A Molecular Dynamics Study of the Epitaxial Growth of Metallic Nanoclusters Softly Deposited on Substrates with Very Different Lattice Parameter

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Abstract. The soft deposition of Cu and Au clusters on Au(001) and Cu(001) surfaces respectively is studied by constant-temperature molecular-dynamics simulations. The initial shape of the nanoclusters is icosahedral or truncated octahedral (Wulff type). Their number of atoms ranges between 12 and 1289 atoms. Bombardment energy is of the order of a few meV/atom. The atomic interactions are mimicked by a many-body potential based on the tight-binding model. The effect of the temperature as activation to get the complete epitaxy is analysed. We have found that Cu clusters manage to align their {002} planes with the substrate by increasing the temperature. However, there is not epitaxial growth in any case since the lattice becomes bcc or important stacking faults are generated. For Au clusters, the alignment of these planes is practically independent of the temperature.

1. Introduction

Interest in completely epitaxial growth of materials has risen due to the growth of the nanoelectronic field [1]. Next generation device fabrication will rely almost completely on the bottom-up technique, which allows in principle a very precise positioning of collection of atoms and hence the capacity to produce nanostructured materials with designed properties. A way to manage such nanostructures is the deposition of size selected clusters on different substrates. Using cluster deposition to grow epitaxial films at soft landing conditions is interesting in magnetic thin-film structures. Cluster assemblies evidence original magnetic properties such as superparamagnetism, magnetic-moment enhancement or surface anisotropy. These effects are influenced by factors such as the symmetry, the local coordination or the interatomic distances, properties determined in turn by the adaptation of the cluster to the substrate.

Small enough clusters with similar lattice parameter as the substrate grow epitaxially with this in systems without lattice misfit [2], but as nanoclusters increase in size, contact epitaxy is no longer complete. This can be altered by heating the system [3] or increasing the deposition energy. However when cluster and substrate have very different lattice parameters, epitaxy is not always guaranteed

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since the strain energy, stored elastically or in dislocations, influences the adaptation. Therefore, it is necessary to know the maximum cluster size for which \{002\} cluster planes align with the same planes of the substrate including effects like heating of the system. In this paper we study the equilibrium structure of metallic nanoclusters deposited at low energy and different temperatures on substrates of very different lattice parameter (misfit of 12.8% for \text{Cu/Au}(001) and 11.35% for \text{Au/Cu}(001)). In a previous work, we found that the nanocluster size for which the alignment is possible at 300 K is smaller than for clusters without lattice misfit [4].

2. Model

The atomic interactions has been described by a many-body potential based on the second-moment approximation of the Friedel tight-binding theory and parameterized by Ackland et al. [5]. The trajectories of the particles have been obtained of a constant-temperature molecular-dynamics method, i.e. simulations were performed in the canonical ensemble proposed by Parrinello et al. [6] and Nosé [7]. Equations of motion were integrated up to 150 ps by using a Nordzieck fifth-order predictor-corrector algorithm [8] and a time step of 0.5 fs. The substrate had \(45\times45\times15\) unit cells and periodic boundary conditions in the directions of the surface plane (\(xy\)-plane) and nonperiodic boundary conditions in the direction of the surface normal (\(-z\) direction). The bottom layer of the substrate was fixed and the top was free (00\(\bar{1}\)) plane. The Cu and Au clusters were given the shape of Wulff-type cuboctahedral polyhedra (CO) with 38, 201, 586, 1289 atoms and icosahedral polyhedra (IC) with 13, 55, 147, 309 atoms [9]. These shapes minimize the binding energy for small nanoclusters of these materials [10,11]. Their dimensions were also optimized to the configuration with minimum energy by using the conjugate-gradient method. Initially, for icosahedra the fivefold axis was parallel to the normal to the substrate surface; and for cuboctahedra a (001) face was parallel to this surface to make easier the epitaxy [12]. Before deposition, cluster and substrate were heated to a specific temperature: 5, 100, 300, 500 and 700 K. In some case, the system after deposited at 300 K was annealing up to 900 K. The deposition energy was 17 meV/atom. This value is slightly lower than the limit to find important plastic effects during deposition [13]. All the same, 100 meV/atom and 500 meV/atoms were also used in some sample for comparison. At the end of each simulation the sample was quenched to 0 K to check the final cluster structure.

