Model Calculations for Copper Clusters on Gold Electrodes

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Abstract

Using the embedded-atom method, the structure of small copper clusters on Au(111) electrodes has been investigated both by static and dynamic calculations. By varying the size of roughly circular clusters, the edge energy per atom is obtained; it agrees quite well with estimates based on experimental results. Small three-dimensional clusters tend to have the shape of a pyramid, whose sides are oriented in the directions of small surface energy. The presence of a cluster is found to distort the underlying lattice of adsorbed copper atoms.

1 Introduction

During the last two decades, the scanning tunneling microscope (STM) has become a versatile tool for the investigation of conducting surfaces. It has not only been used for obtaining images with atomic resolution, but also for the modification of the surface structure. In particular, experimental procedures have been developed for the deposition of small metal clusters on surfaces. In this respect electrochemical interfaces are particularly suited for a controlled modification of surfaces, since two potential differences can be
varied independently: the bias between the electrode and the STM tip, and
the electrode potential with respect to a reference electrode. Thus, Kolb et
al. \[1\] have been able to deposit small copper clusters on the surface
of Au(111) electrodes by first depositing copper on the STM tip and sub-
sequently bringing the tip in contact with the surface. This deposition can
be controlled with great precision, and has given rise to speculations about
possible applications in nanotechnology. Recently, these copper clusters have
attracted further attention because they appear to be stable at electrode po-
tentials at which bulk copper dissolves, an effect which has been attributed
to quantum confinement \[2\].

Since these copper clusters on Au(111) have become to be consid-
ered as a prototype for electrochemical surface modifications, we have performed
model calculations for clusters of various sizes and shapes within the embed-
ded atom method. An important characteristic of the Cu/Au(111) system is
the fact that before the formation of the cluster, which is performed at po-
tentials slightly above the deposition potential for bulk copper, the electrode
is already covered with an epitaxial monolayer of copper atoms. Obviously,
this must be taken into account if the calculations are to be meaningful.

2 Calculation method

Since we are dealing with metallic systems comprising a large number of
atoms, we require a calculation method that allows the treatment of large
systems, but without missing the important many-body properties of metallic
binding. In this respect, the embedded-atom method (EAM) as proposed
by Daw and Baskes \[3\] appears as the natural choice. This model for the
interaction between metallic atoms in condensed phases gives a much better
description of the metallic bond than pair potentials which do not take into
account many-particle effects.

Within the embedded-atom method the total energy $E_{tot}$ of an arrange-
ment of $N$ metal particles is calculated as the sum of individual particles
energies $E_i$:

$$E_{tot} = \sum_{i=1}^{N} E_i$$

where

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

$F_i$ is the embedding function and represents the energy necessary to embed
atom $i$ into the electronic density $\rho_{h,i}$. The latter quantity is calculated at
the position of atom $i$ as the superposition of the individual atomic electronic
densities \( \rho_i(r_{ij}) \) of the other particles in the arrangement:

\[
\rho_{h,i} = \sum_{j \neq i} \rho_i(r_{ij}) \tag{2}
\]

The attractive contribution to the energy is given by the embedding function \( F_i \), which contains the many-body effects. The repulsive interaction between ion cores is represented as a radial pair potential \( V_{ij}(r_{ij}) \), which takes the form of a pseudocoulombic repulsive energy:

\[
V_{ij} = \frac{Z_i(r_{ij})Z_j(r_{ij})}{r_{ij}} \tag{3}
\]

where \( Z_i(r_{ij}) \) may be considered as an effective charge which depends upon the nature of particle \( i \).

We have employed two different versions of EAM potentials. On one hand, we have used the original parameterization of Foiles et al. \[5\] (denoted FDB), which is based on experimental data of pure metals and of several alloys, so as to reproduce such parameters as equilibrium lattice constants, sublimation energies, bulk moduli, elastic constants, vacancy formation energies, and heats of solution. On the other hand, we have used a potential specifically devised by Barrera et al. \[6\] (denoted BTI) to describe the structure and energetics of Cu-Au alloys.

### 3 Results and discussion

#### 3.1 Energetics of copper islands

The clusters generated by electrochemical STM techniques come in various forms and sizes. In this section we focus on flat islands that are only a few monolayers thick. In order to explore the energetics of such clusters we have performed static calculations within the embedded-atom scheme, and assumed a commensurate structure.

Both the energy of adsorption per atom in the bulk of the cluster and edge effects are of interest. In order to separate the two, we have adapted the drop model \[7\] that is often used for the calculation of surface energies to the two-dimensional situation.

