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Epitaxial matching of small metallic nanoclusters in large-misfit systems

J.C. Jiménez-Sáez[a,*], A.M.C. Pérez-Martín[b], J.J. Jiménez-Rodríguez[b]

[a]*Departamento de Física y Química Aplicadas a la Técnica Aeronáutica, E.U.I.T.Aeronáutica, Universidad Politécnica de Madrid (UPM), E-28040 Madrid, Spain*

[b]*Departamento de Electricidad y Electrónica, Facultad de Ciencias Físicas, Universidad Complutense, E-28040 Madrid, Spain*

Abstract

The deposition at low energies of Cu and Au nanoclusters, respectively, on Au(0 0 1) and Cu(0 0 1) substrates is studied by constant-temperature molecular-dynamics simulations. Initially, clusters had icosahedral or Wulff shapes and their number of atoms ranged between 13 and 1289. The deposition energy and the temperature were, respectively, 17 meV/atom and 300 K. Atomic interactions are mimicked by a many-body potential based on the tight-binding model. A different behaviour of the clusters has been found as a function of the number of atoms and of the material. Below 100 atoms, Cu clusters align all their {2 0 0} planes with the substrate but do not achieve epitaxy since either their lattice structure becomes bcc or stacking faults arise. On the contrary, Au clusters with similar number of atoms grow epitaxially but hardly change the distances parallel and perpendicular to the interface in their unit cell. Cu clusters, for their part, fit the parallel distances to the Au lattice parameter. For larger clusters, in general, the alignment or epitaxy is not complete even in the cases of more favourable landing.

Keywords: Molecular dynamics; Cluster deposition; Epitaxy

1. Introduction

Interest in epitaxial growth of materials has risen due to the microelectronics field [1]. The charged cluster model suggests that thin films are actually assembled by nanometer sized clusters [2]. Therefore, the understanding of the processes involved during deposition of nanoclusters would be especially important. Small enough clusters with similar lattice parameter as the substrate align completely epitaxially with this on impact [3]. As nanoclusters grow in size, contact epitaxy stops being complete. This can be compensated for by heating the system [4]. However, when cluster and substrate have very different lattice parameters, contact epitaxy is not always guaranteed since another energy takes part: the strain energy stored either elastically or in dislocations.

In this paper we study the equilibrium structure of metallic clusters deposited on substrates of very different lattice parameter (a misfit of 12.8% for Cu/Au(0 0 1) and 11.35% for Au/Cu(0 0 1)). The influence of the cluster size and of its structure on the epitaxial matching is analysed in the low-energy limit of deposition. Previous results obtained without taking into account deposition effects show that Cu clusters have a much more deformable behaviour and the cluster planes perpendicular to the interface, (2 0 0) and (0 2 0), align epitaxially with the same planes of the substrate [5].

The matching between both cluster and substrate has been studied by different methods. An epitaxy factor and a structure factor assess the degree of adaptation of both lattices. The common neighbour analysis, CNA [6], classifies the types of bond and allows to identify the lattice structure (fcc, bcc, etc.) and a grain analysis [7] allows us to find out whether the deposited-cluster lattice imitates the substrate lattice in orientation.

2. Model

The atomic interactions have 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. [8]. The trajectories of the particles have

*Corresponding author. Tel.: +34 91 39 44376; fax: +34 91 39 45196.
E-mail address: jc.jimenez@upm.es (J.C. Jiménez-Sáez).

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been obtained from a constant-temperature molecular-dynamics method, i.e. simulations were performed in the canonical ensemble proposed by Parrinello et al. [9] and Nosé [10]. Equations of motion were integrated up to 150 ps by using a Nordsieck fifth-order predictor–corrector algorithm [11] and a time step of 0.5 fs.

The substrate had $(45 \times 45 \times 15)$ unit cells and periodic boundary conditions in the directions of the surface plane (xy-plane) and no periodic boundary conditions in the direction of the surface normal ($-z$ direction). The bottom layer of the substrate was fixed and the top was free ($(0\,0\,\bar{1})$ plane). The Cu and Au clusters were given the shape of Wulff-type closed-shell cuboctahedral polyhedra (CO) with 38, 201, 586, 1289 atoms and closed-shell icosahedral polyhedra (IC) with 13, 55, 147, 309 atoms [12,13,]. These shapes have been found to be one of the more common ones and of less binding energy for small nanoclusters of these materials [14,15,]. Initially, their dimensions were optimized to the minimum-energy configuration by using the conjugate-gradient method. Besides, for icosahedra the fivefold axis was parallel to the normal to the substrate surface; and for cuboctahedra a (0 0 1) face was parallel also to this surface to make the epitaxy easier [16]. Before deposition cluster and substrate were heated to 300 K. The deposition energy was 17 meV/atom. This value is slightly lower than the limit to find plastic effects in larger clusters during deposition [17]. At the end of each simulation the sample was quenched to 0 K to check the final cluster structure.

