au(111) and Au(100) surfaces [8, 9].

In summary, UPD systems are very complex ones, as they involve phases of different dimensionalities which are mainly characterized by:

1. Specific adsorption of metal ions
2. Electronic charge transfer
3. Metal adatom-adatom and substrate-adatom interaction, which cannot be rigorously disentangled due to the non-additive property of the metal-metal interaction.
4. Undersaturation and/or supersaturation conditions with respect to the several (iD) phases that may appear on the system.

5. Crystallographic misfit, responsible in many cases for the lack of registry between the adsorbate and the substrate.

6. Cosorption and competitive sorption phenomena of anions as well oxidic species leading also to the formation of low-dimensional anion or oxidic systems in the corresponding undersaturation ranges.

7. The influence of the zero charge potential of the substrate on the electric field conditions at the interface and on adsorption and phase formation phenomena.

8. Surface site exchange processes leading to the formation of iD surface Me-S alloys.

In principle, a general description of the UPD phenomena would require a model incorporating all these items, something that is possible in principle with the current status of the developing of computers but still a formidable task for the small community of theoretical electrochemistry. However, more simple models may be formulated, including some of the points mentioned above, and a number of properties may be inferred for those systems whose salient features correspond to the model selected.

The key features of the present work concentrate on a reliable description of the metal-metal interaction by the EAM, and a lattice model which allows the consideration of relative large systems. Thus we can make the following comments in relation with the points mentioned above: Points 1), 2), 6) and 7) cannot be directly addressed in the present model, since this would require a detailed description of the metal/solution interface, that is only possible using first-principles calculations. Therefore, we shall only deal with the deposition of atoms at different rates, without being concerned on how these rates are related to the corresponding potential changes at the interface. Point 3) is one of the strengths of the present formulation, since the interactions in the EAM have been devised to account for the properties of the metals involved and their alloys. With respect to point 4), in the present work we concentrate on the deposition process, neglecting adatom desorption. So we set supersaturation conditions for the formation of the several low dimensional Me phases. Point 5) is a very complicated one, since
the crystallographic misfit induces in many cases the existence of incommensurate structures, which cannot be addressed by lattice models. Thus, the way to overcome this problem is by choosing a system with a negligible crystallographic misfit. In this respect, the deposition of Ag on Au appears as an optimal candidate. Concerning point 8), site exchange with the substrate could be considered within the present model, but preliminary studies by molecular dynamics show that this effect is not of primary importance in the submonolayer range.

According to the previous discussion, we perform in this work model calculations for Ag deposition on Au(111) and Au(100) surfaces, modelling the metal-metal interactions by the embedded atom method. These systems appear as optimal candidates due to a negligible crystallographic misfit. On the other hand, both Ag and Au atoms are mobile in our model, so that 2D alloys could naturally appear during the course of the simulation but this 2D alloying process has not been observed. Therefore, the aim of this work is to set the basis for a systematic study of a system involving electrochemical phase formation in a Frank-van der Merwe system and emphasize the role of metal-metal interactions in the surface processes accompanying this phenomenon.

2 Some experimental facts of the system
\textbf{Au}(hkl)/\textbf{Ag}^{+}

The system Au(hkl)/Ag\(^{+}\) is a typical example for Me UPD on a foreign substrate S, with strong Me-S interaction but negligible Me-S misfit \((d_{0,Au} = 0, 2884 \text{ nm}, d_{0,Ag} = 0, 2889 \text{ nm})\). Thus, the Frank-van der Merwe or layer by layer growth mechanism is expected to operate in this system. Our previous studies \cite{8, 9} have demonstrated that the Ag UPD on Au(111) and Au(100) occurs in the underpotential range \(0 \leq \Delta E/\text{mV} \leq 720\). For the system Au(100)/Ag\(^{+}\), the formation of an expanded Au(100) – \(c(\sqrt{2} \times 5\sqrt{2})R45^\circ\) Ag overlayer is observed within the potential range \(200 \leq \Delta E/\text{mV} \leq 550\). At lower underpotentials a limited growth of steps occurs and 2D Ag islands are formed involving simultaneous 2D nucleation and growth at steps and flat terraces (Figure 1). The atomic structure on top of islands as well as terraces is quadratic with an interatomic distance of \(d_{0,Ag} = 0.29 \pm 0.01 \text{ nm}\). These morphological and atomic observations indicate that the expanded
structure transforms into a Au(100) − (1 × 1)Ag phase via a first order phase transition. The steps of the 2D Ag islands grow slowly depending on the potential, until a complete Ag UPD monolayer is formed at $\Delta E < 15$ mV. On the other hand, in the system Au(111)/Ag$^+$ the experiments showed an expanded Au(111) − (4 × 4)Ag structure in the range $50 \leq \Delta E / \text{mV} \leq 500$ which is transformed to a Au(111) − (1 × 1)Ag phase at lower underpotentials. The interatomic distance observed ($d_{\text{Ag} \cdots \text{Ag}} = 0.28 \pm 0.01 \text{nm}$) indicates the formation of an hexagonal close-packed Ag monolayer. It is important to note that, in this case, the formation of the condensed 2D Ag phase on Au(111) occurs preferentially at monatomic steps of the substrate, without the formation of 2D islands (Figure 2). The atomic structures and morphologies described above were observed in both sulphate and perchlorate solutions. In addition, electrosorption valency measurements have indicated that coadsorption or competitive adsorption of sulphate or perchlorate anions can be excluded. Nevertheless, as was suggested [8, 9], a nearly constant anion coverage in the entire Ag UPD range cannot be excluded because Ag UPD on Au($hkl$) occurs at positive potentials with respect to the potential of zero charge of Au($hkl$) and Ag($hkl$).

