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Time evolution of Ag-Cu and Ag-Pd core-shell nanoclusters

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Abstract. The possibility of obtaining core-shell nanoparticles by depositing adatoms of a different element B above a cluster of an element A (system B/A) is studied by Molecular Dynamics simulations. We consider the four cases Ag/Cu, Cu/Ag, Ag/Pd and Pd/Ag, which present very different behaviours, and investigate whether it is possible to build up of well-defined core-shell structures.

PACS. 61.46.+w Nanoscale materials: clusters, nanoparticles, nanotubes, and nanocrystals

1 Introduction

Since the observation that strain can change the chemical properties of surfaces [1–3], there has been a considerable interest in the building up of core-shell nanoparticles. A simple mode to prepare a strained surface is to deposit a layer of an element B above a crystal surface of element A. If the two elements present a size mismatch, the overlayer is strained. The use of nanoclusters allows to increase the surface/volume ratio. For this reason, several systems have been studied, such as, for example, considering only transition and noble-metal clusters, the core-shell Pd/Au, Pt/Au, Pd/Pt, Rh/Pt [4], Cu/Ni [5], Ag/Pd [6] and Ag/Cu [7].

An important question which arises concerning these systems is: given two elements, is it possible to obtain a core-shell structure? Here we simulate the growth of free bimetallic nanoclusters by Molecular Dynamics simulations by the method developed in references [8,9]. Our results are relevant also for clusters deposited on inert substrates. We consider both Ag-Cu and Ag-Pd. In our simulations, we start from an initial core of metal A (a truncated octahedron of 201 atoms, TO_{201} in the following) and deposit atoms of metal B above it. Our purpose is to make a comparison at fixed growth conditions but interchanging the role of the two metals. For example, for Ag-Cu, we consider first an initial TO_{201} of Cu and deposit Ag atoms above it, and then we start with an TO_{201} of Ag and deposit Cu atoms. Similarly we proceed for Ag-Pd. The systems studied here behave quite differently for what concerns bulk alloying. Ag-Cu bulk alloys present a large miscibility gap in wide ranges of temperature and concentration [10], and Ag tends to segregate strongly at surfaces [11]. On the other hand, the phase diagram of Ag-Pd alloys displays a continuous series of solid solutions over the whole range of concentrations at high temperatures (around 1200 K) [10]. However, Ag segregates also at Ag-Pd surfaces [12].

The paper is organized as follows. Section 2 contains a brief description of the model and of the simulation method, Section 3 contains the results, and Section 4 the conclusions.

2 Model and methods

The energetic parameters used in our model are derived from the electronic structure in the Tight-Binding Second-Moment Approximation scheme [13]. The band energy of an atom of type i located at site n is proportional to the square root of the second moment of the local density of states, leading to the many-body character of the potential. This band energy term writes:

$$E_n^{i,b} = -\sqrt{\sum_{\substack{m \\ r_{nm}<r_c}} \sum_{j=A,B} p_m^j \xi_{ij}^2 \exp\left[-2q_{ij}\left(\frac{r_{nm}}{r_{ij}^o}-1\right)\right]}, \tag{1}$$

and is counterbalanced by a repulsive term of the Born-Mayer type,

$$E_n^{i,r} = \sum_{\substack{m \\ r_{nm}<r_c}} \sum_{j=A,B} p_m^j A_{ij} \exp\left[-p_{ij}\left(\frac{r_{nm}}{r_{ij}^o}-1\right)\right], \tag{2}$$

where r_{nm} is the distance between the atoms at sites n and m; r_{ii}^o, $i = A, B$, is the nearest neighbor distance in the pure metal i, $r_{ij}^o = (r_{ii}^o + r_{jj}^o)/2$ if $i \neq j$, and r_c is the cut-off distance for the interactions. p_m^j is an occupation number

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equal to 1 or 0 when site m is occupied or not by an atom of type j. For homoatomic interactions ($i = j$), the parameters A_{ij}, p_{ij}, q_{ij}, ξ_{ij}, are fitted to the experimental values of the cohesive energy E_{coh} and lattice parameter (a) and elastic constants (B, C_{44}, C') of the pure metals. The heteroatomic interactions, ($i \neq j$), are fitted on the solubility energy (dissolution enthalpy) of an impurity of A into a bulk of B and of B into A. p_{ij} and q_{ij} are given by the arithmetic average of the pure metals parameters. For more details in the fitting procedure and the values of the parameters see [14,15].

