COMPUTER SIMULATION OF DISTANCE CHANGES IN NANOGAPS

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Resumen

En este trabajo empleamos métodos computacionales para estudiar teóricamente algunos aspectos geométricos de la disolución electroquímica de cobre previamente depositado sobre una punta de microscopio de efecto túnel (STM). El electrodo donde se lleva a cabo la disolución de átomos de cobre es aproximado por un conglomerado aislado y la superficie del sustrato es aproximada por un plano. La simulación se basa en un modelo computacional muy simple (guiado solamente por consideraciones energéticas) y el método del átomo embebido. Se encuentra que el ancho de la nanoseparación D entre la punta del STM y la superficie del sustrato varía en forma discreta, con una distribución de incrementos ΔD con valores más frecuentes en el intervalo 0.1-0.4 Å. Esto se aproxima a resultados de mediciones experimentales.

Abstract

In the present work we employ computational techniques to analyze some geometrical aspects of the electrochemical dissolution of a copper deposit generated on the tip of a Scanning Tunnel Microscope (STM). The electrode where the dissolution occurs is approximated by a metal cluster and the surface of the substrate is emulated by a geometrical plane. The simulation employs a simple computational model (based only on energetic considerations) and the embedded atom method. It was found that the width of the nanogap (D) between the STM tip and the surface should vary in a discrete way, with a distribution of increments ΔD that is maximal between 0.1 and 0.4 Å. This is close to the experimental observation.

Introduction

Experimental studies with small atomic clusters show that some of their properties often differ from those of the corresponding bulk metal. Experimental and theoretical studies performed in the 10 to 100 Å range of particle size [1-6], involving from tens to a few hundreds of atoms, analyze the possibility that under these conditions some remarkable structure relaxation may occur in a relatively short time. The study of the contribution of diverse thermodynamic and dynamic factors to this type of processes appears as a necessary condition to know the limits for controlling the stability and structure of these systems, which are of primary technological relevance.

A novel application of technological research consists in the fabrication of electrodes with a separation of a few nanometers (nm) with the purpose of connecting one or more molecules between them [7-9]. One of the methods devised is based on the mechanic rupture of a nanowire, following the formation of two electrodes [10]. Among

the non mechanical methods is that of electromigration [11] and the electrochemical methods [12, 13]. Mechanical methods allow obtaining a continuous range in the separation between two electrodes (nanogaps) [10]. On the other hand, electrochemical methods involving metal deposition and dissolution do not yield a continuous but a discrete range of nanogaps. This is the case of the experiments of Tao and coworkers [13], who have measured the tunneling current across a nanogap using tunneling microscopy, then translating the measured values of current into distances. In the electrochemical method developed by these authors, Cu atoms are deposited on or dissolved from one of the electrodes, the distance between the electrodes being controlled by a feedback setup. Tao and coworkers have shown that the size of the nanogap between the two electrodes is restricted to take discrete values with changes that are very close to 0.5 Å [13]. This interesting observation is deeply related to the discrete nature of matter. However, these changes in the nanogap are considerably smaller than the distances between the low indexes lattice planes of the fcc structure of Cu (see Table 1). For this reason, Tao and coworkers have postulated that this phenomenon is originated by the existence of relaxation processes, proposing that when an atom is added to the surface an atomic reconfiguration takes place towards more stable atomic structures (magic structures) that originate changes in the nanogap much lower than the expected ones (of the order of 2 Å).

Table 1: *Distances between the low indexes lattice planes of Cu fcc structure.*

Characteristic distances	(Å)
$d_{(a)}$	3.62
$d_{(nn)}$	2.56
$d_{(111)}$	2.08
$d_{(100)}$	1.81
$d_{(110)}$	1.28

Two types of systems were analyzed in the work of Tao. On one side, a couple of Cu electrodes microfabricated on oxidized Si was employed. On the other side, Cu was deposited on a STM tip and the tunneling current between it and a Au substrate was measured as a function of the separation distance. In the present work we use computational methods to study the latter process theoretically. The electrode where the electrodeposition and/or dissolution of Cu atoms take place is approximated by an isolated cluster, and the surface of the substrate is replaced by a plane located at a distance R_p from the center of the cluster.