![Figure 1](image1.png)

**Figure 1.** Steady state of icosahedral Au (a) and Cu (b) clusters with 55 and 147 atoms at different temperatures: 100, 300 and 500 K.

3. Results

In Figure 1 we show the \(xz\)-projection of Cu and Au clusters (55 and 147 atoms) deposited at different temperatures (100K, 300K and 500K) once quenched for comparison. This figure together with other two representing the \(yz\)- and \(xy\)-projections reflect perfectly the different visual alignment of the \{002\} cluster planes with the same type of planes of the substrate. For example, this alignment, although not in a perfect way, is produced in Cu clusters of 55 and 147 atoms when temperature goes, respectively,
from 100 to 300 K and from 300 to 500 K. Concerning with Au clusters of 55 atoms the alignment goes from partial to total when the temperature goes from 100 to 300 K. For 147 atom Au clusters this alignment is neither found at 300 nor at 500 and nor at 700 K. In Table 1 for the Cu clusters and Table 2 for Au clusters this behaviour is pointed out at a variety of temperatures. The temperatures were chosen in order to obtain, when possible, the transition from no alignment to alignment in all the clusters.

Table 1. Epitaxy factor, number of epitaxial atoms $N_{epi}$ and number of atoms with (001) orientation $N_{(001)}$, existence of alignment and epitaxy for the different Cu/Au(001) systems.

| No. of atoms N | Temperature (K) | Final Structure | $<f_{epi}>/f_0$ | $N_{epi}/N$ (%) | $N_{(001)}/N$ (%) | Alignment/Epitaxy |
|----------------|----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| 13 [IC]        | 5              | FCC SF IC DIC   | 2.2             | 8               | 8               | partial/no      |
|                | 100            | FCC sf DIC Bcc  | 1.4             | 38              | 15              | Yes/n           |
|                | 300            | SF DIC BCC      | 1.3             | 38              | 0               | Y/n             |
| 38 [CO]        | 5              | fcc sf IC DIC   | 2.7             | 0               | 5               | n/n             |
|                | 100            | FCC SF DIC BCC  | 1.5             | 34              | 0               | Y/n             |
|                | 300            | SF DIC BCC      | 1.4             | 34              | 0               | Y/n             |
| 55 [IC]        | 100            | fcc SF DIC      | 2.7             | 2               | 7               | n/n             |
|                | 300            | FCC SF dic      | 1.4             | 33              | 36              | Y/n             |
| 147 [IC]       | 300 + annealing| FCC SF ic DIC   | 2.6             | 3               | 22              | n/n             |
| 300 (100 meV)  | FCC SF ic DIC  | 1.8             | 22              | 48              | Y/n             |
| 300 (500 meV)  | FCC SF ic DIC  | 2.9             | 3               | 5               | p/n             |
| 500            | FCC SF dic     | 1.6             | 35              | 39              | Y/n             |
| 201 [CO]       | 300            | fcc DIC BCC     | 1.5             | 28              | 0               | Y/n             |
|                | 500            | FCC SF Bcc      | 1.8             | 13              | 17              | p/n             |
| 309 [IC]       | 300            | FCC SF ic dic   | 2.8             | 5               | 20              | n/n             |
|                | 500            | FCC SF Dic      | 2.2             | 11              | 34              | n/n             |
|                | 700            | FCC SF dic Bcc  | 2.0             | 23              | 12              | p/n             |
| 586 [CO]       | 300            | FCC SF          | 1.3             | 41              | 85              | p/n             |
|                | 700            | FCC sf DIC BCC  | 1.4             | 36              | 22              | Y/n             |
| 1289 [CO]      | 300            | FCC sf          | 0.7             | 80              | 98              | p/p             |