From this brief experimental outlook, it is clear that the model we are presenting in this work is still missing an important number of features to reflect the experimental situation. However, as we shall see below several aspects of the experimental system coincide with the predictions of the model.

### 3 Model and simulation method

#### 3.1 Interatomic potential

The choice of proper interatomic potentials to perform the simulations is one of the key elements of the model. Several methods are available to calculate the total energy of a many-particle metallic system, with a computational effort comparable to that of a pair potential [10]. It is worth mentioning the embedded atom method (EAM) [11], the N-body potentials of Finnis and Sinclair [12], the second-moment approximation or Tight-binding (TB) [10] and the glue model (GM) [13]. In this work we employ the embedded atom method [11] because it reproduces important characteristics of the metallic binding that cannot be obtained using simple pair potentials.

The EAM considers that the total energy $U_{\text{tot}}$ of an arrangement of $N$...
particles may be calculated as the sum of energies $U_i$ corresponding to individual particles

$$U_{tot} = \sum_{i=1}^{N} U_i$$

(4)

where $U_i$ is given by

$$U_i = F_i(\rho_{h,i}) + \frac{1}{2} \sum_{j \neq i} V_{ij}(r_{ij})$$

(5)

$F_i$ is denominated embedding function and represents the energy necessary to embed atom $i$ in the electronic density $\rho_{h,i}$ at the site at which this atom is located. $\rho_{h,i}$ is calculated as the superposition of the individual electronic densities $\rho_i(r_{ij})$:

$$\rho_{h,i} = \sum_{j \neq i} \rho_i(r_{ij})$$

(6)

Thus, the attractive contribution to the EAM potential is given by the embedding energy, which accounts for many-body effects. On the other hand, the repulsion between ion cores is represented through a pair potential $V_{ij}(r_{ij})$, which depends only on the distance between the cores $r_{ij}$:

$$V_{ij} = \frac{Z_i(r_{ij})Z_j(r_{ij})}{r_{ij}}$$

(7)

where $Z_i(r_{ij})$ may be envisaged as a sort of effective charge, dependent on the nature of the particle $i$.

The EAM has been parametrized to fit experimental data like elastic constants, dissolution enthalpies of binary alloys, bulk lattice constants and sublimation heats \[11\]. Pair functionals have been successfully used for surface diffusion studies and adsorption of metals on metallic surfaces \[14, 15, 16\].

3.2 Lattice model

Lattice models for computer simulations have been widely used in studies of nucleation and growth, because they allow simulations with a large number of particles at a relatively low computational cost. The reason for this advantage is the use of fixed rigid lattices that restrict enormously the number of possible configurations for the adsorbate as compared with a model where in
principle all positions in space are available. While continuum Hamiltonians are much more realistic in those cases where epitaxial growth of an adsorbate leads to incommensurate adsorbed phases [17] or to adsorbates with large coincidence cells, the use of lattice models may be justified on the basis of experimental evidence or continuum computer simulations that predict a proper fixed lattice geometry. In the present case, we have strong evidence from simulations within the canonical Monte Carlo method [18] which indicates that at least one of the phases occurring during Ag underpotential deposition on Au(111) and Au(100) possess a pseudomorphic structure. In fact, our continuum MC simulations showed that Ag monolayers adsorbed on Au(111) and Au(100) spontaneously acquired a (1 × 1) coincidence cell in agreement with the experimental finding at low underpotentials. For this reason, we shall employ here a lattice model to represent the square (100) and the hexagonal (111) surface lattices in kinetic Monte Carlo simulations. Square lattices and hexagonal lattices of different sizes with periodical boundary conditions are used in the present work to represent the surface of the electrode. Each lattice node represents an adsorption site for a Ag or a Au atom.

