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Deposition of Ni_{13} and Cu_{13} clusters on Ni(111) and Cu(111) surfaces

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Abstract. The soft deposition of Ni_{13} and Cu_{13} clusters on Ni(111) and Cu(111) surfaces is studied by means of constant-energy molecular-dynamics simulations. The atomic interactions are described by the Embedded Atom Method. It is shown that the shape of the nickel clusters deposited on Cu(111) surfaces remains rather intact, while the copper clusters impacting on Ni(111) surfaces collapse forming double and triple layered products. Furthermore, it is found that for an impact energy of 0.5 eV/atom the structures of all investigated clusters show the lowest similarity to the original structures, except for the case of nickel clusters deposited on a Cu(111) surface. Finally, it is demonstrated that when cluster and substrate are of different materials, it is possible to control whether the deposition results in largely intact clusters on the substrate or in a spreading of the clusters. This separation into *hard* and *soft* clusters can be related to the relative cohesive energy of the crystalline materials.

PACS. 61.46.+w Nanoscale materials – 36.40.-c Atomic and molecular clusters – 68.65.-k Low-dimensional, mesoscopic, and nanoscale systems: structure and nonelectronic properties – 31.15.Ct Semi-empirical and empirical calculations (differential overlap, Huckel, PPP methods, etc.)

1 Introduction

Due to the numerous applications in the nanoindustry, nanodevices, catalysis, etc. [1–3] the deposition of transition and noble metal nanoparticles on diverse substrates has attracted considerable attention among experimentalists and theoreticians over the past decades. Various experimental techniques [4–6] have been developed in order to deposit accurately even very small metal clusters without damaging the surface and keeping the clusters as identifiable entities. Successful growth of monolayers and cluster islands has been achieved with controlled aggregation following atom vapor deposition. Through the use of scanning tunneling microscopy [7,8] it has become possible to deposit and move clusters on the surface. One of the most recent experimental techniques is the Low Energy Cluster Beam Deposition (LECBD) [4] that uses only moderate energies of deposition. With this technique, the surface structure remains largely intact in contrast to experimental methods where the substrate is bombarded with high-energy clusters resulting in thin films formed by the cluster atoms. In that case, the clusters have so large kinetic energies that they melt upon the deposition, lose their initial structures and spread out on the surface, that in turn may suffer from the radiation damage.

Unfortunately, even in the latest experimental set-ups it is not possible to determine the geometry of small or medium-sized clusters, neither in gas phase nor deposited on a substrate. Here, theory can be used in supplementing the experimental studies. However, since theoretical studies of cluster deposition processes on a substrate is computationally extremely demanding when the studies shall consider realistic systems and when attempting to use first-principles methods, semiempirical methods provide a useful alternative for this kind of simulations. In combination with molecular-dynamics (MD) simulations, these methods are very attractive for studying the temporal evolution of the systems of interest. Therefore, several studies of cluster deposition processes for higher impact energy have been reported [9–11]. However, the formation and growth of cluster islands through low-impact-energy deposition have hardly been studied.

The purpose of the present study is to simulate the experimental conditions of the LECBD experiment and, thereby, obtain further details of the cluster deposition that can not be derived in the experiment directly. We shall use the Embedded Atom Method (EAM) in its original version proposed by Daw, Baskes, and Foiles (DBF) [12–14] in describing the interatomic interactions. In a previous study [15] we demonstrated that these semiempirical potentials are accurate for most metals. Very

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recently [16], we have studied the soft deposition of copper clusters on the Cu(111) surface using another version of the EAM, proposed by Voter and Chen [17,18] (VC). We considered different impact energies as well as orientations and sizes of the clusters. For the sake of comparison we shall here include results from that study. As a natural extension we shall here study what happens when the cluster and the substrate are of different metals. Accordingly, we shall study the deposition of copper and nickel clusters on copper and nickel substrates. We shall concentrate on the Cu_{13} and Ni_{13} clusters which are particularly stable according to previous studies [15,19,20].

