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Kinetic Monte Carlo simulation of Pt discontinuous thin film formation adsorbed on Au

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Abstract

The evolution of a non-uniform Pt film adsorbed on Au, in contact with a solution containing $[PtCl_6]^{2-}$ ions was studied by means of lattice gas/kinetic Monte Carlo simulations with pair potentials at 300 K in the canonical ensemble. We found that the evolution of the morphology takes place through two types of exchange: surface diffusion and diffusion mediated by the solution, which occur with different probabilities or rates. These two types of moves were included in the simulation. By means of this dynamic description, it was possible to estimate the exchange rate of Pt atoms on a Au flat surface. A linear dependence was found between the exchange rate and the reciprocal of the number of particles. This function was used to extrapolate the exchange rate to a system of macroscopic size. The standard exchange current density calculated from this value was 5.24×10^{-6} A cm^{-2}. The morphological evolution of the film as a function of the time was also studied.

Keywords: Kinetic Monte Carlo simulation; Pair potentials; Discontinuous platinum deposit

1. Introduction

The modification of a metallic surface by adsorption or desorption processes is of great technological importance due to the possibility of producing surfaces with novel properties. Adžić and coworkers [1] have recently proposed a new metal deposition method to obtain a submonolayer of Pt, a monolayer of Pd, or a bilayer of Ag onto Au(1 1 1) by using a Cu adlayer as a template. In the case of Pt, the resulting deposit is a two-dimensional submonolayer consisting of partially interconnected nanoclusters of monoatomic height. On the other hand, the Pd and Ag films are uniform. The replacement occurs as a spontaneous irreversible redox reaction. In the former of these systems, a Pt^{4+} ion from the solution oxidizes two Cu UPD atoms, while it is simultaneously

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reduced to Pt^0 and deposited onto the Au(1 1 1) surface, which can be described by the following equation:

$$Pt^{+4} + 2Cu^0/Au(1\,1\,1) \leftrightharpoons 2Cu^{+2} + Pt^0/Au(1\,1\,1) \quad (1)$$

The amount of Pt deposited by replacement of a full monolayer of Cu is limited to half of the monolayer because Cu oxidation can supply two electrons per adatom, while four electrons are necessary for the reduction of the Pt^{+4} ion.

In the present work, the morphological evolution of a non-uniform film of Pt adsorbed on Au in contact with a solution containing $[PtCl_6]^{2-}$ ions was studied by means of lattice gas/kinetic Monte Carlo simulations with pair potentials. It was assumed that the metal replacement reaction is fast, and so at an initial time of $t \approx 0$ s, there is a $\theta = 0.5$ Pt deposit randomly distributed on the Au surface. The system was then allowed to evolve via atom diffusion and Pt atom exchange with the corresponding ions in solution. Thus, during the simulation, two types of movements in the exchange sampling were considered: the jumps of an atom to a neighboring site (surface diffusion) or the exchange between an occupied and an unoccupied site independently of the distance between sites (diffusion mediated by the solution). From a physical point of view, the exchange mediated by the solution may be possible due to the fact that the film is in contact with a solution containing Pt^{+4} ions. This exchange consists in:

$$Pt^{+4} + Au(subs) + Pt/Au(subs) \leftrightharpoons Pt/Au(subs) + Pt^{+4} + Au(subs) \quad (2)$$

where two coupled reactions take place, namely the reduction and adsorption of a Pt^{4+} ion on the Au(subs) coupled to the oxidative desorption of a Pt adatom.

By this dynamic description, it was possible to determine the exchange rate and its dependence on the size of the system (number of particles), which was used to extrapolate the exchange rate to the experimental system (a circular area with a diameter of 1 cm [1]). This value can be used to estimate the standard exchange current density for Pt deposition on Au(1 1 1). Finally, the morphological evolution of the film as a function of the time was also studied.

2. Model and simulation method

The experimental STM photograph of Pt/Au(1 1 1) taken from Ref. [1], was processed from an original gray scale photograph in order to obtain a binary black and white image. An area of 100×100 nm^2 was pixelated and transformed into a square lattice of 350×350 sites.