Two further approximations in the present model must also be mentioned. First, we neglect the effect of the presence of solvent molecules. This approximation should not be critical as long as the partial charge on the adatoms is small, thus minimizing the ion-dipole interactions. Second, we also neglect effects related to specific anion adsorption. This may not be true for the experimental system, but thin layer twin electrode experiments gave no indication of any change in the amount of anion adsorption upon building the adsorbed monolayer [1]. On the other hand, the possibility of a nearly constant anion layer on the bare substrate Au(100) as well as on a Ag UPD modified Au(100) has been indicated [3]. In the case of other systems, the adatom-anion interactions have been shown to be very important [19] in playing a decisive role for determining the energetics of the system. This has been recently analyzed by some of us in thermodynamic terms [20].

3.3 Calculation of Gibbs energy of cluster formation.

The initial stages of a phase formation are of primary importance, because the competition of different processes occurring during this phenomenon determine in many practical cases the final structure of the deposit. The thermodynamic foundations of the initial stages of bulk phase formation are well
settled and have been thoroughly discussed in advanced books on the field [1]. For this reason, we shall address here briefly the topics relevant for the present calculations. The free energy change $\Delta G(N)$ produced when a three-dimensional cluster of $N$ atoms is formed on a surface at a certain overpotential $\eta_{3DMe}$ can be written as:

$$\Delta G(N) = -Nze |\eta_{3DMe}| + \Phi(N)$$  \hspace{1cm} (8)

where $z$ is the valence of the deposited ions, $e$ is the elementary charge and $\Phi(N)$ is the energy consumed for the formation of the new interface boundaries. In the 3D case, this quantity is related to the specific surface energies $\sigma_i$ of the facets of the cluster, the specific interface energy $\sigma_{j*}$ and the surface energy of the substrate according to:

$$\Phi(N) = \sum \sigma_i A_i + A_{j*} (\sigma_{j*} - \sigma_{sub})$$  \hspace{1cm} (9)

where $A_i$ denotes the respective surface areas. $\Phi(N)$ can also be calculated within the atomistic model, as long suitable potentials for the system are available. If we called $E_{c+S}$ the energy of a system consisting of a cluster of $N$ atoms of the metal Me on a substrate $S$, $E_S$ the energy of the free substrate, and $E_b$ the binding energy per atom of the bulk adsorbate metal, $\Phi(N)$ would be given by:

$$\Phi(N) = E_{c+S} - E_S - N E_b$$  \hspace{1cm} (10)

If the energy of the atoms in the cluster was equal to that in the bulk, Eq. (10) would yield $\Phi(N) = 0$, and a vanishing small overpotential would be enough for the growth of the new phase according to Eq. (8).

In case of 2D nucleation, which is the current subject of our interest, an equation similar to (8) is valid. However, instead of defining the overpotential with respect to the deposition of bulk Me, it is more suitable to refer to it as the thermodynamic deposition potential of the monolayer. Thus, the excess energy $\Phi_{2D}(N)$ will be calculated from:

$$\Phi_{2D}(N) = E_{c+S} - E_S - N E_{Me}^{mon}$$  \hspace{1cm} (11)

where $E_{Me}^{mon}$ is the binding energy of the Me atoms in the monolayer. In consequence, $\Phi_{2D}(N)$ takes into account the excess energy connected with the occurrence of the border of the 2D islands.
For a given number of atoms \( N \), several values of \( \Phi_{2D}(N) \) can be found depending on the geometry of the 2D cluster. For each \( N \) we have only considered the energy corresponding to most stable configuration. This was obtained by means of a simulated annealing procedure. This technique has often been used to obtain minimal energy structures or to solve ergodicity problems. A suitable way to implement this technique is through the canonical Monte Carlo method at different temperatures. In other words, a given number of atoms, \( N \), is selected, and a simulation allowing the motion of the atoms on the surface is started at a high initial temperature \( T_0 \), in the order of \( 10^3 \) K. The system is later cooled down following a logarithmic law:

\[
T_f = T_0 K^{N_{cycles}}
\]

where \( T_f \) is the final temperature, \( N_{cycles} \) is the number of cooling steps and \( K \) is a positive constant lower than 1. A few hundreds of thousands of Monte Carlo steps are run at each temperature in order to allow an extensive exploration of the configuration space and the simulation stops when \( T_f \) is reached.

### 3.4 Model for Dynamic Monte Carlo simulations

Although Monte Carlo methods have been traditionally related to the study of equilibrium properties, it is possible, if some conditions are fulfilled, to use them to compute the time evolution of a system. The foundations of dynamical Monte Carlo simulations have been discussed by Fichtorn and Weinberg [21] in terms of the theory of Poisson processes. According to this method, the sampling of the system must implicate transition probabilities based on a reasonable dynamic model of the physical phenomena involved. Besides fulfilling the detailed balance criterion, the transition probabilities should reflect a ”dynamic hierarchy ” related to the processes taking place in the system.

In this preliminary study we are mainly interested in nucleation and growth phenomena, therefore, we shall consider only two types of processes related to the growth of the new phase: adsorption of an adatom on the surface and its diffusion in different environments. Since we are neglecting the desorption processes, the results of our model will be valid for relatively large overpotentials for the deposition of the Ag atoms.