In our simulations, B atoms are deposited one by one on the core, and between two subsequent depositions all atoms of the cluster are free to move. The cluster temperature is kept constant by an Andersen thermostat. The time step for the solution of the equation of motion is of 7 fs, while the interval τ between subsequent depositions is of 2.1 ns [8].

3 Results

We show the growth simulations results for the four cases as explained in the introduction. We deposit B atoms above the TO_{201} of A atoms and monitor the cluster as the number of deposited atoms N_{dep} increases by taking several snapshots at each size. If we would cover the TO_{201} by a single-layer shell of atoms of the same species A, we would need a number $N_{geom}^{A} = 204$ of atoms. In our simulation, we cover the TO_{201} of A atoms by adding B atoms, which have a different size: let d_A and d_B be their atomic diameters, respectively. Thus, the geometrical number of B atoms N_{geom} needed to obtain a single layer outer shell is $N_{geom} = N_{geom}^{A} d_A^2 / d_B^2$. We stop our simulations after depositing the maximum between 204 and N_{geom}. In order to give a quantitative account of the development of the structure, we monitor the possible defects in the core-shell structure, either being A atoms on the surface of the cluster (whose number is N_A^{surf}) and the number of B atoms inside the cluster (whose number is N_B^{bulk}). In the ideal case (see Fig. 1), which leads to the formation of a perfect single layer of metal B covering completely cluster A, N_A^{surf} decreases linearly to zero, since B atoms are covering completely the A cluster. Moreover, in the ideal case, B atoms are not incorporated in the A cluster, and therefore N_B^{bulk} is constant and equal to zero until the A core is completely covered by a single-layer shell (with N_A^{surf} reaching zero), and then N_B^{bulk} starts to increase due to the formation of a second layer in the shell itself. In the ideal case, N_A^{surf} and N_B^{bulk} cross at N_{geom} (the minimum number of B atoms needed to cover completely cluster A), the structure has zero defects. However, real good core-shell structures always present a few defects, with a behaviour as in the top right panel of Figure 1. Again, N_A^{surf} decreases almost linearly, but without reaching zero before crossing N_B^{bulk}, which shows a mild increase after a few tens of atoms are deposited. Finally, there are at least two cases in which shells of B atoms cannot be obtained above A cores (low panels of Fig. 1). When there is a strong intermixing at the surface, N_A^{surf} decreases slowly and N_B^{bulk} starts to increase already after the deposition of a few tens of atoms. At the crossing point, the number of defects is very large. Finally, when incorporation of B atoms is fast, *i.e.* when A atoms segregate readily at the surface, N_A^{surf} decreases slightly at the beginning, because some A atoms are initially covered, and then increases due to segregation; N_B^{bulk} starts to increase just at the beginning. In this case, a B shell is never developed above the A core, because A atoms prefer to stay on the surface.

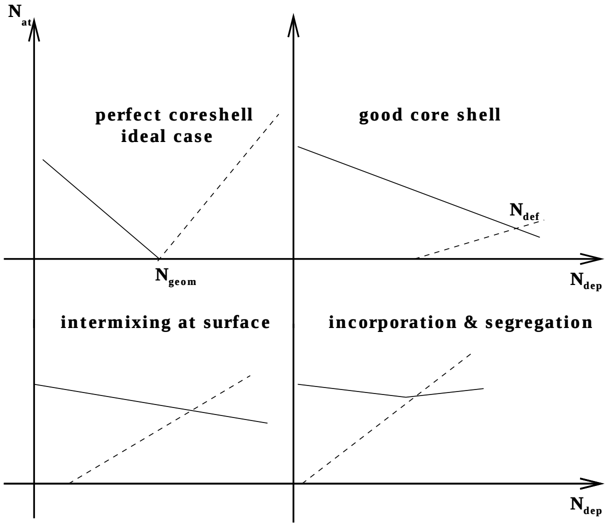

Fig. 1. N_A^{surf} (full line) and N_B^{bulk} (dashed line) are schematically plotted as a function of N_{dep} in four cases (see text).

3.1 Ag-Cu clusters

These metals present a strong tendency to demix, with Ag segregating at the surface. Therefore, this system is a good candidate for the building up of well-defined core-shell clusters, with Ag at the surface. This is indeed the case. In fact, as can be seen from the snapshots in Figures 2 and 3, obtained in a simulation at 400 K, if we deposit Ag atoms on a TO_{201} of Cu, we obtain an almost perfect Ag shell above the Cu core, which has a thickness of a single layer when N_{dep} is around 160. The good quality of the core-shell structure is confirmed by monitoring N_A^{surf} and N_B^{bulk}. N_A^{surf} decreases steadily and almost linearly, while N_B^{bulk} increases slowly. The two quantities cross at $N_{dep}^{*} \simeq 150$, just in the range where the best single-layer core-shell structures are obtained. The behaviour is of the kind shown in the top right panel of Figure 1. We remark that the Ag layer perfectly wets the Cu surface, since its thickness is of one atom in the most part of the surface. There, the number of defects in the core-shell structure is rather low, around 10%. We have simulated also at several different temperatures in the range 300−600 K, obtaining the same kind of behaviour, with a tendency to decrease the number of defects with temperature.