The advantage of the EAM is that it is possible to study larger systems over longer time scales than what is possible with more accurate methods. Nevertheless, the EAM is approximate and, e.g., quantum effects of electrons and of vibrations are only very indirectly included. This means that the details of our conclusions may be altered when using more accurate methods, although we do not believe that our general conclusions will change. Finally, by studying Cu and Ni systems we are considering materials for which the EAM has been found to be particularly precise. Lacking experimental studies on those systems we, therefore, hope also that our work will serve as a motivation for studying those.

The paper is organized as follows. The computational details are described in Section 2 and the main results are presented in Section 3. Finally, we conclude in Section 4.

2 Computational methods

2.1 The embedded-atom method

The interactions between the atoms of the magic Ni_{13}, Cu_{13} clusters and of the surfaces are described through the EAM in the version of Daw, Baskes, and Foiles (DBF) [12–14]. Then the total energy of the system is split into a sum of atomic energies,

$$E_{\mathrm{tot}} = \sum_{i=1}^{N} E_i, \tag{1}$$

with E_i consisting of two parts, i.e., the embedding energy (which is obtained by considering the ith atom as an impurity embedded into the host provided by the rest of the atoms), and pair interactions with all other atoms. Accordingly,

$$E_i = F_i(\rho_i^h) + \frac{1}{2} \sum_{j=1,(j\neq i)}^{N} \phi_{ij}(r_{ij}) \tag{2}$$

where ρ_i^h is the local electron density at site i, F_i is the embedding energy, and ϕ_{ij} is a short-ranged potential between atoms i and j separated by distance r_{ij}.

The local density at site i is assumed being a superposition of atomic electron densities,

$$\rho_i^h = \sum_{j=1,(j\neq i)}^{N} \rho_j^a(r_{ij}), \tag{3}$$

where $\rho_j^a(r_{ij})$ is the spherically averaged atomic electron density provided by atom j at the distance r_{ij}.

The EAM has been successfully applied to many bulk and low-symmetric transition-metal systems such as defects, surface structures and segregation [21]. Furthermore, in our previous studies [15,19,20,22–24] we have tested its accuracy for nickel, copper, and gold clusters and showed that it describes very well the properties of most of those systems, with gold clusters being a possible exception.

In the present study we have studied deposition of a Ni_{13} cluster on the Ni(111) and the Cu(111) surface as well as deposition of a Cu_{13} cluster on the Ni(111) surface. We include our results on the deposition of a Cu_{13} cluster on the Cu(111) surface from our recent study [16]. In that study we did not use the DBF but the VC version of the EAM.

2.2 Molecular-dynamics simulation

Our computational approach is similar to that of our previous work on the deposition of copper clusters on a copper surface [16]. We model the (111) surfaces of the *fcc* copper and nickel crystals using a periodic slab of seven atomic layers and with a dimension of $10a_0 \times 10a_0$ with $a_0 = 3.62$ Å (3.52 Å) being the lattice constant for copper (nickel) for the periodically repeated unit. Periodic boundary conditions are applied parallel to the surface.

Before the deposition process is initiated we orient the icosahedral Cu_{13} and Ni_{13} clusters relative to the surface so that the S_6 symmetry axis of the cluster is perpendicular to the surface.

The equations of motion of the microcanonical (NVE) ensemble are integrated by using the Velocity Verlet algorithm. The time step is set to 2 fs and the total integration time is 50 ps. We consider impact energies of $E_0 = 0.0, 0.1, 0.3, 0.5, 0.7$, and 0.9 eV/atom, which is the range for Low Energy Cluster Beam Deposition experiments.

Both clusters and substrates are initially relaxed to equilibrium at 0 K. Subsequently, the clusters are located near the surface. Then the cluster atoms are given the initial velocity in a direction perpendicular to the substrate, whereas the substrate remains cold. At the end of the simulation the clusters and surfaces are cooled down by means of simulated annealing for a period of 5 ps.