We shall show that the discrete change in the width of the nanogap generates a distribution with the most frequently value found in the 0.1-0.4 Å interval. These results will be obtained only by consideration of the fcc structure of Cu, without the need of assuming atomic rearrangements. Since our results will be based on energetic considerations, the conclusions should be valid for the prediction of thermodynamic features, that is, in the limiting case of very slow deposition or dissolution rates of atoms. Some of Tao's experiments were performed under conditions where the deposition rates of atoms were considerably larger than the exchange rate of ions between the metal and

the solution, that is, very far from equilibrium, where kinetic effects are dominant. However, since the quantization of the tunneling current is observed in a wide range of conditions (fast and low deposition rates), we expect that some of the effects discussed here will be also operative at moderate deposition rates.

Computational details and geometrical model

We have used a semiempirical approach to simulate atomic clusters made of several hundreds of atoms. The present choice is the embedded atom method (EAM) [14], a many-body potential able to provide a reliable description of static and kinetic properties of transition metals for bulk systems, as well as for systems involving surfaces. The EAM provides interesting advantages with respect to more general models such as the Lennard-Jones one, since the consideration of many-body properties by the former yields a better description of cohesion out of equilibrium. Within this formalism, the total energy of the system is given by:

$$E_{total} = \sum_i E_i$$

$$E_i = F_i(\boldsymbol{\rho}_{h,i}) + \frac{1}{2}\sum_{j(\neq i)} \Phi_{ij}(R_{ij})$$

$$\boldsymbol{\rho}_{h,i} = \sum_{j(\neq i)} \boldsymbol{\rho}_j^{\sigma}(R_{ij})$$

Within this model the total energy of the cluster E_{total} is written as the sum of the contributions of each atom E_i. Each atom is assigned an energy term that is function of the electronic density $\boldsymbol{\rho}_{ij}$ at the point where the atom is located. This is calculated as the sum of the electronic densities of the isolated atoms $\boldsymbol{\rho}_j^{\sigma}(R_{ij})$. While the term $\sum_{j(\neq i)} \Phi_{ij}(R_{ij})$ is a sum of repulsive pseudocoulombic potentials, the parameters of the functional form $F_i(\boldsymbol{\rho}_{h,i})$ are obtained from a fit of experimental properties (sublimation energies, elastic constants, etc).

As a first approximation to an STM tip, we employed a nanocluster that we disassemble atom by atom, using as criterion for extracting an atom the total energy of the cluster. In other words, the atom to be removed is selected by attempting the extraction of each of the atoms of the cluster, starting from the same initial configuration with *n* atoms. The atom delivering the most negative energy change will be removed yielding a cluster with *n-1* atoms. When several equivalent alternatives result, a random choice is made between them. The procedure is then repeated with the *n-1* atoms cluster, and so on.

This can be symbolically written:

$$Cu_n \longrightarrow Cu_{n-1} + Cu \qquad \Delta E_{total}$$
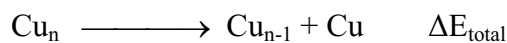
where ΔE_{total} corresponds to the energy change of the system upon removal of the atom selected. The initial configuration (state 1, Figure 1) consists of a 1709 atoms structure. This is prepared from the fcc structure of Cu according to the following. For a given