If we deposit Cu on an Ag core, the behaviour is completely different, and resembles closely the bottom right

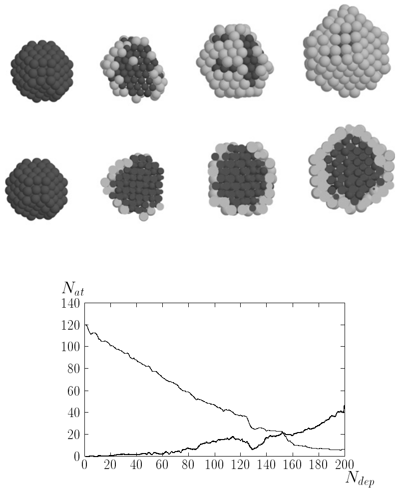

Fig. 2. Growth sequence from a simulation of the deposition of Ag atoms on a TO_{201} of Cu at $T = 400$ K. Starting form left, we show the initial Cu cluster and then snapshots taken at $N_{dep} = 50$, 100, and 204. In the first row we show the cluster surface, in the second row its inner structure. Clearly, a well-defined single-layer Ag shell is developed above the Cu core. Below the sequences, we report a plot of N_A^{surf} (thinline) and N_B^{bulk} (thickline) as a function of N_{dep}; the crossing is at $\simeq 155$, with ∼20 defects.

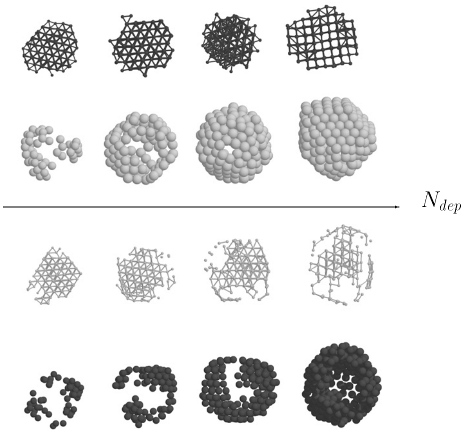

Fig. 3. The sequences of Figure 2 (Ag deposited above Cu, first and second row) and Figure 4 (Cu deposited above Ag, third and fourth row) are given in representations which show separately A and B atoms of the same cluster (Ag atoms in the second and third row, Cu atoms in the first and fourth row). We remark that in the case of Cu deposited on Ag, the Ag atoms (see the third row) are found either in a outer shell, or in a small nucleus at the centre of the cluster.

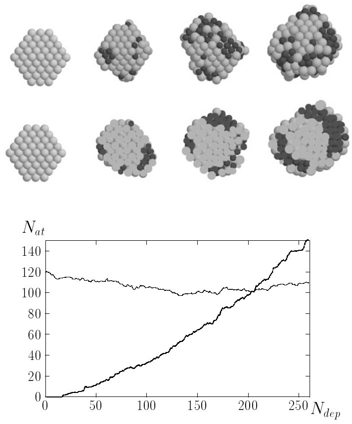

Fig. 4. The same as in Figure 2, but for the deposition of Cu above a TO_{201} of Ag. At the crossing the number of defects is very large, the majority of surface atoms being of Ag.

panel of Figure 1, as can be seen in Figures 3 and 4 where results from a typical simulation at the same $T = 400$ K are reported. The incorporation of the Cu atoms, with Ag readily segregating at the surface, is so fast that good core-shell structures are never obtained. Indeed, N_A^{surf} stays almost constant during the whole simulation instead of decreasing linearly, and N_B^{bulk} increases fast. The number of defects in the core-shell structure is always high, so high that even the term of core-shell Cu/Ag structure cannot be applied to. The same kind of behaviour is recovered at 300 K; on the other hand, at higher temperatures, the incorporation of Cu is faster. It is practically impossible to obtain a Cu shell covering an Ag cluster at already room temperature. The results of our simulations indicate that core-shell structures with an Ag shell would be easily obtained also by the deposition of Cu above an Ag core, producing an outer Ag layer which wets the surface.