3 Results and discussion

Limiting the summation in equation (1) to the 13 atoms of the cluster, we can introduce a total energy of the cluster. This corresponds to splitting the energy of the interaction between cluster and substrate into two equally large half-parts that each is attributed to one of the subsystems. In particularly the variation of the total energy of the cluster with deposition parameters (like impact energy and geometry) can be used in analysing the outcome of the

Table 1. The relative total energy (in eV) of the clusters after the collision with the surface as a function of the impact energy in eV/atom. The total energies of the initial, isolated structures obtained with the EAM are shown for comparison (denoted 'EAM'). 'A/B' denotes the A_{13} cluster deposited on the B(111) surface. Notice that for the Cu/Cu simulation we use the VC potential, whereas we for the others use the DBF potential. Thereby, the isolated Cu clusters have slightly different total energies.

Impact energy	Ni/Ni	Cu/Cu	Cu/Ni	Ni/Cu
0	−47.14	−36.66	−37.64	−48.46
0.1	−47.10	−37.67	−37.60	−48.46
0.3	−47.52	−37.67	−37.51	−48.46
0.5	−47.88	−37.79	−37.79	−48.43
0.7	−47.79	−36.80	−37.76	−48.46
0.9	−47.61	−36.96	−37.77	−47.61
EAM	−44.87	−33.50	−34.37	−44.87

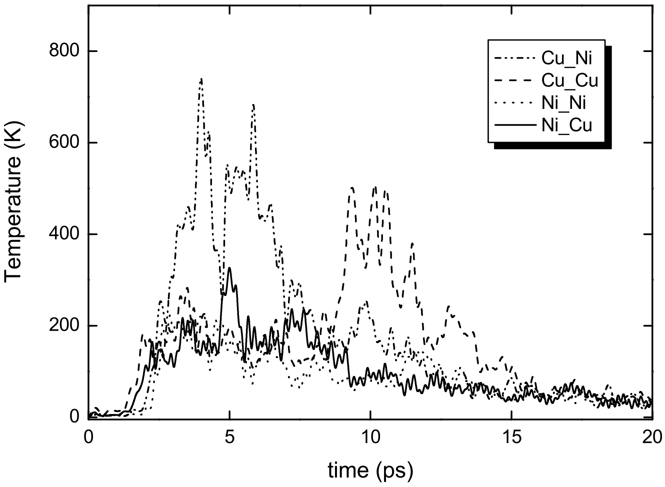

Fig. 1. The internal temperatures of Cu_{13} deposited on Ni(111), Cu_{13} deposited on Cu(111), Ni_{13} deposited on Ni(111), and Ni_{13} deposited on Cu(111) at an impact energy of 0.0 eV/atom as functions of the time. A_B marks the A cluster deposited on the B substrate.

deposition. Table 1 shows this quantity for all different impact energies and cluster/substrate combinations.

In all cases, the attractive interactions between substrate and cluster lead to a lowering of the total energy of the cluster when being deposited on the substrate. For clusters deposited on the Ni(111) surfaces the most stable structures are obtained at impact energies of 0.5 eV/atom. This result is consistent with our previous findings for Cu-Cu interactions described with another version of the EAM potential [16]. On the other hand, a nickel cluster deposited on a Cu(111) surface keeps its structure intact up to impact energies of 0.9 eV/atom, where the compact shape is distorted by the removal of a single atom from the cluster and substitution of this by a copper atom from the surface.

In Figure 1 we show the evolution of the internal temperature of the clusters as a function of time in the case that the depositions are driven only by attractive forces, i.e., for an impact energy of $E_0 = 0.0$ eV/atom. The internal temperature is defined as follows. We define the position of the center of mass of the cluster,

$$\boldsymbol{R}_0 = \frac{1}{N} \sum_i \boldsymbol{R}_i, \tag{4}$$

with $N = 13$ being the number of atoms in the cluster and $\boldsymbol{R}_i$ their positions. Subsequently,

$$\frac{3}{2} NkT = \frac{1}{2} m \sum_{i=1}^{N} \left[|\dot{\boldsymbol{R}}_i|^2 - |\dot{\boldsymbol{R}}_0|^2 \right], \tag{5}$$

with m being the mass of a cluster atom and the dots represent time derivatives, defines the internal temperature. As seen in Figure 1, the clusters with the highest internal temperatures are the copper ones, independently of the substrate, whereas the nickel clusters have much lower internal temperatures. Since the higher internal temperatures imply that the atoms are more mobile, this finding can be explained through the lower binding energies of the Cu clusters than of the Ni clusters (cf. the lowest row in Tab. 1).