2.1. Lattice gas model

The Au substrate surface was assumed to be smooth, without defects, and was represented through square lattices of 25×25, 50×50, 100×100, 150×150, 200×200, and 350×350 adsorption sites with periodic boundary conditions. The adsorption sites may be occupied (by a Pt atom) or vacant in order to represent the Pt/Au system with a Pt coverage of 0.5. The initial configuration consisted of N Pt adatoms adsorbed at random in order to represent the first fast electron transfer that allowed the replacement of Cu by Pt atoms at random positions. Thus the following simulation considered the rearrangement of this system.

Pair potentials were used to represent the interaction between the particles with a Hamiltonian of the form:

$$H = -\frac{1}{2}\sum_{\langle i,j\rangle} \varepsilon_{ij} n_i n_j - \sum_i \varepsilon_i n_i \quad (3)$$

where n_i denotes the occupation number of the site (0 if the site is unoccupied or 1 if it is occupied); ε_{ij} is the interaction energy between the particle at site i and the nearest neighbor particle at site j (in this case, $\varepsilon_{ij} > 0$ because the interaction is attractive), and ε_i is the energy associated with the adsorption on site i. The first sum runs over all the nearest neighbor pairs of sites. A similar pair potential Hamiltonian has been employed by Plapp and coworkers [2,3] in studies of dynamic spinodal decomposition of binary alloys with vacancies

(ABv systems). This Hamiltonian is equivalent to the classical Ising model [4,5].

The site energy ε_i in Eq. (3) was found to be equal to the binding energy of a single Pt atom on a Au surface, $\varepsilon_{Pt} = 4.617$ eV. The interaction energy ε_{ij} was equal to $\varepsilon_{Pt-Pt} = 0.148$ eV, corresponding to the average Pt–Pt interaction in a Pt monolayer on Au. These are reasonable values proposed from our experience with the embedded atom method [6].

2.2. Simulation method

The Kinetic Monte Carlo (KMC) simulations were performed in the canonical ensemble at 300 K with pair potentials. The exchange sampling employed takes into account two types of movements, the jump of a particle to a nearest neighbor vacant site (surface diffusion) and to a more distant vacant site (diffusion mediated by the solution) [4,7].

The KMC simulations may predict the evolution of the morphology of the system as a function of the physical time. We briefly recall the KMC procedure. A vector containing all the events must be constructed and one of them is randomly selected to occur, and the time advanced an increment Δt selected from an exponential distribution containing a random number η and the sum of all the rates of the processes v_T that may occur in the system [8].

In the case of the present problem, for each step of the simulation, v_T is given by:

$$v_T = \sum_{i=1}^{n_{diff}} v_i^{diff} + \sum_{j=1}^{n_{exch}} v_j^{exch} \tag{4}$$

where v_i^{diff} is the rate of each of the diffusion events that may occur at a certain time of the simulation t, and v_j^{exch} is the corresponding rate for the exchange of a particle with a vacant site on the surface. n_{diff} and n_{exch} are in turn the total number of diffusion and exchange events that may occur in the system respectively. If diffusion steps to nearest neighbors is assumed, n_{diff} can be calculated by looking at the number of unoccupied sites close to each adsorbed particle and adding up this number for all particles. On the other hand, n_{exch} can be obtained by adding up the possible exchanges of each particle with all the free sites on the surface.

In order to calculate the time for the simulation, we must make some assumptions for the diffusion rates. As stated above, a diffusion rate can be given the form:

$$v_i^{diff} = v_i e^{-E_i/k_B T} \tag{5}$$

where v_i is an attempt frequency and E_i denotes the activation energy. In a first approximation, we shall consider v_i to be the same for all environments, say v_{av}, and make E_i dependent on the environment of the initial state according to:

$$E_i = E_{free}^{diff} - g(\Delta n_i)\varepsilon_{Pt-Pt}$$
$$g(\Delta n_i)\begin{cases} = \Delta n_i & \text{if } \Delta n_i \leqslant 0 \\ = 0 & \text{if } \Delta n_i > 0 \end{cases} \tag{6}$$