To illustrate the model used for the dynamic calculations, we show in Figure 3 a-c the diffusion of a Ag atom on a Au(100) surface in three different
environments. In Figure 3a, a Ag adatom jumps between two equivalent sites without any near neighbors. In Figure 3b, it has one Ag neighboring atom in the initial position and none in the final state and in figure 3c the jump is again between two equivalent positions with one Au nearest neighbor. The corresponding potential energy curves calculated by the EAM at each stage of the diffusion are shown in Figure 3d. From these curves we obtain the two important quantities required to perform the dynamic MC simulation: the attempt frequency for overcoming the diffusion barrier, calculated for the curvature of the potential energy surface at the initial state, and the activation energy, by taking the difference between the energy at the saddle point and the corresponding value at the initial minimum. These curves were constructed for all possible environments and involved 729 and 6561 energy curves in the case of the (100) and (111) faces respectively.

In the case of the adsorption rates, we assumed the same rate for all free sites. A more realistic calculation should also take into account different rates on different environments. This would require a complete knowledge of the degree of solvation of the discharging ion and detailed information of the different transition states in different environments. This information is not available for the present system but could be easily introduced in our modelling. Experimental evidence show that electrodeposition of metal ions on native or foreign substrates take place preferentially at 0D and 1D surface inhomogeneities such as kink and monoatomic steps. In the case of foreign substrates, 0D metal clusters are preferentially formed at these inhomogeneities. We have addressed the role of different types of defects by means of thermodynamic Monte Carlo studies in previous work, confirming this expectation. In the present work, we study the deposition phenomena from a kinetic point of view, analyzing the influence of the deposition rate on the formation and growth of the 2-D phase on a foreign surface with a relatively small number of defects.

4 Results and discussion

4.1 Static calculations

4.1.1 2D Ag cluster formation on Au(100) and Au(111) surfaces.

Figure 4 shows the Gibbs energy of 2D Ag cluster formation on Au(100) as a function of size $N$, calculated according to the method described in section
3.3. Since we are using an atomistic model, our curves are discontinuous. For this reason, we have fitted our curve for $\eta_{2DAg} = 0$ by means of a square root law, and later employed it to draw the corresponding continuous lines for $|\eta_{2DAg}| > 0$. With this information we were able to calculate the size of the 2D critical clusters for different overvoltages, as reported in Table 1a. The sizes of the critical clusters are relatively large as compared with the values estimated for nucleation of Ag on a Ag(100) quasi perfect surface \[1\], given in Table 2b. In other words, the overpotentials for nucleation are considerably larger when Ag nucleates on the foreign Au(100) surface.

Figure 5 shows the Gibbs energy of a 2D Ag cluster formation on Au(111) at different overpotentials. It can be noticed that for a given overpotential, the maximum in the curve appears at larger $N$ than in the case of the Au(100) surface, that is, the energy for the formation of border atoms from atoms located in the monolayer is larger for the adsorbate on the (111) face. This fact can be understood in terms of the relative energy change for this process. In the case of an adsorbate in the (100) monolayer, it has eight nearest neighbors: 4 Au substrate atoms plus 4 Ag atoms belonging to the monolayer. This coordination changes to seven (4 Au + 3 Ag) for a border atom. In the case of the (111) adsorbate, the change is from nine (3 Au + 6 Ag) to seven (3 Au + 4 Ag) at the border, that is, the change of coordination to produce a border atom from the monolayer is more important in the case of the more compact adsorbate, originating a stronger energy change. This is somehow the 2D analogous of the qualitative justification why more open faces exhibit a larger surface energy than the more compact ones.

4.1.2 Diffusion of single Ag atoms on Au(100) and Au(111)

The growth of a 2D phase after nucleation involves a number of elementary steps that should be considered in a general formulation of the phenomenon. This has been analyzed in detail in specialized texts on the field\[1\], hence we simply enumerate them here:

1. Bulk diffusion of the discharging ions.
2. Adatom electrodeposition and electodesorption.
3. Surface diffusion of the discharged adatoms and diffusion of adatoms along the steps.
4. Direct attachment to steps or kink sites.

The relative rates of these processes govern the overall rate and it is of key importance for the modelling of each system to determine the one(s) ruling the whole process. For example, in the case of the growth of a 2D Ag cluster on Ag(100) quasi perfect faces, step 2 is very fast under the usual deposition conditions yielding an unusually high exchange current density of Ag atoms. In this way, the average random surface displacement of adatoms during their stay at the surface is small and surface diffusion plays only a subordinate role.

The high exchange current density of Ag atoms has also dramatic effects during the deposition of the second Ag monolayer on Au(111), producing very noisy STM pictures under these conditions. On the contrary, images obtained for the growth of Ag islands on Au(100) are stable and clear [8] (Figure 1b, 1c), denoting that the exchange current for Ag atoms on Au surfaces is considerably lower. On these grounds, we assume in our simulations and the following considerations that atom deposition occurs under conditions where atom exchange is negligible.