Moreover, when the copper cluster is deposited on the nickel substrate it obtains a rather high internal temperature during the first 2–3 ps of the simulation and after some further 5 ps the temperature drops again. On the other hand, when the same cluster is deposited on the copper substrate, the internal temperature does not reach as high an absolute value (notice, that in this case the simulations were initiated at a larger distance between cluster and substrate, so that at the beginning the cluster was moving as a whole towards the substrate and first after some 5 ps the structure of the cluster starts changing structure leading to an increase in the internal temperature). Again, the higher mobility of copper atoms (lower binding energy of the crystal) than of nickel atoms makes it easier for the copper substrate to absorb the impact energy from the collision process, leading to a more soft landing of the clusters. In particular for the deposition of Cu_{13} on Cu, initially most of the impact energy is absorbed by the substrate that deforms so much that the cluster partly enters the surface. First then the cluster experiences larger structural changes, indicated by the late decrease in the inner temperature for this system.

Furthermore, due to the larger cohesive energy and smaller lattice constant of nickel, it is favourable for a deposited copper cluster to spread out on the surface instead of staying intact. That this occurs is seen in Figure 2. The deposition of Cu_{13} on Cu(111) at negligible attractive forces results in the formation of a distorted icosahedron, cf. Figure 3, and the cluster atoms are not spread on the surface. Here, the maximal internal temperature of 500 K is not sufficient to break the cluster bonds. According to our previous results [16] the minimal impact energy needed to disturb significantly this cluster is at least 0.5 eV/atom.

Further information on the resulting cluster structures due to the deposition can be obtained by looking at the

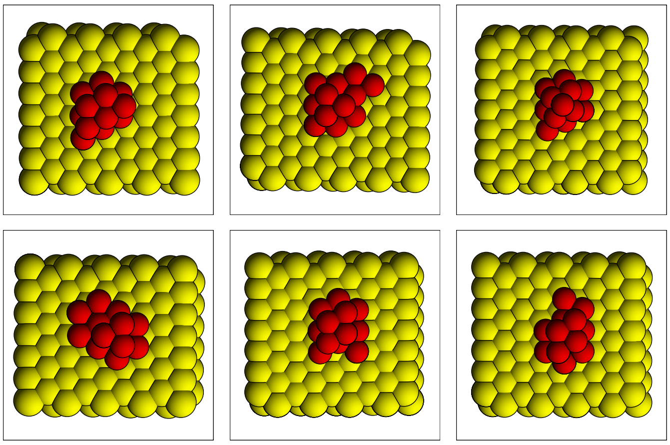

Fig. 2. (Color online) The final products of Cu_{13} clusters with different deposition energies after deposition on the Ni surface. The impact energies are (top, left) 0.0, (top, middle) 0.1, (top, right) 0.3, (bottom, left) 0.5, (bottom, middle) 0.7, and (bottom, right) 0.9 eV/atom.