where Δn_i is equal to the change in the number of neighboring sites occupied by other adsorbates, and E_{free}^{diff} represents the activation energy for the diffusion of a free particle (no neighbors). Thus the diffusion rate in Eq. (5) can be written as:

$$v_i^{diff} = v_{free}^{diff} e^{g(\Delta n_i)\varepsilon_{Pt-Pt}/k_B T} \tag{7}$$

where $v_{free}^{diff} = v_{av} e^{-E_{free}^{diff}/k_B T}$ is the diffusion rate of a free particle.

In the case of the exchange rate between particles, we have made a similar consideration. With all the assumptions mentioned, Eq. (4) becomes:

$$v_T = v_{free}^{diff} \sum_{i=1}^{n_{diff}} e^{g(\Delta n_i)\varepsilon_{Pt-Pt}/k_B T} + v_{free}^{exch} \sum_{j=1}^{n_{exch}} e^{g(\Delta n_j)\varepsilon_{Pt-Pt}/k_B T} \tag{8}$$

v_{free}^{exch} is the exchange rate of a free particle with an unoccupied site surrounded by empty sites.

We can now define the ratio of exchange to diffusion rates as $f = v_{free}^{exch}/v_{free}^{diff}$ and rewrite the previous equation as:

$$v_T = v_{free}^{diff} \left[\sum_{i=1}^{n_{diff}} e^{g(\Delta n_i)\varepsilon_{Pt-Pt}/k_B T} + f \sum_{j=1}^{n_{exch}} e^{g(\Delta n_j)\varepsilon_{Pt-Pt}/k_B T} \right] \tag{9}$$

Eq. (9) allows now to establish a correlation with the physical time, defined in terms of the free diffusion characteristic time $t_{diff} = \frac{1}{v_{free}^{diff}}$.

Using Eq. (9), the time advance in the simulation is given by:

$$\frac{\Delta t}{t_{\mathrm{diff}}} = -\frac{\ln \eta}{\left[\sum_{i=1}^{n_{\mathrm{diff}}} \mathrm{e}^{g(\Delta n_i)\varepsilon_{\mathrm{Pt-Pt}}/k_{\mathrm{B}}T} + f\sum_{j=1}^{n_{\mathrm{exch}}} \mathrm{e}^{g(\Delta n_j)\varepsilon_{\mathrm{Pt-Pt}}/k_{\mathrm{B}}T}\right]} \tag{10}$$

Then, for a given configuration, the time increase can be defined according to Eq. (10). With this purpose, the sums in the denominator must be calculated, and f is a parameter that can be introduced in the simulation to represent the relative rates of the exchange and diffusion processes.

$v_{\mathrm{free}}^{\mathrm{diff}}$ can be estimated from the activation energy $E_{\mathrm{free}}^{\mathrm{diff}}$ for the diffusion of a single adatom on a surface which is equal to 0.85 eV (calculated with the embedded atom method) and employing the pre-exponential factor $v_{\mathrm{av}} = 1 \times 10^{12}\ \mathrm{s}^{-1}$, proposed by Haftel and Einstein [9]. The resulting diffusion rate of a free Pt atom on Au is equal to $v_{\mathrm{free}}^{\mathrm{diff}} = 6.34 \times 10^{-3}\ \mathrm{s}^{-1}$. Simulations with this $v_{\mathrm{free}}^{\mathrm{diff}}$ and different f allow to determine $v_{\mathrm{free}}^{\mathrm{exch}}$.

Since the experimental image of the deposited Pt structure was obtained after 180 s [1], we performed simulations within this time interval.

The shape factor S as defined by Levy et al. [10] was used to characterize the shape of the clusters. According to this idea, a cluster is characterized by the number N of atoms (size) and the number of bonds b in it. The ratio $S = b/N$ is therefore employed to characterize the shape of a cluster. A regular cluster (square or round) of large size ($N \to \infty$) is characterized by $S \to Z/2$ (where $Z = 4$ is the coordination number).