choice of the coordinate origin on one of the atoms of the lattice, we draw a large sphere enclosing Cu atoms. This sphere is then intersected by (111) and (100) lattice planes that are located at a distance of the center of the sphere that satisfies the Wulff relationship[15] and all the atoms out of the resulting volume are removed, remaining the 1709 mentioned above. The choice of this structure, based on the fcc structure of the bulk metal is made because we attempt to emulate a deposit on a bulk metal. In the case of very small clusters, more stable structures than the fcc can be found [16]. However, the experimental studies are made on a massive tip (or electrode) that provides an external field that will preserve the fcc structure of the metal.
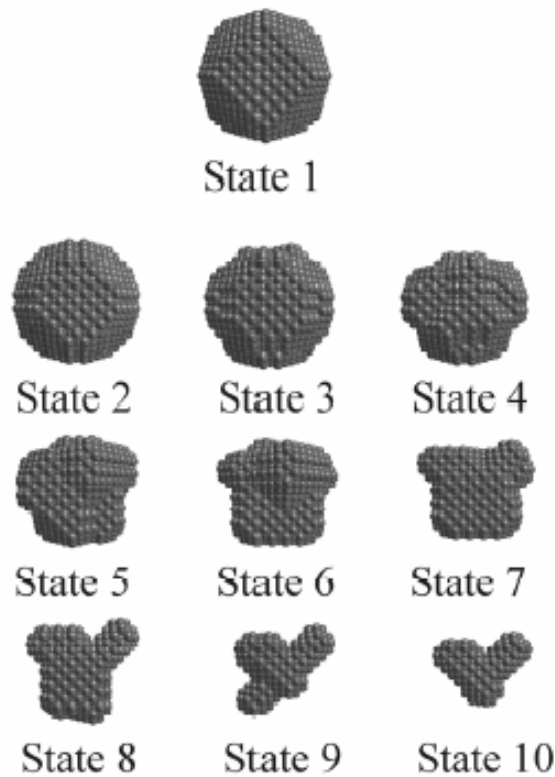

Figure 1: *Some configurational states for the dissolution of a 1709 atoms cluster.*

The experiments of Tao and coworkers [13] involve measurements of the tunneling current between an STM tip on which the metal is deposited and a substrate as a function of time. This current is transformed in a distance scale by means of a previous calibration. In order to mimic the experimental measurements, we shall calculate the closest distance between the cluster and an arbitrary plane representing the surface of the substrate. Figure 2a shows a scheme of the border of a cluster and a plane P, whose orientation is characterized by the unit vector **û.** We also show there the distances (d_1, d_2 and d_3) between different atoms at the border of the cluster and the plane P. The closest distance between the cluster and the plane, labeled with D, is given in this case by the distance d_1. Since the tunneling current decays exponentially with the distance, it is

reasonable to assume that practically all the current flows between the surface and the atom closest to it, located at the distance D. Since the clusters are constructed on the basis of an fcc structure, we shall define the corresponding planes (jkl), like for example (111), (100), (110) or higher indices. It is useful to denote with $\mathbf{R}_{jkl}$ the vector normal to the (jkl) plane of the cluster.
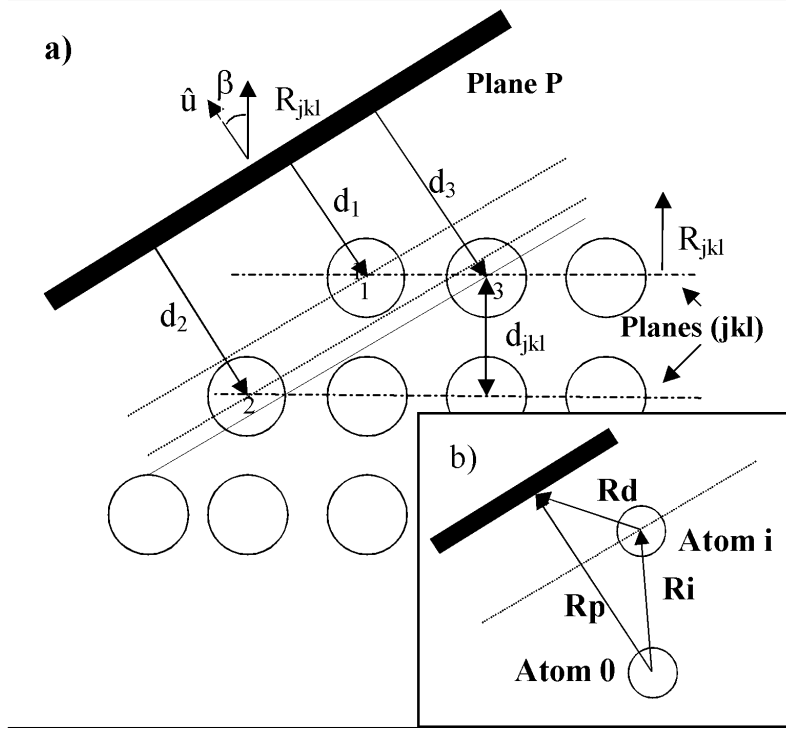