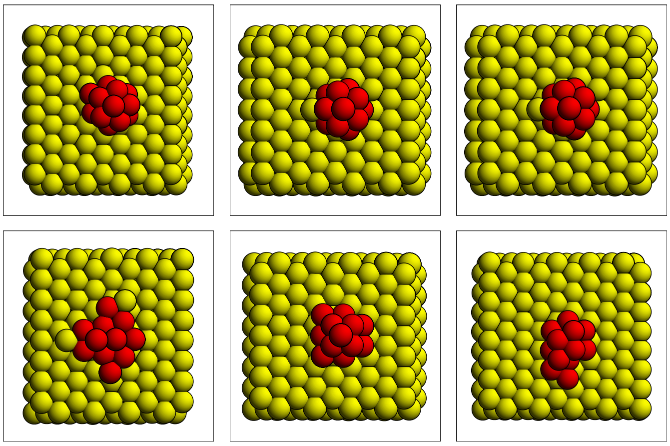

Fig. 3. (Color online) The final products of Cu_{13} clusters with different deposition energies after deposition on the Cu surface. The presentation is as in Figure 2.

Table 2. The height of the cluster (in Å) after the collision with the surface as a function of the impact energy in eV/atom. A/B labels the A cluster deposited on the B surface.

	Ni/Ni	Cu/Cu	Cu/Ni	Ni/Cu
0	5.741	5.365	4.135	5.364
0.1	5.822	5.295	3.955	5.377
0.3	5.301	5.349	5.742	5.295
0.5	3.905	3.609	3.954	5.254
0.7	5.134	5.564	4.014	5.157
0.9	5.693	4.042	4.006	5.289

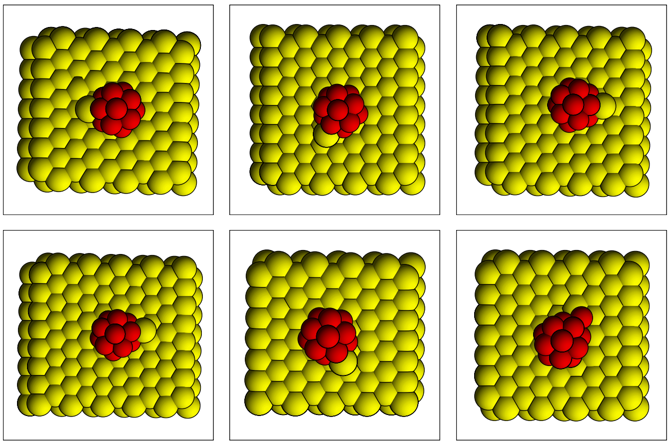

Fig. 4. (Color online) The final products of Ni_{13} clusters with different deposition energies after deposition on the Cu surface. The presentation is as in Figure 2.

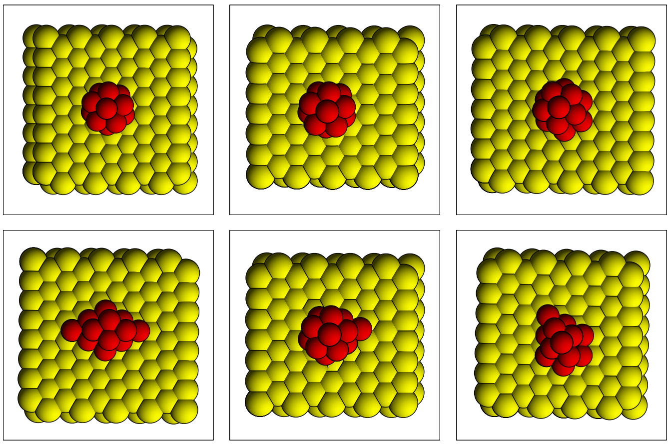

Fig. 5. (Color online) The final products of Ni_{13} clusters with different deposition energies after deposition on the Ni surface. The presentation is as in Figure 2.

height of the clusters measured as the positions of the atoms above the first plane of substrate atoms without the deposited cluster. This parameter is given in Table 2 as a function of the deposition energy. It can be seen that at a deposition energy of 0.5 eV/atom there is a minimum in the cluster height, except for the Ni_{13} cluster deposited on Cu(111) that has a minimum for an impact energy of 0.7 eV/atom. Again, the stronger interatomic bonds for Ni than for Cu may explain this shift to higher impact energies.