The diffusion coefficients $D_{hkl}$ of a Ag single atom on the Au surfaces can be calculated from:

$$D_{hkl} = \frac{na^2\nu}{4}e^{-\frac{E_a}{kT}}$$

where $a$ is the distance between adsorption sites, $\nu$ is the attempt frequency, $E_a$ is the activation energy for diffusion and $n = 4$ or 3 for the (100) and (111) faces respectively. We obtained $D_{100} = 3.3 \times 10^3 \text{Å}^2 s^{-1}$ and $D_{111} = 1.2 \times 10^{10} \text{Å}^2 s^{-1}$, indicating that the diffusion on the (111) face is much faster than the same process on the (100) face. These figures already give us a very important hint to predict the type of nucleation and growth behavior in these two faces under the usual experimental conditions in voltammetry. In fact, let us consider an experiment where the reduction current density producing adatoms, $i$, is of the order of 1 $\mu A/cm^2$, and let us assume that the surface presents terraces of the order of $40 \times 40 \text{ nm}^2$. The number of atoms originated at the terrace per unit time will thus be of the order of $10^2 s^{-1}$. We will denote this number with $\frac{1}{\tau}$. Thus, once an atom is deposited, it has the chance to diffuse the length:

$$d_{hkl} \simeq \sqrt{2 D_{hkl} \tau}$$
before any other atom is deposited on the average on the same terrace. If we replace in this equation the \( D_{hkl} \) obtained, we get \( d_{100} \approx 8 \text{Å} \) and \( d_{111} \approx 1.5 \times 10^4 \text{Å} \) respectively. Thus, while on the Au(100) face the deposited Ag atoms may meet other atoms for the nucleation and growth of the 2D phase, the Ag atoms deposited on the Au(111) surface will diffuse unhindered to the border of the terraces and produce the 2D growth there. Since the diffusion barriers are usually higher on (100) surfaces than on (111) ones, we expect that this should be a rather general result, also valid for other upd systems. It is worth mentioning that, as shown in section 2, the experimental Ag/Au(hkl) upd system presents a similar behavior, in that the growth of the 2D phase occurs at the border of steps on the (111) face, and in the form of islands on the (100) face, besides a limited growth at steps.

4.2 Dynamic Monte Carlo simulations.

4.2.1 Ag on Au(100)

We discuss here the results obtained with the simulation 2D box shown in Figure 6, which is relatively small as compared with real terraces, but should yield the correct qualitative features. We consider 1600 adsorption sites distributed over a 115 × 115 Å² square lattice, delimited by two rows of monoatomic high Au steps on each side. Periodic boundary conditions were applied in the direction parallel to the borders. Real surfaces present a more complex topology, with different kinds of 0D and 1D inhomogeneities like kinks or roughened steps. However, our simulation could also represent a situation where kink or steps are already decorated by 0D or 1D silver phases. We only allowed for the deposition of Ag atoms on the terraces at different rates \( v_{ads} \). We varied \( v_{ads} \) between \( 10^{-4} \text{ s}^{-1} \) and \( 10^2 \text{ s}^{-1} \) per free adsorption site, corresponding to potentiostatic conditions with an initial current density (\( \Theta \rightarrow 0 \)) ranging between \( 2 \times 10^{-2} \mu A/cm^2 \) and \( 2 \times 10^4 \mu A/cm^2 \). Although we made several sets of simulations, we discuss here some representative examples to obtain a physical insight into the phenomena taking place in each case.

For the slowest rate (\( 10^{-4} \text{ s}^{-1} \)) we typically observed initially a single particle diffusing on the surface towards the Au border step and then remaining attached to the border and diffusing parallel to it. Diffusion along the borders is relatively fast with respect to surface diffusion, since \( D_{100}^{\text{border}} = 1.7 \times 10^5 \text{Å}^2\text{s}^{-1} \). About 15 seconds later, a second particle entered and diffused to the
opposite side, followed by others that behaved in the same way. Two Ag stripes parallel to the Au borders grew in this way, being completed at about 650 seconds. After that a second row started to grow. Diffusion of Ag on the Ag border also showed a diffusion coefficient of the order of $2 \times 10^5 \text{Å}^2\text{s}^{-1}$.

In this simulation, no Ag island formation was evident on the surface and the growth occurred at the Au border. The third Ag row was completed at about 1800 seconds.

When the adsorption rate was $v_{\text{ads}} = 10^{-3} \text{s}^{-1}$, all the particles deposited up to 50 seconds were found to diffuse to the borders. At that time, a dimer was formed, which initially diffused on the surface and later was fixed by addition of more particles. At 170 s a trimer was formed, giving place to a second island. At 700 seconds, the coalescence started to take place between the growing islands and the growth at the Au borders. At 7250 seconds, only a single vacancy remained on the surface, diffusing with $D_{\text{vacancy}} = 4.2 \times 10^3 \text{Å}^2\text{s}^{-1}$.