Figure 2: *a) Scheme of the border of a nanocluster close to the plane P representing the substrate. Atoms 1, 2 and 3 are the atoms located closer to the plane. b) Relationship between the vectors Rp, Ri and Rd=Rp-Ri.*

Figure 2b illustrates the calculation of the distance from an atom to a given plane, which we have located outside the surface. We denote with $\mathbf{R}_p$ the vector perpendicular to the plane representing the substrate, setting its origin at the center of our coordinate system and with $\mathbf{R}_i$ the vector defining the position of the *ith* atom of the cluster. We then define the vector $\mathbf{R}_d$ as the difference:

$$\mathbf{R}_d = \mathbf{R}_p - \mathbf{R}_i$$

so that the distance D will be given by:

$$D = \frac{\mathbf{R}_p \cdot (\mathbf{R}_p - \mathbf{R}_i)}{|\mathbf{R}_p|} = \mathbf{R}_d \cdot \hat{\mathbf{u}}$$

From figure 2a we notice that if atom 1 is removed from the cluster, atom 2 turns to be active for the tunneling process. In this way, D changes from d_1 to d_2. At this point we

start to understand that the distance D should take in principle discrete values, and that its variation should be strongly dependent on the way in which the cluster dissolves. It is also evident that the changes in D will be sensitive to the relative orientation of the plane P with respect to the surface of the cluster.

Discussion

Figure 1 shows the starting configuration (state 1, 1709 atoms) and intermediate states for the dissolution of a Cu cluster. At the beginning of atom removal (state 2) the first atoms disappearing are those at the border between two (111) faces. This involves 12 groups of 3 atoms each and leads to the appearance of (110) faces, that closely follows the prediction of the Wulff construction. Non symmetric clusters are generated starting from state 3, being small hexagonal structures made of 7 atoms found very often.
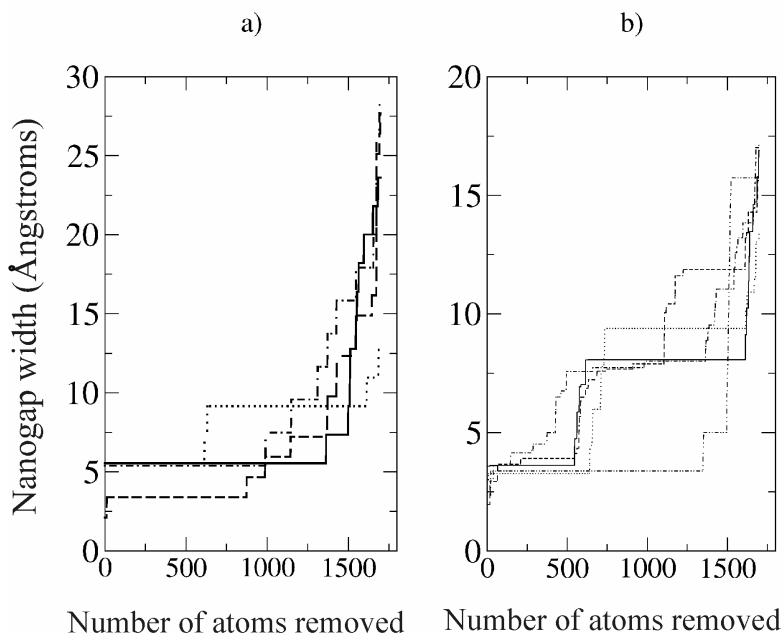

Figure 3: Nanogap width as a function of the number of atoms removed from the cluster for a) some specific orientations of the plane P ....(100), ──── ($\bar{1}$00), ── . ($\bar{1}\bar{1}\bar{1}$), ── ── . ($\bar{1}\bar{1}$0). *b) five orientations of the plane P chosen at random.*