When simply viewing the final products of the depositions, Figures 2, 3, 4, and 5, it is immediately seen that the shape of the Ni_{13} icosahedron deposited on a Cu(111) surface remains very well kept for all impact energies (see Fig. 4). On the other hand, the Cu_{13} icosahedron spreads out on the Ni(111) surface forming double layers for all impact energies except for a deposition energy of 0.3 eV/atom, where the final structure is a symmetrical pyramid (see Fig. 2). Also this finding is due to the fact that Ni-Ni bonds are much stronger than Cu-Cu bonds (nickel possesses a higher cohesive energy of 4.45 eV than copper (3.51 eV) [25]).

As Figures 3 and 5 show, the final products of deposition of Ni_{13} and Cu_{13} clusters on surfaces of the same atom type, are very similar for the lowest impact energies. However, while at a higher deposition energy of 0.5 eV/atom, the Cu_{13} cluster spreads out on the Ni(111) surface forming a slightly deformed monolayer, the Ni_{13} cluster forms

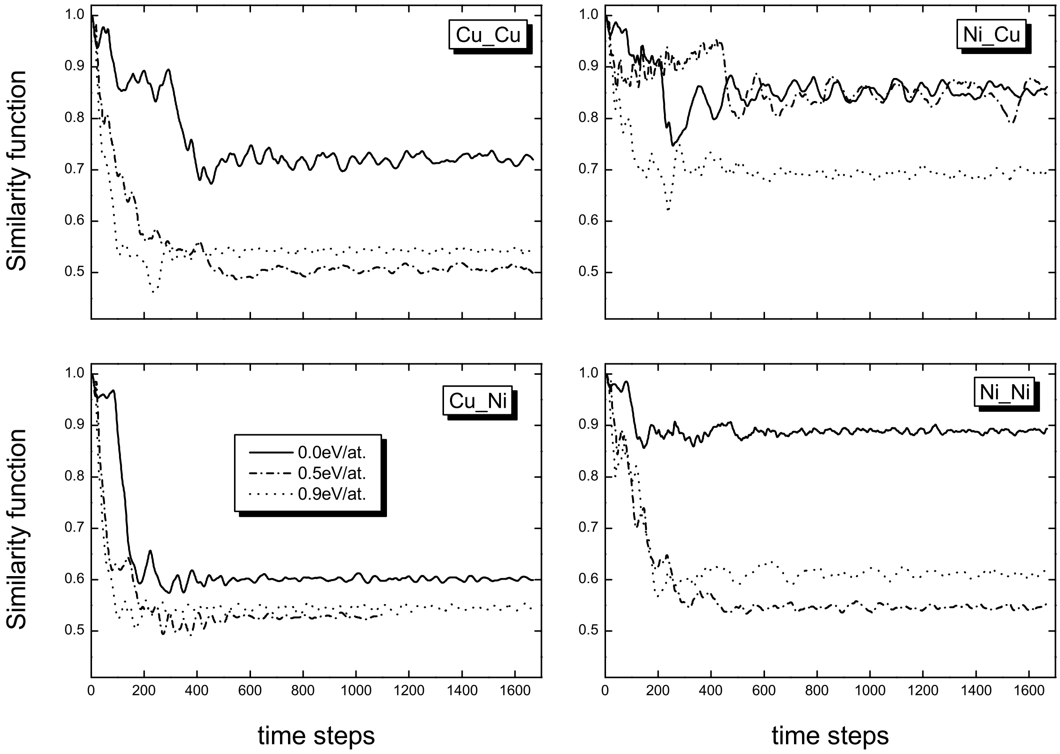

Fig. 6. The evolution of the similarity functions with time for the simulations with cluster energies of 0.0, 0.5, and 0.9 eV/atom. A_B marks the A cluster deposited on the B substrate.

only a double layer on the Cu(111) surface. For an impact energy of 0.7 eV/atom the Ni_{13} cluster remains relatively intact, with one atom substituted by a surface atom. At the same impact energy, the Cu_{13} cluster forms a symmetrical pyramid. A similar pyramid appears first at an impact energy of 0.9 eV/atom for the Ni_{13} cluster, whereas at this energy the Cu_{13} cluster collapses forming a double layer. All these results allow us to coin the nickel and copper clusters as being *hard* and *soft*, respectively.

