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Interface formation by low energy deposition of core-shell Ag-Co nanoclusters on Ag(100)

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Abstract. Molecular Dynamics is used to study the formation of an interface between a single crystalline Ag matrix and core-shell AgCo nanoclusters deposited with energies ranging from 0.25 eV to 1.5 eV per atom. As a consequence of the slowing down, clusters deform, may become epitaxial with the substrate and keep their core-shell structure. The consequences of the cluster-surface interaction are studied in detail for a realistic size and energy range and the accumulation of clusters is modelled. It is found that the interface formed is no more than a few atomic layers thick and that both the cobalt cluster cores and the silver shells display limited epitaxy with the substrate. The effect is not much energy dependent and is larger for the Ag shells that for the Co cores.

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1 Introduction

The interest of nanoparticles resides in the wide range of specific properties directly related to their nanometer size. For instance, as metallic particles are concerned, chemical, magnetic, electronic as well as optical properties are different than in macroscopic bulk metals. Hence, controlling size of nanoparticles allows controlling their properties. Further, non elemental particles have an additional degree of freedom, composition, which allows wider tuning of properties related to size.

It is known that, in principle, equilibrium macroscopic phases of alloys may be retrieved in nanoparticles [1]. However, due to the enhanced surface to volume ratio, segregation may be much enhanced in nanoparticles providing structures with a stoichiometric core surrounded by a segregated shell with significantly different composition. An additional difference with macroscopic systems comes from the fact that nanoparticles may be synthesized in highly non equilibrium thermodynamic conditions allowing virtually any composition [2–4]. This way, surface segregation states may be obtained, still more different than at macroscopic surfaces. As a limiting case of segregation, nanoparticles can be formed in which total phase separation takes place, giving rise to a core-shell structure. Such systems, obtained experimentally [5] are also predicted by modelling at the atomic scale [6–8]. They are the subject of theoretical studies both using thermodynamic techniques inspired from macroscopic approaches [9] and at the atomic scale [1,10]. The conditions for the occurrence of a core-shell structure and its dependence on composition, size and temperature is discussed in [11]. Although several papers report about experimental studies of nanoparticles in a particle beam [12], most of nanoparticle properties can nowadays only be measured when they are deposited of embedded into a matrix. In order to use the original properties that nanoparticles display in applications, it is obviously also necessary to either support them on a substrate surface, to embed them in a matrix or to assemble them. This raises two new questions, namely, the extent to which their properties are retained by the embedding, deposition or assembling processes and possible new properties specific to the interface between a particle and a matrix, a surface or between them. These questions, already addressed at the mesoscopic and atomic scale, in several studies [13–23] are huge and still far from being completely settled. Recently, the study was extended to phase separated particles formed by cobalt and silver [23] and this latter study is still extended in the present paper.

In [23], the $Co_{10}Ag_{191}$and $Co_{285}Ag_{301}$ particles slowing down on a Ag (100) substrate was analyzed in detail. It was also found that, whatever the cluster size and energy — in the range investigated —, damage is produced in the substrate. Ag cluster atoms were found to flow from the cluster surface and dissipate their initial kinetic energy by diffusing toward more distant isolated adatom sites or

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small monolayer islands, well-separated from the cluster area. The smallest cluster accommodates epitaxially with the substrate. This accommodation is inhibited in the case of the larger one. Therefore, the memory of the initial cluster morphology, fully lost in the case of the smallest cluster is partially preserved after the impact of the largest one. This is a size effect. The study is here extended to clusters having no special morphology and the effect of size and deposition energy is systematically studied. Using realistic conditions, the formation of a cluster-substrate interface is also modelled and its characteristics are predicted.

The atomic scale model used is summarized in Section 2, Section 3 is devoted to the cluster slowing down and Section 4 to the interface formation. A conclusion is presented in Section 5.

2 The model

We use Molecular Dynamics (MD) to simulate Low Energy Cluster Beam Deposition (LECBD) [24,25] in realistic conditions with slowing down energies ranging from 0.25 to 1.5 eV/at. and sizes ranging from 200 to 3000 atoms.

The MD model employed is already described elsewhere [21]. Forces are derived from an Embedded Atom Model potential (EAM) proposed in [26] and account, in addition, for a contribution of electron-phonon coupling [21]. Its application to binary systems is discussed in [19] and, in the case of deposition of CoAg clusters on a Ag substrate, in [23].