The run with $v_{\text{ads}} = 10^{-2} \text{s}^{-1}$ presented several interesting features, since at this deposition rate (corresponding to $\approx 2 \mu\text{A/cm}^2$) the number of islands appearing in our simulation box allows for statistical analysis. For example, the number of islands was followed as a function of time. In the simulation probed, the number of islands reached a maximum of 7 at about 15 seconds (Figure 7), decreasing later and generating islands of vacancies at $t \approx 400$ s. At $t = 630$ s, only a vacancy remained diffusing on the surface and the surface was completely covered by Ag atoms at $t = 860$ s. In Figure 8 we show snapshots of a simulation with this adsorption rate.

In the case of deposition rates of $10^{-1} \text{s}^{-1}$ and larger, a coexistence of growing islands and diffusing particles is observed from the very beginning of the simulation. Typical times for the completion of the monolayer are reported in Table 2. It can be noticed that they follow the expected logarithmic law.

Figure 9 shows the number of islands as a function of the coverage degree for different deposition rates. Each of the curves represents an average over six simulation runs. It can be noticed there how the number of islands increases with the deposition rate, with a maximum in the range $0.1 < \Theta < 0.2$ which is progressively better defined at the higher rates.

Unfortunately there are no experiments available for the present simulation conditions, consequently a direct comparison is not possible. STM-voltammetric experiments where the deposition rate is of the same order of magnitude as some of our results ($i \approx 2 \mu\text{A/cm}^2$, corresponding to $v_{\text{ads}} = \ldots$)
show the occurrence of growing islands, generated at times of the order of a few seconds, which correspond to the simulation times where the islands appear in our simulations. It must be stressed, however, that the deposition history in the experiment is completely different, since the pseudomorphous phase appears after the voltammetric formation of an expanded Au(100) – c(\sqrt{2} \times 5\sqrt{2})R45°Ag phase which is not considered in the present model.

4.2.2 Ag on Au(111)

The simulation box was analogous to that of the Au(111) face, and the adsorption rates were varied between $10^{-3} \leq v_{\text{ads}}/s^{-1} \leq 10^8$. Since the activation barriers on this surface are very low, the absolute-rates model employed to calculate the transitions of atoms on the surface should deliver only qualitative predictions. Furthermore, some transitions on these surfaces were not activated at all. We assigned to these processes an arbitrarily high rate, so they made a negligible contribution to the time accumulation in the simulation and we were able to follow the relatively slow processes occurring on the surface.

In the case of the Au(111) surface, the adsorption sites constitute an hexagonal lattice. Two kinds of adsorption sites occur, usually denoted as 'hcp' and 'fcc', depending on the position of the adsorbing atom with respect to the second lattice plane of substrate. In our model these sites have practically the same energy, but the lattices they define cannot be filled simultaneously due to steric hindrances. Thus, under some simulation conditions two domains (one fcc and one hcp) of the adsorbate appear, with a corresponding domain border.

For $v_{\text{ads}} \leq 10^3$ s$^{-1}$, all atoms reached the border of the box. However, since we are dealing now with the (111) face, the borders are no longer equivalent. One of them exhibits a facet with square symmetry (that we shall label \{100\}) and the other presents three fold sites \{111\}. In the case of the \{100\} border, we obtained straight Ag stripes parallel to the step, while a triangle like decoration was found in the case of the \{111\} step (Figure 10). This different type of growth occurs in our model on kinetic ground as a consequence of the fact that only jumps between nearest neighbors are allowed. Molecular dynamic calculations would be very helpful to elucidate this point.

For $v_{\text{ads}} = 10^4$ s$^{-1}$ we observed more than one Ag atom diffusing simul-
taneously on the surface, building in some cases dimers that also diffuse.

For \( v_{ads} = 10^5 \) s\(^{-1}\) we observed the formation of islands on the surface, initially triangular like. Domains of sites corresponding to adsorption on fcc or hcp sites are formed. The surface becomes completely filled at \( t = 7 \times 10^{-5} \) s

For \( 10^6 \leq v_{ads}/s-1 \leq 10^8 \) hcp and fcc domains are formed on the surface (Figure 11), with the domain border fluctuating rapidly within one near neighbor distance.

According to the simulation results for this phase, we conclude that for the deposition rates under which the experiments are undertaken (corresponding to \( 0.1 \leq v_{ads}/s-1 \leq 1 \)), no islands should be formed on the surface. Surface diffusion is fast and allows the atoms to reach neighboring steps on the surface, where nucleation and growth occur. Although the Ag deposition on Au(111) seems to be a rather complex process, including the formation of a number of expanded faces, we think that these findings, that are based on the fast diffusional behavior of Ag on Au(111), should be at least qualitatively valid.

