CLUSTERS DEPOSITION ON SURFACE AN ATOMIC SCALE STUDY BY COMPUTER SIMULATION METHOD

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Abstract. A nanoparticle contains from a few atoms for the smallest ones to several thousand for the largest ones considered here. The properties of an atom result from quantization and the same is true for the molecules they form. The same is thus true for the smallest nanoparticles. At the other edge, many of the properties of macroscopic materials are well described by a classical approach and nanoparticles appear as objects at the fringing field between quantum and classical behaviors. In the study of their properties, using either a quantum or a classical approach, atomic scale methods appear as naturally well-suited. Atoms are considered as individual objects interacting via their outer shell electrons only. However even with such an approximation, solving the Schrödinger equation becomes quickly prohibitively heavy as the number of atoms involved increases. For the heaviest elements, relativistic effects make the problem even heavier. In this case, the classical approach is the only one presently practical. Ab initio calculation is frequently used to predict small particles configurations as well as their electronic and magnetic properties. In principle, the method is exact. Uncertainties about the origin of correlation exchange however, and also the complexity of setting up efficient numerical algorithms suggest the need of experimental confirmation in many cases. The classical approach to atomic interactions makes use of semi-empirical models fitted on atomic collision properties at high energy (of the order of core electron binding energies or higher) and on solid state properties at low energies (of the order of cohesive energies or lower). Interaction between atoms in a nanoparticle and the interaction of nanoparticles with surfaces presented in this report belong to the latter category. For these, interaction potentials are set up as functionals of the local electron density or of hopping integrals and parameterized on the basis of a range of microscopic and macroscopic properties of bulk materials. Obviously, the correct prediction of other properties is not warranted and comparison with experiment is necessary.

Keywords: computer simulation, cluster, slowing down, nanocluster, deposition, monolayer, morphology, structure, damage, deformation, electron-phonon coupling.

1. Introduction

In the present paper, this question will not be addressed as a whole. The case of noble elemental clusters deposited on a crystalline substrate having the same elemental nature was the
The case of metallic alloy clusters and nanostructured films formed by their accumulation was discussed in [3]. The present study focuses on bi-metallic clusters formed by non-miscible elements. Such clusters can be synthesised outside thermodynamic equilibrium. The case of the Co-Ag system is selected, as it has already been the subject of several experimental [4] and modelling [5] studies. Truncated octahedral Co$_x$Ag$_{201-x}$ isolated clusters, with $0 \leq x \leq 201$ were already studied by means of a Metropolis Monte Carlo method [6]. They have an fcc structure and 201 is the smallest number of atoms with which an ideal compact truncated octahedron can be constructed. The spatial distribution of Co and Ag in this cluster was shown to be the consequence of a balance between Ag position relaxation and Co binding. This balance is temperature dependent. When the amount of Ag is sufficient, it systematically forms a layer around a Co core. However, when Co atoms are only a few (no more than 10), they are located just beneath the cluster surface, either as one oblate group beneath a facet, or as subgroups of no more than 5 atoms beneath a vertex.

The slowing down of such a cluster, with x=10, is here studied in detail in comparison with a bigger one, Co$_{285}$Ag$_{301}$. This latter cluster is also an ideal truncated octahedron and it has a core-shell structure. The stoechiometry is such that the core is pure Co and the shell is made of one monolayer of Ag. The substrate Ag surface has {100} orientation and the slowing down occurs at room temperature. These two clusters undergo different transformations upon impact, related to their different size and structure and it is the purpose of the present paper to identify the consequences of the impact on these transformations. The section II briefly describes the Molecular Dynamics (MD) model employed and the slowing down conditions. The detailed study of the cluster slowing down is presented in section III where a distinction is made between a statistical analysis over several slowing down histories and an analysis cluster by cluster. An overall picture of the slowing down and related cluster modifications emerges, which is summarised in section 3.

2. The model

The MD model employed is already described elsewhere [7] and will only be briefly summarised. The equations of motion of the atoms in the system are integrated stepwise in time with the algorithm in [8]. Forces are derived from a Embedded Atom Model potential (EAM) proposed in [9-11] and account, in addition, for a contribution of electron-phonon coupling. This is done by means of a friction term which governs the exchange of energy between the ionic and the electronic systems, assuming a constant electronic temperature. It is shown in [7] how an approximate model can be established to evaluate the strength of the coupling with no adjustable parameters. The physical quantities needed are known from experiment in the case of pure elements, and it is assumed that the electronic density at the Fermi level is one electron per atom.

Table 1. Physical quantities used to estimate the characteristic electron-phonon coupling time in Ag.