The major parameter which governs the interatomic interactions in the system is, of course, the potential, assessed on the basis of equilibrium properties [10,14]. The difference with the present case is the impact of the clusters on a surface, involving energies up to 1.5 eV per atom, which is much higher than those involved at thermal equilibrium. However, at this energy, the shortest Ag-Ag separation distance involved in the simulations presented below is 2.124 Å at 1.5 eV/at. It is similar for Co-Co and Ag-Co pairs at the same energy. Such distances are still of the order of the first neighbour distance for which the EAM potential is designed. Before any substantial atomic displacement, the cluster impact is known to induce one collective excitation which propagates as a wave — sometimes considered as a shock wave — and dissipates within the crystal. The length scale of this phenomenon is larger than typical box sizes used in MD simulations with the potential consequence of spurious boundary effects. The modelled substrate is 48 atomic layers thick and the energy carried by this collective excitation is damped by artificial friction forces applied to boundary atoms close to the simulation box surface opposite to the surface of incidence. These forces are released after a time of the order of the time needed by a sound wave to propagate through the whole model substrate thickness.

In order to evaluate the modification of the clusters as a result of their impact on a Ag substrate surface, a set of characterisation functions is used.

An aspect ratio is used to measure the cluster deformation upon impact. In a coordinate system where x and y are parallel to the surface and the z-axis to the inward normal, the aspect ratio will be measured as the arithmetic mean of l/L_x and l/L_y. Here l is the distance between the cluster atoms having the largest and the smallest z-coordinate, L_x is the distance between cluster atoms with the lowest and highest x-coordinate and L_y similarly. The undeformed initial clusters have all an aspect ratio close to unity.

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.

$$S = \frac{1}{N} \sum_{j=1}^{N} e^{i\mathbf{k}\cdot\mathbf{r}_j}. \tag{1}$$

In this expression, $\mathbf{k}$ is the wave vector, $\mathbf{r}_j$ is the position of the atom j and N is the total number of atoms in the cluster. $|S|^2$ is measured with $\mathbf{k} = (4\pi/a_0)\,(0,0,1)$, normal to the surface, where a_0 is the substrate lattice parameter. Lateral accommodation study would require the use of additional $\mathbf{k}$-vectors but will not be considered here. When clusters are accumulated on a substrate, as is the case in the following discussion, the structure factor is also measured in thin slabs (one lattice unit thick) in the vicinity of the interface in order to measure epitaxial accommodation as a function of the distance from the interface plane. The number of atoms N in equation (1) is then taken as the number of atoms in the slab where $|S|^2$ is measured.

A pair distribution function is used to characterise order in the clusters,

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

where δ 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

The clusters used in this slowing down study are those which equilibrium thermodynamic properties are discussed in [11]. Energy dependence is studied for one $Ag_{500}Co_{500}$ cluster, keeping all other incidence conditions constant.

The maximum cluster penetration is given in Figure 1 in terms of substrate atomic layers as a function of the incident energy. The results are representative of the other cluster sizes considered. In [23], repeating the slowing

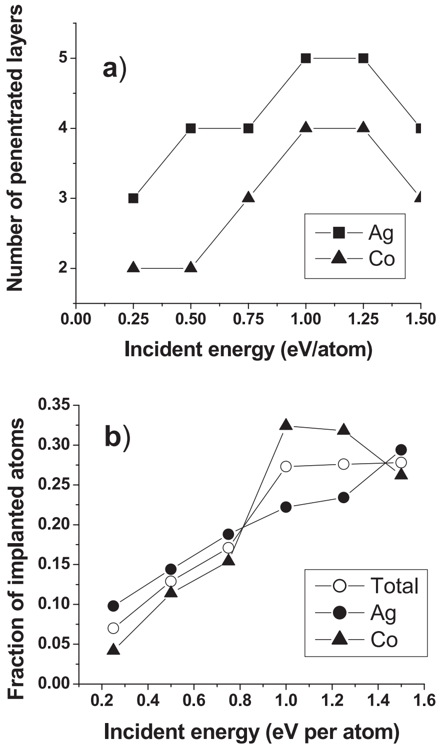

Fig. 1. Energy dependence of the penetration of $Ag_{500}Co_{500}$ clusters. (a) Maximal penetration of the Ag and the Co components; (b) fraction of implanted cluster atoms.

down with initial cluster orientations and impact points at random, it was shown that statistical fluctuations were quite small, of the order of the size of the points in Figure 1. It is found that 0.25 eV/at are sufficient for cluster atoms to penetrate up to 3 atomic layers. However, whatever the incident energy in the range considered, no atom penetrates more than 5 layers, representing less than 2 lattice distances. The distinction is made between penetrations of each of the elements forming the clusters. For both species, a trend for an increase of penetration with the energy of incidence is observed. The results at 1 eV/at and higher energies however show that, in this energy range, no further energy dependence is to be seen. Consistently with [23], Co atoms are found to penetrate at most to the fourth atomic layer. It is only at energies higher than 0.5 eV/at that the effect of the impact is sizeable.