5 Conclusions

Inspired in puzzling experimental results, we have modeled the underpotential deposition for a Frank-van der Merwe system on (111) and (100) faces by means of a lattice model employing a realistic potential for the metal-metal interactions. From a thermodynamic viewpoint, the present static calculations indicate that the overpotentials for Ag nucleation on Au will be larger for the (111) than for the (100) face. The reason for this behaviour is the larger energy that is required to generate the borders of the growing Ag clusters in the former case.

If a negligible exchange current for adatoms is assumed, kinetic simulations by means of dynamic Monte Carlo indicate that the nucleation and growth should take place with characteristic time of tenths of seconds in the case of the Au(100) face and of the order of milliseconds in the case of the Au(111) face. Therefore, if Ag is deposited at intermediate rates on both surfaces, island growth should occur on Au(100) but not on Au(111). It must be stressed that this behaviour is a purely kinetic effect. On thermodynamic grounds, the growth of the 2D phase should always start at steps and not on the terraces.

It must be emphasized that these conclusions are all drawn from a model
which is free from any adjustable parameters. A desirable improvement of the present model is to consider the electrodesorption of adatoms in different environments that involves a model for electron transfer in this system. Work in this direction is in progress.

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References

[1] E. Budevski, G. Staikov and W. J. Lorenz, *Electrochemical Phase Formation and Growth*, VCH Weinheim, (1996).

[2] W. J. Lorenz and G. Staikov, *Proceedings of the Sixth Symposium on Electrode Processes*, Vol. 96-8, p. 189, The Electrochemical Society, Pennington NJ, (1996).

[3] W. J. Lorenz and G. Staikov, *Proceedings of the Conference "Electron and Ion Charge Transfer in Condensed Systems",* Trieste, Italy, July 15-19 1996, ed. by A. A. Kornyshev, M. Tosi, and J Ulstrup, p. 241, World Scientific, Singapore-New Jersey-London-Hong Kong, (1997).

[4] G. Staikov, W. J. Lorenz, and E. Budevski, *Imaging of Surfaces and Interfaces - Frontiers in Electrochemistry*, Vol. 5, p. 1, edited by P. Ross and J. Lipkowski, Wiley-VCH, Weinheim (1999).

[5] W. J. Lorenz, W. Wiesbeck, and G. Staikov. *Proceedings of the "International Symposium in Honor of Norio Sato: Passivity and Localized Corrosion”,* Vol. 99-27, p. 655, The Electrochemical Society, Pennington, USA, (1999).

[6] W. J. Lorenz, W. Wiesbeck, and G. Staikov, *Proceedings of the "Second International Symposium on Pits and Pores: Formation, Properties, and Significance for Advanced Materials”,* The Electrochemical Society, Pennington, USA, in press.

[7] M. C. Giménez, M. G. Del Pópolo and E. P. M. Leiva, *Electrochim. Acta*, 45, 699-712, (1999).

[8] S. G. García, PhD. Thesis, Universidad Nacional del Sur, Bahía Blanca, Argentina (1997).

[9] S. G. García, D. Salinas, C. Mayer, E. Schmidt, G. Staikov, W. J. Lorenz, *Electrochim. Acta* 43, 3007 (1998).
[10] Carlsson, *Solid State Physics*, 43, H. Ehrenreich, H. Seitz, and D. Turnbull, p. 1, Academic Press, New York, (1990).

[11] S. M. Foiles, M. I. Baskes and M. S. Daw, *Phys. Rev. B* 33 7983 (1986).

[12] M. W. Finnis and J. E. Sinclair, *Philos. Mag. A* 50 ,45 (1984).

[13] F. Ercolessi, E. Tosatti and M. Parrinello, *Phys. Rev. Lett.* 57, 719 (1986).

[14] C.L. Liu, J. M. Cohen, J.B. Adams and A. F. Voter. *Surface Science* 253, 334 (1991).

[15] M. I. Haftel, *Phys. Rev. B*, 48, 2611 (1993).

[16] M.G. Del Pópolo, E.P.M. Leiva, *J. Electroanal. Chem.* 440, 271 (1997).

[17] M. G. Samant, M. F. Toney, G. L. Borges, L. Blum and O. R. Melroy, *J. Phys. Chem.* 92, 220 (1998).

[18] M.C. Gimenez, M. G. Del Pópolo and E.P.M. Leiva. “Portucalensis”, *Conference on Electrified Interfaces*, Porto, Portugal,(1998).

[19] Zhichao Shi, Shijie Wu and J. Lipkowski, *Electrochimica Acta*, 40, 9 (1995).

[20] C. G. Sánchez, M. G. Del Pópolo and E.P.M. Leiva, *Surface Science*, 421, 59-72 (1999).