In a more general way, it is possible to define the mean value of S for a deposit with a given distribution of islands or for a discontinuous film, according to:

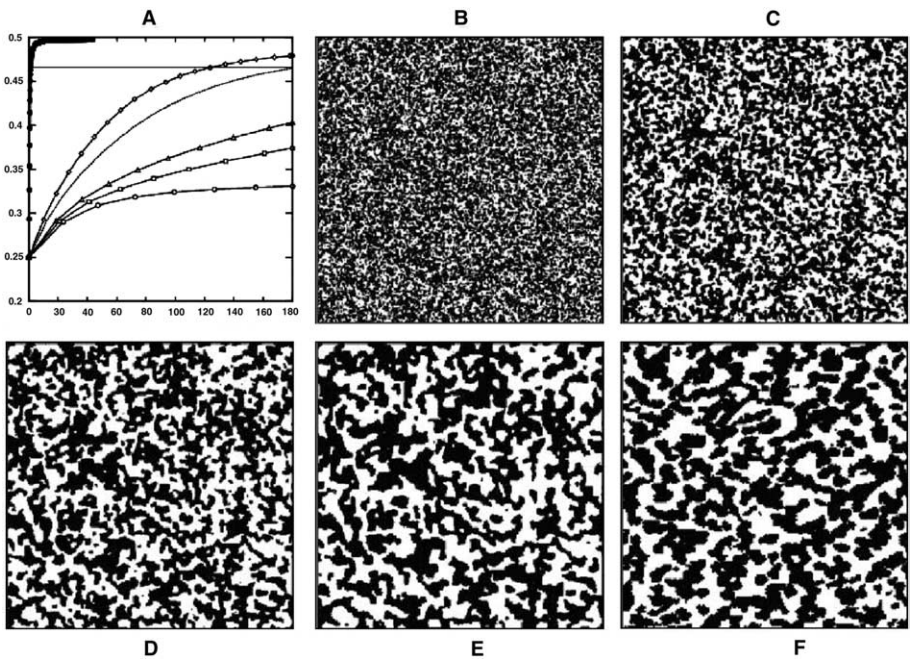

Fig. 1. Kinetic Monte Carlo simulation of a Pt deposit on Au at 300 K and $\theta = 0.5$; $100 \times 100\ \mathrm{nm}^2$; Pt (black) and vacant (white) dots respectively. (A) Change of the shape factor of the deposit as a function of time for different f (exchange rate/diffusion rate). Circle: $f = 0$; square $f = 1 \times 10^{-3}$; triangle $f = 5 \times 10^{-3}$; diamond $f = 1 \times 10^{-2}$; full circle $f = 1$. Solid line: the experimental shape factor value; dashed line: $f = 1.095 \times 10^{-2}$. B–E are the frames of the simulation with $f = 1.095 \times 10^{-2}$ at different times. (B) $t = 50$ s; (C) $t = 100$ s; (D) $t = 150$ s; (E) $t = 180$ s; (F) Pt/Au(1 1 1) experimental morphology taken from Ref. [1].

$$\overline{S} = \frac{\left(\frac{1}{2}\sum_{i=1}^{Z} i v_i\right)}{\sum_{i=0}^{Z} v_i} \tag{11}$$

where i denotes the number of bonds and v_i is the number of atoms with i bonds.

3. Results and discussion

The initial configuration of the Pt film adsorbed on Au was selected at random and the morphological evolution of the Pt film was studied as a function of the physical time by means of the KMC described above.

First, a system of 350×350 sites with an area of 100×100 nm^2 (which is the size of the experimental photograph) was selected. For this system size, there is only one ratio f (exchange rate/diffusion rate) which achieves the experimental shape factor (0.4559) in 180 s. This is shown in Fig. 1A, where the change of shape factor as a function of the time is plotted for different f values. The ratio $f = 1.095 \times 10^{-2}$ reaches the experimental shape factor in 180 s so that the exchange rate of a Pt atom for this system size would be equal to $v_{\text{free}}^{\text{exch}} = 6.945 \times 10^{-5}$ s^{-1}.