Another parameter which describe atoms, namely, the number of cluster atoms sitting below the level of the surface after impact. This fraction is found to be an increasing function of the incident energy. It however levels off at impact energies above 1 eV/at. and is never found higher than 30 percent. Because of the core-shell structure of the incident cluster, at low energy, more Ag than Co atoms penetrate. The balance changes however when the impact energy is above 0.75 eV/at. This is the consequence of the fact that, during the impact, the silver shell partially disrupts and that silver atoms flow from the cluster shell to adatom sites on the surface, in the close vicinity of the cluster. This phenomenon was already found in [23] where the formation of a step around the Co core and of isolated adatoms was discussed. Above 1 eV/at., the incident Co core deforms. The energy spent in its plastic deformation is no more available for penetration, hence the levelling in the energy dependence of the number of penetrating atoms.

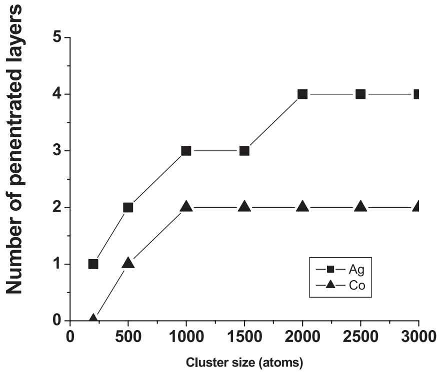

Fig. 2. Maximal penetration of the Ag and the Co components. The deposition energy is 0.25 eV/at.

Size dependence is studied in the case of 0.25 eV/atom slowing down energy. The maximal penetration depth of the incident clusters is shown in Figure 2 as a function of cluster size. The maximal penetration depth is a fast increasing function of size as far as the clusters are small (no more than 1000 atoms). No size effect is found for bigger clusters. Again as a consequence of the core-shell structure, Ag atoms reach larger depths than Co atoms and the effect increases with cluster size. The surface to volume ratio decreases with size. Thus, if the stoichiometry is maintained constant, it results in increasing the thickness of the Ag shell and this explains the difference in the maximal penetrations observed.

As the largest clusters are concerned, the both the maximal penetration and the fraction of implanted atoms are found size independent. This implies that the number of atoms within the same surface layer increases and thus that the implanted fraction of the cluster undergoes some lateral spreading.

The incident energy dependence the aspect ratio is shown in Figure 3 for the $Ag_{500}Co_{500}$ cluster, which is not found to be significantly dependent on the cluster size. Consistently with the maximal penetration characteristics, the aspect ratio decreases with increasing slowing down energy. This decrease is monotonic. Because its cohesion is stronger, the Co core deforms less than the Ag shell, systematically.

The case of smallest cluster is exceptional. In this case, the cluster is fully destroyed in the early stage of the impact. It then recovers and, as already discussed in [23], it rebuilds epitaxially.

4 Interface formation

The lattice mismatch between Ag and Co, before impact, induces a large strain in the Ag lattice [11], it contributes

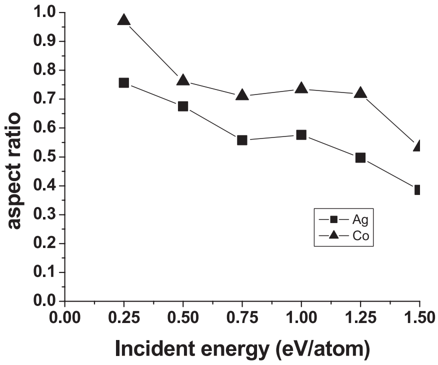

Fig. 3. Aspect ratio of the $Ag_{500}Co_{500}$ cluster as a function of the energy of incidence.