The concept of *hard* and *soft* clusters can be further quantified through the evolution of the cluster shape with the simulation time. In order to compare the structures of the deposited products with their initial structures we use the so-called similarity functions introduced by us in previous studies [19,20]. For each atom we define its radial distance

$$r_n = |\boldsymbol{R}_n - \boldsymbol{R}_0|. \tag{6}$$

These are sorted in increasing order. At any time in the simulation we compare these with the sorted radial distances for the initial structure, $\{r'_n\}$. From

$$q = \left[\frac{1}{N}\sum_{n=1}^{N}(r_n - r'_n)^2\right]^{1/2}, \tag{7}$$

the similarity function is defined as

$$S = \frac{1}{1 + q/u_l} \tag{8}$$

($u_l = 1$ Å), which approaches 1 if the cluster has changed structure very little.

The results are shown in Figure 6. The similarity function for nickel deposited on a copper surface stays at a higher value than the one for copper deposited on a nickel surface. This supports the consensus of *hard* nickel and *soft* copper clusters. In contrast to these results, the nickel cluster readily spreads on its homoatomic surface, producing a symmetric bilayered structure at an impact energy of 0.5 eV/atom, as indicated by the low values seen in Figure 6. It can also be seen in the figure that when depositing a cluster on a surface of the same type of atoms the separation into hard and soft clusters becomes less relevant (see also Figs. 3 and 5).

A further relevant question is whether the substrate dictates the structure of the deposited cluster, i.e., to which extent the deposition can be classified as being epitaxial. To this purpose we use an 'index of epitaxy', I, [16] defined through

$$I = \frac{1}{1 + q/u_l^2}, \tag{9}$$

with

$$q = \sum_{i}^{N} |\boldsymbol{R}_i - \boldsymbol{R}_c|^2 \tag{10}$$

where $|\boldsymbol{R}_i - \boldsymbol{R}_c|$ is the distance between the position of the ith atom of the cluster and the closest-lying fictitious atom in the infinite ideal crystal formed by the substrate (notice that thereby I can also become close to 1 even when the cluster and the substrate are far apart). When I reaches 1, perfect epitaxy is obtained.