Figs. 1B–E show the evolution of the morphology as a function of the time for $f = 1.095 \times 10^{-2}$. The frames correspond to 50 s, 100 s, 150 s, 180 s with shape factors $\frac{\overline{S}(t)}{Z}$ of 0.3688, 0.4260, 0.4552, 0.4651 respectively. The frame at 50 s (Fig. 1B) is a discontinuous film which has thin branches and becomes more compact as a function of the time. The morphology shown in Fig. 1E has a shape factor of 0.4651 which is close to that obtained for the experimental photograph (0.4659). The latter is shown in Fig. 1F, as a binary black and white image processed from the original photograph taken from Ref. [1]. It can be observed that Fig. 1E and F present similar structures.

The experimental picture shown in Fig. 1F represents a window on the complete surface which is a circular area of 1 cm in diameter [1]. As the estimated exchange rate $v_{\text{free}}^{\text{exch}}$ depends on the size of the system, it was evaluated for different system sizes (25×25, 50×50, 100×100, 150×150, 200×200, and 350×350 adsorption sites). In Fig. 2

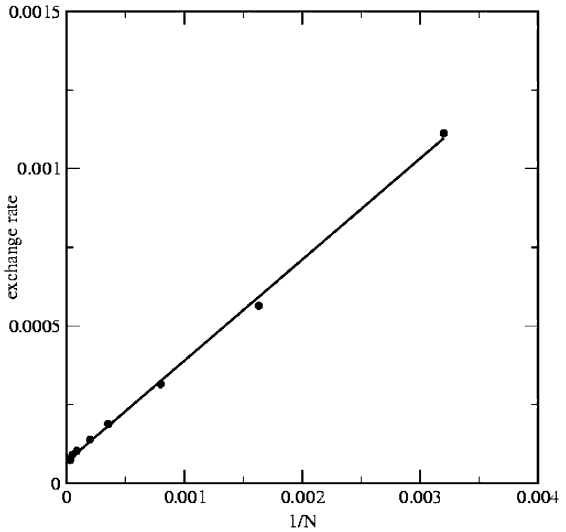

Fig. 2. Exchange rate for a Pt atom on a flat surface $v_{\text{exch}}^{\text{free}}$ (no neighbors) as function of the reciprocal number of particles. The black full circles correspond to $v_{\text{exch}}^{\text{free}}$ values obtained for systems of 25×25, 50×50, 75×75, 100×100, 150×150, 200×200, 250×250, and 350×350 adsorption sites. The line corresponds to a least-square fit.

$v_{\text{free}}^{\text{exch}}$ is shown as a function of the reciprocal of the number of particles, where a linear relationship can be observed. Thus a linear function of the type:

$$v_{\text{exch}}^{\text{free}}\left(\frac{1}{N}\right) = \beta + \alpha\frac{1}{N} \tag{12}$$

was fitted by least squares, obtaining $\alpha = 0.322 \pm 0.005$ and $\beta = (6.8 \pm 0.6) \times 10^{-5}$. These values were used to extrapolate the exchange rate of the experimental system. Since the latter is of macroscopic size, we have $v_{\text{free}}^{\text{exch}} \approx \beta$, which can be employed to estimate the exchange current density i_{exch} of Pt atoms on a flat Au surface according to [11]:

$$i_{\text{exch}} = \frac{v_{\text{exch}} z e_0 c^{1/2}}{s} \tag{13}$$

where z denotes the number of electrons transferred, e_0 is the elementary charge, s represents the atomic surface and the c is the concentration ($c_{[PtCl_6]^{2-}} = 0.1$ mM $PtCl_6^{2-}$ is the concentration of the solution [1]). This results in a standard exchange current density i_{exch}^0 ($c_{[PtCl_6]^{2-}} = 1$ M

$PtCl_6^{2-}$) of Pt atoms on a flat Au surface equal to 5.24×10^{-6} A cm^{-2}.

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