The matching between both cluster and substrate has been studied by different methods. The common neighbour analysis, CNA [14,15], classifies the bond types and allows to identify the lattice structures (fcc, body centred cubic (bcc), icosahedral (ic), distorted icosahedral (dic) and stacking faults (sf)). A grain analysis [12,13,15] obtains the local lattice unit vectors of the cluster, and specifically the number of atoms with (001) orientation $N_{(001)}$ either fcc (similar to the substrate) or bcc. Finally, an epitaxial factor assesses numerically the degree of adaptation of both lattices [3,4]: In every cluster, we have calculated the parameter $F_{epi} = \sum_{i=1}^{N} \min \left( \arccos \left| \mathbf{u}_{id} \cdot \mathbf{u}_{n} \right| \right)$ for every atom. This parameter is the result of the comparison of the actual bond directions with the ones corresponding to the ideal bonds in the substrate. Specifically, the $n$ position vectors from an atom to their nearest neighbours $\mathbf{u}_{nn}$ (indexed $j$) are calculated and normalized and the same with an ideal atom in a perfect substrate lattice $\mathbf{u}_{id}$ (in an fcc lattice, these $n$ vectors correspond to the twelve $<110>$ directions, each indexed $j$). For every atom the dot products are calculated for all the combinations of ideal vectors and the vectors to the nearest neighbours, and then the $n$ minimum values are added to $F_{epi}$. For a better comparison, a normalized parameter $f_{epi}$ defined as the parameter $F_{epi}$ divided by the number of nearest neighbours is obtained. A visual study of deposited clusters and the distributions of the normalized parameters reveals that a criterion for epitaxy of an atom is a $f_{epi}$ value inferior to $f_0=0.15$ rad. This rule allows us to select those atoms with epitaxial structure $N_{epi}$. 
In Table 1 and Table 2 we show the results of the parameters previously defined. The lattice structures found in the interior of these clusters were: fcc, sf, ic, dic or bcc corresponding to the number of average bonds per atom of each one of these lattice types. If this number is about one, it appears in small letters and if it is larger, it appears in capital letters. In these tables, the “epitaxy factor” is also shown, that is, the average value for all cluster atoms of the normalized parameter $<f_{\text{epi}}>$ divided by $f_0$. A value of the epitaxy factor lower than 0.5 give rise to coherent epitaxy, and between 0.5 and 1.0 to semicoherent (or partial) epitaxy, that is, with stacking faults [4]. We also indicate in these tables both the number of epitaxial atoms $N_{\text{epi}}$ and of atoms with (001) orientation $N_{(001)}$ divided by the number of cluster atoms $N$ for all studied systems.

### Table 2. Epitaxy factor, number of epitaxial atoms $N_{\text{epi}}$ and number of atoms with (001) orientation $N_{(001)}$, existence of alignment and epitaxy for the different Au/Cu(001) systems.

| No. of atoms $N$ | Temperature (K) | Final Structure | $<f_{\text{epi}}>/f_0$ | $N_{\text{epi}}$ / $N$ (%) | $N_{(001)}$ / $N$ (%) | Alignment/Epitaxy |
|------------------|-----------------|-----------------|------------------------|-----------------------------|------------------------|-------------------|
| 13 [IC]          | 5               | FCC             | 0.4                    | 85                          | 100                    | Y/Y               |
|                  | 100             | FCC             | 0.3                    | 100                         | 100                    | Y/Y               |
|                  | 300             | FCC             | 0.4                    | 100                         | 100                    | Y/Y               |
|                  | 38 [CO]         | FCC SF dic      | 1.5                    | 34                          | 42                     | n/n               |
|                  | 100             | FCC SF          | 0.9                    | 68                          | 84                     | p/p               |
|                  | 300             | FCC             | 0.4                    | 97                          | 100                    | Y/Y               |
|                  | 55 [IC]         | FCC SF dic      | 1.5                    | 44                          | 65                     | p/n               |
|                  | 300             | FCC             | 0.4                    | 100                         | 98                     | Y/Y               |
|                  | 300 + annealing | FCC SF dic      | 1.7                    | 16                          | 69                     | n/n               |
|                  | 300 (100 meV)   | FCC SF          | 1.8                    | 31                          | 44                     | n/n               |
|                  | 300 (500 meV)   | FCC SF          | 1.0                    | 59                          | 76                     | p/p               |
|                  | 500             | FCC SF dic      | 1.1                    | 42                          | 82                     | p/n               |
|                  | 700             | FCC SF dic      | 1.5                    | 41                          | 56                     | n/n               |
|                  | 201 [CO]        | FCC SF dic      | 1.9                    | 22                          | 34                     | n/n               |
|                  | 500             | FCC SF dic      | 2.0                    | 22                          | 36                     | n/n               |
|                  | 700             | FCC SF          | 1.0                    | 60                          | 80                     | p/p               |
|                  | 309 [IC]        | FCC SF dic      | 2.3                    | 13                          | 33                     | n/n               |
|                  | 586 [CO]        | FCC SF          | 0.3                    | 99                          | 95                     | Y/Y               |
|                  | 1289 [CO]       | FCC SF          | 0.6                    | 86                          | 97                     | p/p               |