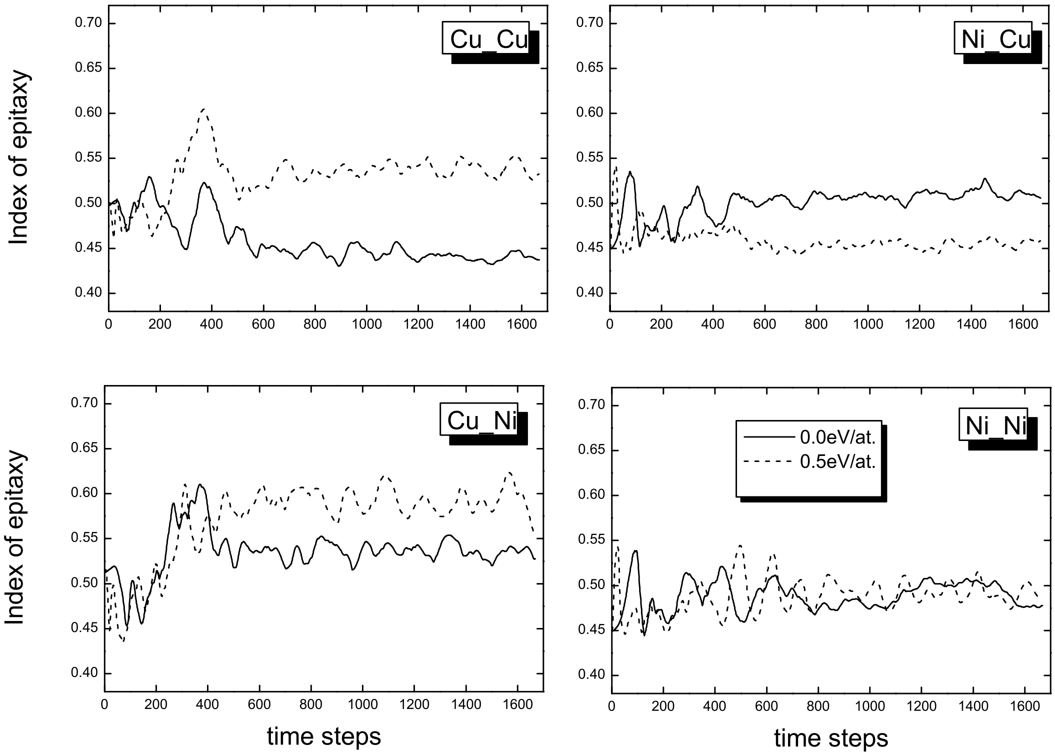

Fig. 7. The evolution of the index of epitaxy with time for the simulations with cluster impact energies of 0.0 and 0.9 eV/atom. A_B marks the A cluster deposited on the B substrate.

In agreement with our previous study [16], there is no direct relationship between the impact energy and the value of I. In Figure 7 we show I for impact energies of 0.0 and 0.5 eV/atom. In all cases I is well below 1 which implies that the interatomic forces within the clusters are sufficiently strong to keep the cluster fairly intact and prevent epitaxial spreading on the surface. It is again seen that the nickel clusters are *harder* than the copper clusters, since I stays roughly constant. A similar behaviour is observed also for the highest impact energy of 0.9 eV/atom, which is not shown here. On the other hand, the *softer* copper clusters show an increasing index of epitaxy, which reflects the spreading of these cluster on the Ni(111) and Cu(111) surfaces. The highest indices of epitaxy are obtained for the combination Cu_{13} deposited on Ni(111). In this case, the cluster forms double layers for all impact energies, except for $E_0 = 0.3$ eV/atom, where a symmetric pyramid is obtained (see also Fig. 2).

4 Conclusions

In the present work we have studied the structural rearrangements of nickel and copper clusters softly deposited on Ni(111) and Cu(111) surfaces. We have used constant-energy molecular-dynamics simulations with impact energies being typical of the Low Energy Cluster Beam Deposition experiment. The main point of this study was to investigate the differences in the structural and energetic properties of the final products when comparing depositions with homoatomic and heteroatomic interactions. According to our findings we conclude that in the case of heteroatomic interactions the cohesive energy of the bulk element is a crucial factor influencing the shape of the final structures. Thus, the deposition of Cu_{13} on a Ni(111) surface results in an overall spreading of the cluster due to the lower cohesive energy of copper, whereas the deposition of the nickel cluster on a Cu(111) surface leads to relatively small changes of the initial structure.

This may be the most interesting outcome of our study, i.e., that when clusters of one type of metal are deposited on another type of metal, it is possible to distinguish between *hard* and *soft* clusters, depending on whether the cohesive energy of the cluster material is larger or smaller than that of the substrate material. Then, *soft* clusters tend to spread on the substrate even at modest impact energies, whereas *hard* clusters largely remain intact also at slightly higher impact energies.

Moreover, it turned out that a deposition energy of 0.5 eV/atom could be favorable for the production of monolayers in the case of Cu_{13} cluster deposited on Cu(111) and Ni(111) surfaces, and the formation of double layers in the case of Ni_{13} cluster deposited on Ni(111).

Finally, we add that our study not at all aims at being exhaustive. We have only considered two types of cluster and substrate metals, only one cluster size and substrate surface, and only one impact geometry. As we have found in our recent study [16], varying the cluster size and impact geometry may very easily change details of the outcome of the deposition. Furthermore, in some preliminary studies we also found that by changing the approximate method used in describing the interatomic interactions (specifically, we considered the DBF potential instead of the VC potential for the Cu on Cu deposition), slightly different results will be found. Nevertheless, we are convinced that our main conclusions remain valid, also when taking such extensions into account.

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