[21] K.A. Fichthorn and W.H. Weinberg, *J.Chem. Phys.* 95, 1090 (1991).
7 Tables

Table 1:

a) Size $N_{\text{crit}}$ of the 2-D critical cluster of Ag on Au(100) for different overvoltages $\eta$, calculated from the embedded atom method and a simulated annealing procedure.

| $N_{\text{crit}}$ | $|\eta_{2DMe}| / eV$ |
|-------------------|---------------------|
| 313               | 10                  |
| 78                | 20                  |
| 34                | 30                  |
| 20                | 40                  |
| 9                 | 60                  |
| 5                 | 80                  |
| 3                 | 100                 |
| 1                 | 170                 |

b) Sizes of critical clusters estimated for nucleation of Ag on a Ag(100) quasi perfect surface, as reported in ref. [1].

| $N_{\text{crit}}$ | $|\eta_{2DMe}| / eV$ |
|-------------------|---------------------|
| 67                | 6                   |
| 25                | 10                  |
Table 2: Average times required for the completion of the monolayer $\tau_{\text{mon}}$ for different adsorption rates per site $v_{\text{ads}}$. These times correspond to values averaged over 6 simulation runs.

| $v_{\text{ads}}/s^{-1}$ | $\tau_{\text{mon}}/s$ |
|-------------------------|------------------------|
| $10^{-4}$               | $6.7 \times 10^4$     |
| $10^{-3}$               | $8.3 \times 10^3$     |
| $10^{-2}$               | $7.50 \times 10^2$    |
| $10^{-1}$               | 70                    |
| 1                       | 7                     |
| $10^1$                  | 0.69                  |
| $10^2$                  | 0.067                 |
8 Figure Captions

Figure 1 In situ STM images of Ag UPD in the system Au(100)/5 × 10⁻³M AgClO₄ + 5 × 10⁻¹M HClO₄ at T = 298K. a) ΔE = 700 mV, b) ΔE = 200 mV, c) ΔE = 20 mV. I_{tip} = 20 nA.

Figure 2 In situ STM images of Ag UPD in the system Au(111)/5 × 10⁻³M AgClO₄ + 5 × 10⁻¹M HClO₄ at T = 298K. a) ΔE = 700 mV, b) ΔE = 278 mV, c) ΔE = 27 mV. I_{tip} = 15 nA.

Figure 3: a-c) Sample environments for the motion of a Ag atom on a Au(100) surface d) potential energy as a function of the distance along the diffusion path for the environments shown in a-c.

Figure 4 Gibbs energy of 2D Ag cluster formation on Au(100) as a function of size N at different overpotentials η_{2DME}.

Figure 5 Gibbs energy of 2D Ag cluster formation on Au(111) as a function of size N at different overpotentials η_{2DME}.

Figure 6: One half of the simulation box employed to represent Ag nucleation and growth on a Au(100) surface.

Figure 7: Number of islands as a function of time for a deposition rate of 10⁻² s⁻¹.

Figure 8. Snapshots of a simulation with the Au(100) surface, v_{ads} = 10⁻² s⁻¹. t₁=1.7 s, t₂=5.7 s, t₃= 19 s, t₄= 42 s, t₅= 76 s, t₆=101 s. Grey squares are Ag adatoms, black squares represent Au border atoms.

Figure 9 Number of islands as a function of the coverage degree for different deposition rates v. Each curve represents an average over six simulation runs.

Figure 10. Snapshots of a simulation with the Au(111) surface v_{ads} = 10³ s⁻¹. Simulation times are t₁= 0.8 s, t₂=4 s, t₃= 6.6 s, t₄= 13 s, t₅= 42 s, t₆=87 s. The upper border corresponds to the {100} step and the lower border to the {111} step.

Figure 11. Snapshots of a simulation with the Au(111) surface v_{ads} = 10⁵ s⁻¹. Circles and diamonds denote fcc and hcp adsorption sites respectively. Filled and empty sites are represented by filled and empty figures respectively. The simulation time was 1.46 × 10⁻⁷ s.
This figure "Figure1.jpg" is available in "jpg" format from:

http://arxiv.org/ps/cond-mat/0106122v1
This figure "Figure2.jpg" is available in "jpg" format from:

http://arxiv.org/ps/cond-mat/0106122v1
Ag on Au(100)

Number of atoms, $N$

Energy (eV)

$\eta = 0$ mV

$\eta = 10$ mV

$\eta = 20$ mV

$\eta = 30$ mV

$\eta = 40$ mV

$\eta = 50$ mV
Ag on Au(111)

Number of atoms, $N$

Energy (eV)

- $\eta = 0$ mV
- $\eta = 20$ mV
- $\eta = 40$ mV
- $\eta = 60$ mV
- $\eta = 80$ mV
- $\eta = 100$ mV
Ag/Au(100)

Number of islands

\( \Theta \)

- \( v = 0.001 \) 1/s
- \( v = 0.01 \) 1/s
- \( v = 0.1 \) 1/s
- \( v = 1.0 \) 1/s
- \( v = 10.0 \) 1/s