In order to calculate properties for a Cu island adsorbed on a surface, we use a two-dimensional version of the drop model. Thus, we split the energy of a two-dimensional cluster into a bulk and a surface contribution; for a circular cluster we may write:

\[
E = 4\pi R^2 e_s + 2\pi Re_l \tag{4}
\]
where $R$ is the radius of the cluster, $e_s$ the energy per unit surface of the cluster, and $e_l$ the energy per unit boundary length. Rearrangement gives:

$$\frac{E}{\pi R} = e_s + \frac{2}{R} e_l$$

(5)

so that the two contributions $e_s$ and $e_l$ can be determined by a plot of the total system energy $E$ vs. $1/R$. However, such a plot gave a fair scattering of data particularly for small clusters, where the deviations from the spherical shape are noticeable. We have therefore modified eq. (4) a little and written:

$$E = u_{s}n_{s} + u_{l}n_{l}$$

(6)

where $u_{s}$ and $u_{l}$ denote the energy per bulk atom and per boundary atom, respectively, and $n_{s}$ and $n_{l}$ denote the numbers of bulk and of boundary atom. Rearrangement now leads to:

$$\frac{E}{n_{t}} = u_{s} + (u_{l} - u_{s}) \frac{n_{l}}{n_{t}}$$

(7)

where $n_{t} = n_{s} + n_{l}$ is the total number of atoms in the cluster.

A typical plot of $E/n_{t}$ vs. $n_{l}/n_{t}$ is shown in Fig. 1. The fit to a straight line is excellent, so that both the bulk adsorption energy $u_{s}$ and the quantity $\Delta u_{\text{step}} = (u_{l} - u_{s})$, which is the energy required to form a step atom from a bulk atom, can be determined with good accuracy. A few results are shown if Fig. 2; they have been obtained both with the BTI and with the FDB potentials, which here give quite similar results.

The adsorption energy $u_{s}$ per bulk atom is highest for the cluster that is one monolayer high, where all the copper atoms are bonded directly to the gold surface. For clusters that are two or three layers high, the adsorption energies are the same within the accuracy of the calculation. In contrast, the energy for step formation is lowest for the monolayer, indicating that the Cu-Cu bond is weakened by the stronger Cu-Au bond. The energy per atom required to form a double step is particularly large, so that clusters of pyramidal shape are favored. These results bear witness to the fact that in metallic bonding the bond energies are not additive.

Because of the circular geometry assumed for the Cu island, calculations for step formation of figures 2a-2c correspond to an average over different orientations on the surface. Calculations can also be performed for different directions on the surface, as shown in figure 2d. As expected, the step formation energy is lower for the formation of more compact steps, so these should predominate.

The step-formation energy is difficult to measure, but estimates can be obtained from the growth and the stability of copper clusters. Xia et al. [9]
estimate the step energy to be of the order of 0.4 to 0.5 eV, which is quite in line with our calculations.

3.2 Atom dynamics simulations

In order to explore structures that are not necessarily commensurate with the Au(111) substrate, we performed molecular-dynamics simulations within the embedded-atom scheme. At first, we tested the two different potentials employed in this work and performed calculations for a Cu monolayer adsorbed on Au(111). The system consisted of a slab of Au atoms eight layers thick, four of them mobile, covered with a Cu layer. Each of these layers consisted of 196 atoms; cyclic boundary conditions were imposed parallel to the surface. For the the interactions between the particles a cut-off radius of 7 Å was employed. The time step was set at 0.2 fs, and the simulations ran over 4 ns.

Although the energetic predictions of the two parameterizations employed here are very similar, as shown in the previous section, they result in rather different structures for the adsorbed Cu monolayer. In the case of the FDB potentials the monolayer is compressed, leading to holes and domains with an incommensurate structure (see Fig. 3a). In contrast, the BTI potentials, which are based on data for Cu-Au alloys, predict a commensurate (1 × 1) structure, which correspond to the experimental observation in the electrochemical system (see Fig. 3b). It is worth mentioning that although both structures show strong differences while observed in direct space, the Fourier transforms of the corresponding averaged atomic densities lead to a hexagonal pattern with the same lattice parameter, with considerably more diffuse spots in the case of the FDB potentials. Because of its better agreement with the experimental finding, we shall use only the BTI potentials in the following simulations. However, the tendency of the copper atoms to form compressed structures is real – it is caused by the shorter lattice constant of bulk copper – and will also be found in the simulations with the BTI potentials reported below.

To investigate the properties of copper clusters adsorbed on a Au(111) surface we have performed atom dynamics simulations with Cu clusters containing between 55 and 125 atoms with different starting configurations such as a cylindrical or an inverted pyramidal structure; typical runs lasted between 4 ns and 10 ns. Since a full statistical analysis requires a higher number of runs than we have undertaken so far, we shall only give here some representative results which show the main features of the investigated system.

Figure 4 shows the atomic arrangement for a Cu cluster that is 7-layers high. The pyramidal structure is favored by the step energies (see previous
section) and was obtained with various starting configurations. It is instruc-
tive to consider the time-averaged atomic density as a function of the distance
perpendicular to the surface (Fig. 4b). The decreasing height of the peaks
and their decreasing area reflect the pyramidal structure of the cluster. Note
that the peaks become broader with increasing distance, since the atoms in
the top layers are more mobile. An analysis of the distance between lattice
planes yields values in the range of 2.00 to 2.02 Å for the Cu planes closer to
the surface. In bulk copper the distance between lattice planes in the (111)
direction is 2.09 Å, so the clusters are somewhat contracted. This is under-
standable in terms of bond order arguments: The lower coordination of the
atoms at the boundary of the layer yields a stronger binding between the
layers, with a concomitant lowering of the interlattice distance.