<table>
<thead>
<tr>
<th>Debye temperature (K)</th>
<th>Conduction electronic density (m$^{-3}$)</th>
<th>Thermal conductivity (W/m.K)</th>
<th>Fermi energy (J)</th>
<th>Atomic mass (kg)</th>
<th>Coupling time (ps)</th>
</tr>
</thead>
<tbody>
<tr>
<td>215.0</td>
<td>5.86e$^{28}$</td>
<td>418.0</td>
<td>0.8796e$^{18}$</td>
<td>1.791e$^{-25}$</td>
<td>22.557</td>
</tr>
</tbody>
</table>

The electron-phonon coupling contributes to dissipate the energy brought by the cluster in the impact and enhances the local cooling of the system. As compared to elemental systems, more complexity occurs in the present case as we have to deal with two different metallic elements that are not homogeneously distributed. The approximated electron-phonon coupling model employed is unsuitable to correctly describe the transport of heat by the electronic system through an interface between two elemental subsystems as in a core-shell structured cluster. It is considered here that, since the substrate is pure silver, it will be sufficient to model the electron-phonon coupling for pure...
silver and to neglect the difference with cobalt. The physical quantities used to estimate the electron-phonon coupling in Ag, and the characteristic coupling time deduced at room electronic temperature are given in table 1.

A structure factor is used to measure the epitaxial accommodation of the clusters with the substrate. It is measured inside the cluster and gives information about the periodicity in one direction.

$$S = \frac{1}{N} \sum_{j=1}^{N} e^{i k r_j}$$

(1)

In this expression, \(k\) is the wave vector, \(r_j\) is the position of the atom \(j\) and \(N\) is the total number of atoms in the cluster. If the periodicity in the direction of \(k\) corresponds to the inverse of \(|k|\), then the value of \(|S|^2\) is unity. If there is no such periodicity in this direction, \(|S|^2\) is zero. In order to measure the epitaxial accommodation of the deposited cluster with the substrate, substrate lattice wave vectors are used

$$k = \frac{4\pi}{a_0} (h, k, l)$$

(2)

Where \(a_0\) is the substrate lattice parameter, and \(h, k\) and \(l\) are Miller indices of lattice directions.

A pair correlation function is used to characterise short-range order in the clusters,

$$g(r) = \frac{1}{2(N-1)} \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} \delta(r_{ij} - r)$$

(3)

Where \(\delta\) is the Dirac function, \(N\) is the number of atoms in the cluster and \(r_{ij}\) the distance between atoms \(i\) and \(j\) in the cluster. The pair correlation function gives the number of atomic pairs separated by a given distance, \(r\). This function is calculated separately for the different kinds of pairs: Co-Co, Ag-Ag and Ag-Co. It is characteristic of the lattice structure.

3. Cluster slowing down

If one defines the impact characteristic time as the time needed for the cluster to convert its centre of mass kinetic energy into potential energy, and this potential energy to convert into kinetic energy into the whole system, it can be estimated as of the order of 5 ps, which is smaller than the electron-phonon coupling time at room temperature (20 ps). The slowing down of a cluster is followed during 150 ps in order to track possible thermally activated processes. At the end of these 150 ps MD evolution, particle trajectories are fully decorrelated from the initial trajectories and the system is in a thermal equilibrium state which may be metastable. Whether this state has a sufficiently long lifetime to be observed is not known and this question needs comparison with experiment to be settled. However, if an incident cluster undergoes modifications because of the impact, the probability to retrieve its initial state once deposited is vanishingly small. These modifications may thus be considered as permanent, whatever further thermally activated modifications are still possible.

The discussion of the slowing down of the clusters on a Ag (100) surface will be split into two parts. The first one focuses on statistical aspects and the second one to individual aspects, where the sensitivity of the final state of the cluster on the slowing down conditions is examined.

In order to mimic a uniform collimated beam, the slowing down, always at normal incidence, is repeated ten times with the same cluster with a given initial kinetic energy, selecting the impact points on the surface and its orientations with respect to the surface at random. Each impact is followed during 150 ps at room temperature. Within the 150 ps evolution time considered,
thermally stimulated configuration modifications may have a sufficiently high probability to take place.

The slowing down is characterised by several significant features. These can be illustrated with the help of figure 1 which represents a cut in the cluster before its deposition and in the cluster-substrate system after 150 ps evolution. The $\text{Co}_{285}\text{Ag}_{301}$ cluster is represented and the slowing down energy is 0.5 eV/atom. The final system is characterised by a limited penetration of the cluster into the substrate.

It undergoes some deformation accompanied by structural accommodation of the cluster with the substrate, which is limited in the case of fig.1. At the same time, the upper part of the cluster may retain its initial atomic arrangement. It the case of fig.1, some damage is created in the substrate and the Ag cluster shell tends to spread on the substrate surface. While the Co core is only moderately affected by the slowing down, the Ag lattice, which is already distorted initially, undergoes further deformation as a consequence of the impact.

All these characteristics of course depend on the incident energy as well as on the cluster size, composition and energy. We now turn to their systematic study for $\text{Co}_{285}\text{Ag}_{301}$ and $\text{Co}_{10}\text{Ag}_{191}$.

The first characteristic of the slowing down in the energy range considered is the penetration of the clusters into the substrate and the related damage. Surface damage production induced by the soft landing of Co atoms was already studied, both experimentally and by MD in [5] and surface tunnelling microscopy showed it to be significant. The situation may be different if the incident Co atoms are bound inside clusters as in the present case.