3. Results and discussion

Fig. 1 shows different stages of the deposition process of two icosahedral Au clusters of 147 and 55 atoms respectively. During the first deposition stages of the system with 147 atoms and due to the relocation processes [18], local orderings with shape of connected "nanowires" form inside the cluster (see 15 ps plot). This phenomenon also happens in Wulff Au clusters although to a lesser extended. Only in the cases of clusters with fewer atoms, these nanowires once deposited are placed producing the alignment of the (2 0 0), (0 2 0) and (0 0 2) planes with the substrate. Visually, the steady state of Cu clusters with similar number of atoms (55 and 147) is analogous to the Au case. The alignment for all systems is pointed out in Table 1. Only clusters deposited in very favourable conditions with more of 55 atoms, Wulff polyhedra, manage to align total or partially their {0 0 2} planes with the substrate. This result contrasts with that obtained in clusters with similar lattice parameter [4] where the alignment is achieved with clusters of the order of 150 atoms.

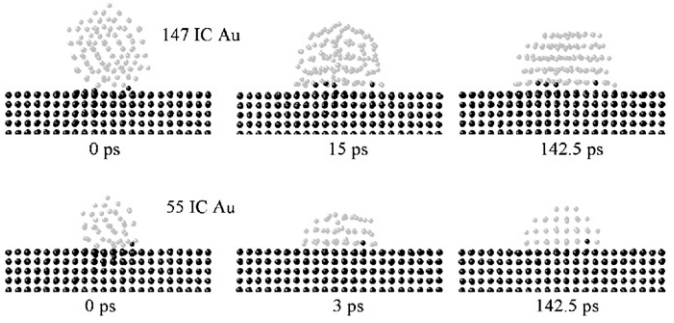

Fig. 1. Snapshots of the deposition of icosahedral Au clusters with 147 (above) and 55 (below) atoms. The viewing direction is [0 1 0].

In order to numerically analyse the epitaxy of the cluster, we calculates the epitaxy factor [19]: $F_{\mathrm{epi}} = \sum_{i=1}^{n} \min_{j}(\arccos|\boldsymbol{u}_{id}^{j} \cdot \boldsymbol{u}_{nn}^{i}|)$ for every atom, which is a measure of the epitaxy of the atom compared to the substrate. This parameter compares the lattice directions of atoms in the cluster to their n nearest neighbours to the 12 lattice directions of the substrate (indexed j): $\langle 0\,1\,1 \rangle$, $\langle 1\,1\,0 \rangle$ and $\langle 1\,0\,1 \rangle$. F_{epi} is calculated as a sum over the n nearest neighbours of an atom (indexed i). In this formula the ideal neighbour vectors are unit vectors marked $\boldsymbol{u}_{id}$ and the unit vectors for each atom to its nearest neighbours are marked $\boldsymbol{u}_{nn}$. For every atom the dot product is calculated for all the combinations of ideal vectors and the vectors to the nearest neighbours, and the n minimum values are added to the F_{epi}. We have separated the contributions of F_{epi} in planes: F_{xy} obtained from the 4 vectors $\boldsymbol{u}_{id} = \langle 1\,1\,0 \rangle/\sqrt{2}$, and the same for F_{yz} ($\boldsymbol{u}_{id} = \langle 0\,1\,1 \rangle/\sqrt{2}$) and F_{xz}. For a better comparison, a normalized factor f defined as the factor F divided by the number of nearest neighbours in planes or total (4 for f_{xy} and 12 for f_{epi} if all neighbours are present) is obtained. A visual study of deposited clusters and of the distributions of the normalized epitaxy factors reveals that a criterion for epitaxy of an atom is a f value inferior to $f_0 = 0.15$ rad. This rule allows us to select those atoms with epitaxial structure in planes, N_{yz}, N_{xz}, N_{xy}, or total, N_{epi}.

In Table 1 we show the average value of the normalized epitaxy factor, $\langle f \rangle$, for all cluster atoms divided by f_0 and the number of epitaxial atoms divided by the number of cluster atoms for all studied systems. Moreover, by a study of grains [16,17] we obtained the number of atoms $N_{(0\,0\,1)}$ with (0 0 1) orientation either fcc (similar to the substrate) or bcc. This last number is in general larger than N_{epi} since it does not take into account defects around the atom [7]. In Cu clusters with 13 (IC), 38 (CO) and 201 (CO) atoms, this rule is not verified. CNA [16,17] shows that the lattice structure of these clusters is bcc-like according to hypotheses made by others authors in the growth of Cu monolayers on Au [20]. The (0 0 1) bcc Cu lattice fits the substrate if its [1 0 0] and [0 1 0] directions are rotated 45° around the [0 0 1] axis. So the angular positioning of the first neighbours of an atom (14 in total) is similar in xy-planes to the substrate, but slightly different in the rest of the planes. Due to this an elevated number of epitaxial atoms N_{xy} is found in these systems; and although there is alignment, there is not epitaxy. Besides, there are two first