The number $N_{(001)}$ is in general larger than $N_{\text{epi}}$ since it does not take into account defects around the atom. This rule is not verified in those cases where the lattice structure becomes totally or partially bcc as shown Table 1. Examples are the Cu clusters with 13 (300 K), 38 (100 and 300 K), 201 (300 K) and 586 atoms (700 K). The cause is that this structure is rotated 45° about the z-axis [4]. All these systems manage to align like that their {002} planes with the substrate, but obviously do not achieve the epitaxy. The bcc lattice appears also in the growth of Cu monolayers on Au [16]. Another way by which Cu clusters align their (002) planes is preserving the fcc structure but generating stacking faults. The Cu cluster with 55 (300 K) or 147 (500 K) atoms are examples of this latter method. The temperature also influences this effect. Thus, for icosahedral Cu clusters the temperature for which the alignment is achieved increases with the number of atoms [3]. If the deposition energy per atom increases (see the results of the cluster with 147 atoms), also the alignment improves without changing significantly the structure. Wulff clusters show a different behaviour since the better positioning of their atoms before deposition favours notably the alignment. In these clusters only very low temperatures or large sizes can impede this. The low temperatures also cause the appearance of the icosahedral bond even in Wulff Cu clusters. Besides unlike Au, for Cu clusters the annealing achieves the alignment of planes. Just only a few fully epitaxial clusters were found. As an example, let us point
out two cases of Au clusters: small size clusters and big size Wulff clusters. In both cases, at not very low temperatures, clusters are able to minimize the stacking fault appearance growing epitaxially.

In Au clusters the existence of alignment implies epitaxy. Nevertheless, in a previous work it was found that the atomic distances in Au are not adapted to the Cu atomic distances [4]. For icosahedral clusters the temperature at which alignment takes place is almost independent of the number of atoms. In fact in clusters of 147 atoms there is not a temperature to get it. On the contrary, this cluster at higher energy is able to get some degree of alignment. The behaviour of Wulff clusters of larger sizes are similar to Cu [12,13]. They have partial epitaxy in the steady state since after the reconstruction the clusters get back to a state structurally almost equal as when they initially landed onto the substrate. There is even a case in which the landing is perfect; that is, for the 586 atom cluster. Finally, let us say that there is neither bcc nor icosahedral structures in Au clusters.

4. Conclusions

The deposition at low energy and different temperatures of small Cu and Au clusters with icosahedral and Wulff shapes are studied by molecular dynamics. Cu clusters manage to align their {002} planes with the substrate either turning their lattice structure into bcc or generating stacking faults. Obviously in any case, they do not achieve the epitaxy. For icosahedral Cu clusters the temperature for which the alignment is achieved increases with the number of atoms. For Wulff Cu or Au clusters the better positioning of the atoms before deposition favours notably the alignment. Thus big size Wulff clusters have a partial epitaxy due to the reconstruction undergone leaving them almost as they were when initially landed onto the substrate. We have only found fully epitaxy in Au clusters of small sizes and in some cases of clusters with Wulff shape. For these clusters alignment implies epitaxy. For icosahedral Au clusters the alignment depends on the temperature but is almost insensible to the number of atoms. Besides, if the deposition energy increases, the alignment also improves in both types of clusters.

5. References

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