3.2 Ag-Pd clusters

Well-defined core-shell structures are obtained also by the deposition of Ag atoms on a TO_{201} of Pd. As in the case of Ag above Cu, a single layer of Ag is obtained in a wide range of temperatures. However, since the tendency of Ag to segregate is weaker on Pd than on Cu, a few more defects are usually present in the structures. Let us analyze the case represented in Figure 5, where T is kept at 500 K. N_A^{surf} decreases almost linearly also in this system, and N_B^{bulk} is practically zero up to $N_{dep} = 80$, and then increases slowly. The crossing of these two quantities is found at $N_{dep}^* \simeq 180$, which is very close to N_{geom}, and there we find about 20 defects. Again, Ag is wetting the Pd core almost perfectly. This kind of behaviour is reproduced in a wide range of temperatures (say from 300 to 600 K), with a slight tendency to increase the number of defects with temperature.

On the contrary, depositing Pd above an Ag cluster, it is again difficult to obtain good core-shell clusters. In fact, there are always some incorporations of Pd adatoms into the cluster surface. The incorporation is not as fast as in the case of deposition of Cu above Ag, but leads to structures with many defects (about 90 at the crossing for the simulation shown in Fig. 6), which is about four times larger than what is obtained by the deposition of Ag above Pd in the same conditions of temperature and flux. In this case, one has strong intermixing at the surface (as in the bottom left panel of Fig. 1) which contains always a large proportion of atoms of both species. Simulating

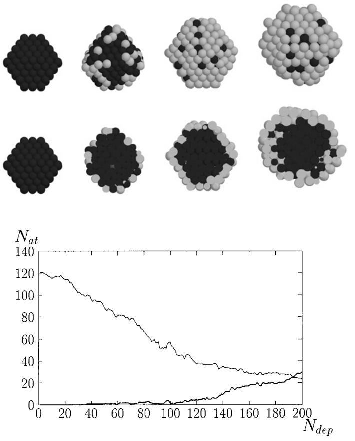

Fig. 5. The same as in Figure 2, but for the deposition of Ag above a TO_{201} of Pd. Here, as in the case of Ag deposited on Cu, a single-layer shell around $\simeq 190$ with a few defects is obtained.

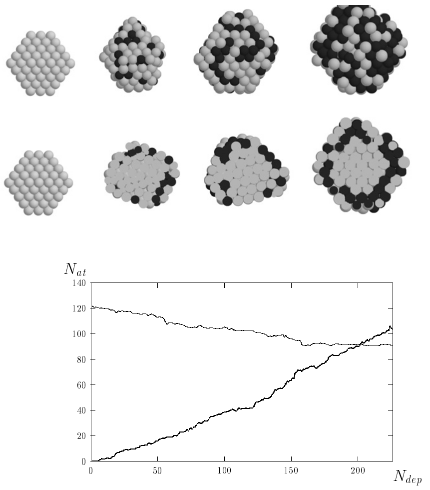

Fig. 6. The same as in Figure 2, but for the deposition of Pd above a TO_{201} of Ag. A well developed Pd layer above the Ag core is never developed, and at the end the cluster surface contains roughly the same number of atoms of both species.

at lower temperatures, for example at 300 K, there is an improvement in the number of defects (in the sense that N_A^{surf} and N_B^{bulk} cross at a lower value, say around 60), but the cluster shape itself becomes highly irregular. This is due mainly to the fact that interlayer mobility becomes difficult at low temperatures, so that there is no hope to obtain regular shells of a thickness of a single layer on the time scale of the simulation.

4 Conclusions

We have simulated the growth of core-shell structures in the cases of two different bimetallic systems, Ag-Cu and Ag-Pd, in order to investigate the possibility of obtaining well-defined shells of a thickness of a single layer. For each system, we have inverted the role of the two metals. In the deposition of Ag above Cu or of Ag above Pd, very good core-shell structures are indeed obtained in a wide range of temperatures. This indicates that these structures should be quite stable. In both cases, we obtain that Ag is almost perfectly wetting the core, already on the time scale of the simulation, and in a wide range of temperatures. The behaviour is of the kind represented in the top right panel of Figure 1. The situation is completely different when Ag is the starting core. Depositing Cu above Ag, the incorporation of the incoming adatoms and the segregation of Ag are very fast so that one obtains readily a structure with an outer Ag shell. This finding is in agreement with the strong tendency of Ag to segregate at the surface. Depositing Pd above Ag, incorporation is never negligible, even at low temperatures. We remark finally that our results not only can be relevant for free clusters, but also for clusters deposited on inert substrates [16].

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