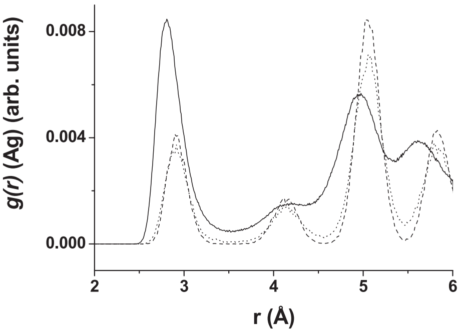

Fig. 4. Pair correlation function in Ag. The straight line represents the Ag pair correlation function measured in the free $Ag_{500}Co_{500}$ cluster, the dashed line in the Ag substrate and the dotted line in the cluster layer just above the interface.

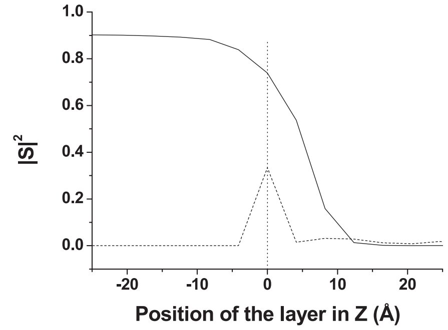

Fig. 5. Square module of the structure factor measured in Ag (solid line) and in Co (dotted line) in the vicinity of the interface between the substrate and the cluster layer (shown by a vertical dashed line).

to the partial loss of core-shell structure and only allow a poor epitaxial accommodation of the Co lattice with the Ag substrate [23]. In this section, the properties of the interface formed by core-shell cluster slowing down between the nanostructured layer formed by the core-shell deposited clusters and the Ag (001) surface are examined.

Clusters are consider to slow down one after the other within time intervals of 150 ps, which is the time evolution considered for a single cluster slowing down in the previous section. For each impact, one cluster is selected at random according to a realistic close to log-normal size distribution [27] with a mode at 2.5 nm. The number of deposited clusters is sufficient to completely cover the substrate surface, making the study of an overall interface possible. The surface area is $36a_0 \times 36a_0$ (a_0 is the lattice distance in Ag). We here discuss results for the 0.25 eV/at slowing down which also pertains to the other slowing down energies. Pair correlation functions (Eq. (2)) are used to characterize the crystallinity at short range. Figure 4 shows a comparison between pair correlation functions measured in the substrate layer just below the surface and the nanostructured Ag layer just above the surface. Both layers have the thickness of one Ag lattice distance. It is seen that all the crystalline features showing up in the substrate also show up in the cluster layer, even the second neighbour peak lacking in the isolated cluster function. The peaks in the nanostructured Ag subsystem are only a little broader than beneath the surface, because of distortions induced by the presence of cobalt. The effect of this distortion is however smaller than in the free clusters where the Ag-Ag separation distances are systematically shifted toward lower values, due to the smaller Co-Co separations at the core-shell interfaces. The impact does not alter the ordering of Co.

Figure 5 shows the structure factor measured as a function of the distance from the interface in both the Ag and the Co subsystems. The analysis is limited to 2.5 nm on both sides of the interface. At the interface, the epitaxy of the Ag subsystem clearly appears but quickly decreases with distance from the interface in the nanostructured layer. Co does undergo the influence of the Ag substrate structure at the interface. The effect on the structure factor is however limited because of the difference in lattice distances and the strong binding of Co cores with respect to silver which hampers accommodation.

5 Conclusion

The results in the present study can be summarized as follows. When slowing down on a Ag crystalline surface, only the smallest ones undergo profound reorganization and, in all cases, the core-shell structure is preserved to a large extent. In the energy range considered, the penetration of the clusters into the substrate is limited to a few atomic layers and is found energy dependent. The fraction of cluster atoms penetrating the substrate surface is not significantly size dependent. It is limited to a few percent. The Co core and Ag shell deformations subsequent to impact are different. Deformation of the Co cores is less pronounced because Ag is loosely bound to the cores and flows to the substrate surface during the impact. As a result of the accumulation of clusters on the surface, the interface formed is crystalline and Ag originating from the clusters is epitaxial. The epitaxy of the Co subsystem is much lower, though significant. The epitaxial accommodation quickly vanishes with distance from the interface. This suggests the lack of correlation between the substrate and a nanostructured film formed by deposition at distances larger than a couple of nanometres.

The modelling of thick films is in progress and their specific properties will be discussed in a later report.

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