The presence of a cluster induces a rearrangement of the copper mono-
layer underneath. In fact, several atoms initially belonging to the cluster
are incorporated into the monolayer during the simulations, making it more
compact after equilibration. This effect is illustrated in fig. 5, where a cluster
is shown along with the structure of the Cu monolayer in contact with the
Au(111) surface. The presence of the cluster strongly distorts the monolayer
and creates dislocations.

The compression of the monolayer can be quantitatively expressed through
the average distance to the nearest neighbors. Figure 5c shows a correspond-
ing contour plot for the copper atoms in the monolayer. The data were ob-
tained by averaging the distance of each particle to its nearest neighbors,
and by further averaging over 1000 time steps. It is evident that the presence
of the cluster produces a dramatic decrease of the nearest-neighbor distance
in the monolayer; the minimal values are around 2.67 Å, which is somewhat
larger than the value for bulk copper (2.55 Å), but much smaller than the
distance between Au atoms on the Au(111) surface (2.88 Å). Figure 5c also
reveals the shape of the basis of the cluster, which resembles that of a trun-
cated equilateral triangle. This can be understood as follows: According to
the static calculations of the previous sections, steps should preferentially oc-
cur in the more compact < 110 > directions. Two kinds of facets arise in these
directions, which depending on their structure are usually denoted as {111}
and {100} faces, respectively. These facets originate the growth of faces of
pyramids that resemble the (111) and (100) fcc faces respectively, which are
known to have different surface energies. Since the embedded atom method
predicts, in qualitative agreement with experiment, a lower surface energy
for the (111) surface, this is the facet that is expected to predominate, and
the pyramids should exhibit hexagonal bases, where the sides corresponding
to the {111} facets should be considerably larger than those of the {100}
facets.
The clusters generated by these simulations are stable within the time that can reasonably be covered in a simulation. They are not stable in an absolute sense since it would generally be favorable to spread them out into a monolayer. However, real copper clusters, if they are chemically pure, should also be in a metastable state, since the average binding energy in a cluster is always less than that of the bulk material. Electrochemical experiments with such clusters are usually performed in sulphate solutions; in the region near the equilibrium potential for the Cu/Cu$^{2+}$ system copper is covered by a layer of adsorbed sulphate ions, which may increase their stability.

4 Conclusions

The embedded-atom method, which we have employed, is particularly suited to treat large ensembles of metal atoms; both static and dynamic calculations can be performed with relative ease [10]. Since the interaction parameters have been fitted to experimental data, we expect the method to give qualitatively correct results and to provide good estimates for binding and step-formation energies. We think that our results for copper on Au(111) are encouraging, and that the method can be applied to similar systems and give valuable information about the properties of metal clusters on metal electrodes.

Our calculations do not explain the extra stability of copper clusters observed by Kolb et al. [2]. However, our method is not suited to investigate quantum confinement, which these authors believe to be the cause of this effect. On the other hand, metal dissolution is a comparatively slow process: it involves the solvation of the dissolved ion, and thus requires $10^{-12} - 10^{-11}$ s. On this timescale, the copper clusters can freely exchange electrons with the underlying substrate. The very fact that these clusters can be imaged with the STM shows that such an exchange occurs without a major hindrance. Therefore the explanation for this stability has to be sought elsewhere. Preliminary energetic considerations with the present calculation method, indicate that the admixture of gold to copper clusters may improve their stability. This will be the subject of further investigations.

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Figures

1. Binding energy per atom for a Cu island adsorbed on a clean Au(111) surface as a function of the fraction of atoms that belong to the border of the island.

2. Energy per surface atom $u_s$ and energy required to generate an atom at a step from an atom on the surface of the island $\Delta u_{\text{step}}$ for several systems. FDB denotes the results obtained with the potentials of Foiles et al. [5] and BTI indicates the corresponding results with the potentials of Barrera et al. [6]. An island with circular shape was assumed in all cases. (a) Cu island on Au(111). (b) Cu island on a pseudomorphic layer of Cu adsorbed on Au(111). (c) Two-atom high Cu island on a pseudomorphic layer of Cu adsorbed on Au(111). (d) Step formation energy for different directions on the surface. The calculations were performed with the BTI potentials.

3. Final structures obtained after 4 ns in an atom-dynamics simulation for a Cu monolayer adsorbed on Au(111). (a) Potentials of Foiles et al. (FDB) [5]; (b) potentials of Barrera et al. (BTI) [6].

4. Atomic arrangement (a), and Cu atom density (b) as a function of the distance perpendicular to the surface for a 7-layers high Cu cluster formed on a Au(111) surface.

5. Compression of the Cu monolayer induced by the presence of a cluster. (a) Atomic arrangement of the cluster. (b) Structure of the Cu layer in contact with the Au(111) surface. (c) Contour plot of the distance between nearest neighbors in the Cu monolayer. The contour lines start at a distance of 2.65 Å, are separated by 0.05 Å, and end at 2.95 Å. The geometric arrangement is shown for comparison.
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