Figure 3a shows the variation of the distance D as a function of the number of atoms taken away from the cluster for orientations of the plane P corresponding to the low index planes, given by the unit vector **û**, normal to the plane P (Fig. 2a). We shall denote here with (hkl) the direction perpendicular to the plane labeled with these indices, so that when we refer, for example, to the (100), we shall be addressing the direction of the x axis coordinate. It is found that according to the trivial expectation, the distance D increases with the dissolution of the cluster in a stepwise fashion, with increments ΔD corresponding to the distance between lattice planes. For example, when we analyze the

directions (100) and $(\bar{1}00)$, ΔD is close to 1.81 Å, which is the distance between 100 lattice planes (see Table 1). The same occurs for the (111) and (110) directions. On the other hand, when the direction that defines the plane P is chosen at random, as shown in Figure 3b, the changes in ΔD are still stepwise, but the changes in ΔD are no longer uniform. Some interesting questions arise from these results. Which is the probability of obtaining a given ΔD? Which is the shape of the probability distribution for ΔD? In order to answer these points, different planes (of the order of 5000) were generated at random, and the frequencies of the different ΔD were computed. A histogram for the observed frequency of ΔD is shown in figure 4. We see there that the distribution function appears to show a maximum in the region between 0.1 and 0.4 Å, then decreasing and showing again a secondary maximum around 2.50 Å, with a subsequent steep decrease.
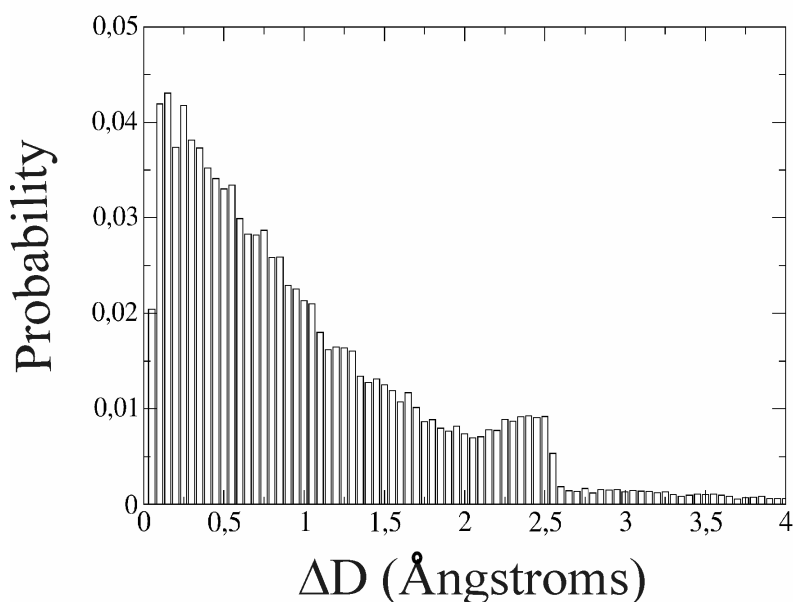

Figure 4: *Probability of obtaining a certain change ΔD in the width of the nanogap. The histogram was constructed by averaging over 5000 planes oriented at random.*

Conclusions

We have proposed a first approximation to the study of the behavior of nanogaps generated by electrochemical growth-dissolution processes. The present model is guided by simple energetic and geometrical considerations. According to the present predictions, the changes in the nanogap values ΔD depend on the relative orientation of the two electrodes. If the relative orientation of a nanoelectrode with respect to a plane surface is such that the surface is parallel to one of the low index lattice planes of the former, the ΔD values will correspond to the distance between these lattice planes. On the other hand, if a random distribution of orientations is chosen, a ΔD distribution results in a maximum value in the range 0.1-0.4 Å. In must be stressed that the present model is based only on energetic considerations, no kinetics elements being considered, so that its

application should be restricted to deposition or dissolution conditions not far from equilibrium.

Acknowledgements

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