At the low energies considered (no more than 1.5 eV per atom), the cluster penetration, if any, is only partial. Co is always found regrouped into one cluster surrounded by a layer of silver. When it penetrates, the cluster displaces Ag atoms from the substrate with the consequence of the formation of add-atoms. For both clusters, the fraction of cluster atoms with final positions below the substrate surface is the same and is close to linearly increasing with the slowing down energy. It is close to 3 percent at 0.25 eV/at and 30 percent at 1.5 eV/at. According to a rule of volume conservation, in the case of the smallest cluster, the number of substrate atoms displaced above the surface is exactly equal to the number of cluster atoms below this surface. It is somewhat smaller for the larger cluster since the volume per Co atoms below the surface is less than the volume per Ag atoms in the substrate.
Figure 2 shows the maximal penetration depth of the incident clusters (fig.2a) and the height of the layer formed by substrate atoms above the surface (fig.2b) as functions of the incident energy. The distinction is made between the penetration of each of the elements forming the incident clusters. The results are averaged over ten independent slowing downs at each energy and the standard errors on the mean are given. Not surprisingly, the maximal penetration is a monotonically increasing function of the incident energy and it is limited to 4 atomic layers for the largest cluster. The smallest cluster does not penetrate two layers, in the average, at the highest energy considered. The largest cluster systematically penetrates deeper than the smallest one. Systematically as well, Co, initially surrounded by Ag atoms has less penetration than Ag and still remains surrounded by its silver shell. Except for the smallest cluster with incident energy lower than 0.5 eV/atom, Co and Ag atoms are always found at least one layer deep in the substrate. This suggests that, in real experiments, substrate damage would be particularly difficult to avoid.

As a consequence of the impact, Ag atoms leave the cluster and form add-atoms. Add-atoms are either found regrouped and forming a step at the periphery of the cluster, or they are found isolated at larger distances from the cluster. The latter, in their large majority, are found to originate from the cluster itself while the former are substrate atoms displaced during the penetration of the cluster. Part of the induced damage can be appreciated in fig. 2b where it is shown that displaced Ag atoms form layers around the cluster which height, in the average, is also an increasing function of the incident energy. This means that a configuration with a compact two or three atomic layer step at the periphery of the cluster is energetically better favourable than a single monolayer configuration extending on a larger area.

In all cases, \( w_r \) is larger than \( w_l \), except for the Co-Co peaks that are close to symmetrical. The peak asymmetry in the free cluster, which is the most pronounced for the Ag-Co pairs, is consistent, in principle, with an anharmonic character of thermal vibrations. If this was true, anharmonicity would also contribute to the peak structure after deposition. Anharmonicity is not sufficient to explain the asymmetry.

Indeed, while \( w_l \) is quite small at 0K, \( w_r \) is significant, indicating distortion toward large separations. The increase of \( w_l \) and \( w_r \) from 0K to 300K are similar, indicating that the effect of anharmonicity is small. Hence, among the different possible contributions to the first peak structure, lattice distortion appears to be the dominant effect.

4. Summary
The present study embraces several aspects of cluster modification subsequent to their slowing down. The comparison of these aspects in the case of well-defined different clusters is
made and the picture which emerges is as follows: Whatever the cluster size and energy –in the range investigated-, damage is produced in the substrate. Not surprisingly, the amount of damage increases with the slowing down energy. This damage results in the formation of add-atoms at the substrate surface either originating from the cluster or from the substrate. The latter result from the partial penetration of the cluster and form a step at the periphery of the cluster, which may be several atomic layers high. The former flow from the cluster surface and dissipate their initial kinetic energy by diffusing toward more distant isolated add-atom sites or small monolayer islands, well-separated from the cluster area.

The core-shell structure of a cluster enhances this flow, decreasing this way part of the excess energy associated with the interface between the core and the shell. The impact does not induce dissociation of the Co groups in the cluster, whatever the stoechiometry. As already known from previous work, both experimental and numerical, small clusters accommodate epitaxially with the substrate. This accommodation is however inhibited when the Co core is large enough. Since this one does not dissociate upon impact, it can only accommodate with the substrate by a rigid rotation which turns out to be hardly induced. Therefore, core-shell clusters –depending on the binding energy of the core- may display defects resulting from the competition between epitaxial accommodation and the random core orientation. The lattice in the free clusters is distorted and this distortion is enhanced by the impact. The memory of the initial cluster morphology is partially preserved after the impact of the larger cluster, both as the core and the shell are concerned. No such memory effect was found for the small cluster, which morphology is destroyed by the impact and its reshaping is governed by the epitaxial accommodation. This process is only partial for the larger cluster considered, within the simulation time of 150 ps.

Hence, at the atomic level, the cluster-substrate system displays a complex structure after deposition and the memory of the initial geometrical properties is only partial. This may have consequences relevant to catalysis, magnetic and optical properties and further work is in progress to gather a better insight about the possibilities to monitor the consequences of the cluster-surface interaction.

References.