

Molecular Dynamics Study of the Energetic Impact of Ag₁₉ on Pd(100): An Interpretation of Mass-Selected Clusters Deposition Experiments

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We have studied the dynamical processes and the structural modifications induced by the collision of a Ag₁₉ cluster on the (100) substrate of Pd at impact energies $E_{i1} = 20$ eV and $E_{i2} = 95$ eV, by using embedded atom potentials. Our numerical study mimics a recent series of experimental results aiming at low-energy deposition of well-defined metallic clusters on metallic surfaces. We show that the degree of implantation and cluster fragmentation is directly related to the impact energy. A transition from a three-dimensional to a two-dimensional heterogeneous adsorbed structure is observed with increasing impact energy, in a way qualitatively consistent with the experiments. Chemical disorder in the upper substrate layers is common to both energies of deposition. This provides important indications to achieve optimal conditions for cluster deposition, leading to the controlled fabrication of adlayers having a precise chemical nature.

1. Introduction

Nanostructures created via adsorption on surfaces can be obtained either by depositing atoms from the gas phase via thermal evaporation or by increasing the size of the constitutive units brought in contact with the substrate, i.e., by depositing clusters of a given size. A crucial parameter to be considered when devising a cluster deposition experiment is the impact energy involved in the collision process. Ideally, if the main interest is the creation of nanostructures maintaining properties close to those of their parent units, this energy should be kept as low as possible to minimize surface damage and atomic implantation. Although the deposition at very low impact energies of selected clusters having a narrow distribution of sizes is still an unachieved goal, it is nowadays possible to work at impact energies as small as ~ 1 eV/atom, as shown in a series of experiments performed on the system Ag_n⁺/Pd(100).^{1,2}

Three different sizes for the Ag clusters have been considered (Ag₁⁺, Ag₇⁺, Ag₁₉⁺) for impact energies equal to $E_{i1} = 20$ eV and $E_{i2} = 95$ eV and in the range of temperature $80 \text{ K} < T < 400 \text{ K}$. By using specular reflected thermal helium scattering, these investigations allowed one to infer the extent of lateral aggregation of adstructures and point defects via the evaluation of the effective cluster cross section Σ_{exp} for diffuse scattering. This quantity is obtained from the attenuation of the helium specular intensity, and its definition relies on the geometrical overlap approach. According to this approximation, which behaves reliably in a large number of cases, Σ_{exp} can be obtained from the geometrical overlap of simple cross sections centered at each defect on the surface (adatom, substitutional impurity, vacancy),³ thereby providing an indirect view of the modifications to the surface morphology induced by the impact.⁴ The low-coverage limit of the cross section corresponds to the value associated with the isolated atom, $\Sigma_{\text{exp}} = 109 \text{ \AA}^2 = 14.4\sigma_{\text{Pd(100)}}$ (where $\sigma_{\text{Pd(100)}}$, the surface unit cell, is equal to 7.56 \AA^2 in our case).

Even before the actual realization of metal-on-metal cluster deposition experiments, classical molecular dynamics (MD) simulations were employed to predict the behavior of several combinations of cluster–substrate transition and noble metal

systems made of Cu,^{5,6} Ni, and Al.⁶ More recently, the same approach has yielded results for relatively small (Cu₁₃/Cu(100))⁷ and large (Mo₁₀₄₃/Mo(100))⁸ clusters. A realistic modeling of interatomic interactions in metals with filled or nearly filled d-shells is represented by the embedded atom method scheme (EAM).⁹ This approach has been explicitly conceived to describe energetics and dynamics of large, disordered metallic systems and allows to study phenomena that would be otherwise intractable within the framework of ab initio techniques. The usefulness of nanoscale numerical approaches to mimic cluster–surface interactions stands out especially at low temperatures. In this region the time interval spanned by the simulations, which can hardly extend beyond 10^{-10} s, becomes adequate to describe the atomic rearrangements that follow the collision and last a few picoseconds.

Over the past three years we have undertaken a major research effort to investigate by MD the behavior of the system Ag_n/Pd(100). We are interested in obtaining an estimate of the degree of atomic implantation, defect creation, and surface mixing resulting from the collision process. A more stringent comparison with the experiments is reached at low temperatures by extracting the values of the cross sections from the calculated population of the surface defects. These latter (adatoms, substitutional impurities, vacancies) are easily quantified at the end of the simulations and, in analogy with the experimental analysis, provide average classical cross sections via the geometrical overlap approach.¹⁰

In ref 4 we showed that simulations and experiments are in good agreement in the case of collisions of Ag atoms at energies $E_{i1} = 20$ eV and $E_{i2} = 95$ eV on the Pd(100) substrate. However the cross sections calculated by accounting for Ag implantation underestimate the experimental value for E_{i1} , i.e., $\Sigma_{\text{exp}} = 32.0\sigma_{\text{Pd(100)}}$, $\Sigma_{\text{cal}} \sim 21\sigma_{\text{Pd(100)}}$, while the opposite is true for E_{i2} with $\Sigma_{\text{exp}} = 53\sigma_{\text{Pd(100)}}$ and $\Sigma_{\text{cal}} \sim 70\sigma_{\text{Pd(100)}}$. The results show that higher collision energies lead to deeper implantation and very limited adsorption on the upper layer. On the other hand, at $E_{i1} = 20$ eV, implantation in the second layer is absent and accommodation of the colliding atom at stable adsorption sites occurs frequently.

When going from atomic to cluster collisions on surfaces, an additional crucial factor influences the final structure of the global systems, i.e., cluster fragmentation. This determines the degree of the transformation from an initial, compact cluster structure to a collection of two or possibly three-dimensional units adsorbed or embedded on the substrate. The case of Ag₁₉⁺/Pd(100) is of particular interest especially at the lower impact energy E_{i1} (~ 1 eV/atom). This condition is very close to a supposedly nondestructive “soft landing”, with the cluster expected to keep memory of its original properties after the deposition. The results of ref 2 indicate a strong reduction of the cross section at both impact energies for Ag₁₉⁺/Pd(100) with respect to the case of Ag₇⁺/Pd(100).¹¹ This corresponds to a lower extent of fragmentation and, in turn, to an enhanced compactness of the larger cluster. Even though the Ag₁₉⁺ clusters become most likely two-dimensional after the collision, the structures obtained at $E_{i2} = 95$ eV (5 eV/atom) are significantly more compact than those obtained in the case of Ag₇⁺ at a lower impact energy per atom, $E_{i1} = 20$ eV (2.86 eV/atom). Furthermore, when the temperature increases, a dynamical restructuring takes place, giving rise to more ordered cluster structures.

In this paper we investigate by molecular dynamics simulations the behavior of the Ag₁₉/Pd(100) system resulting from the impact of the cluster on the substrate at energies $E_{i1} = 20$ eV and $E_{i2} = 95$ eV. Our results can be used as a complement to the experimental data of ref 2 in the region of low temperatures, where atomic mobility is suppressed and the only relevant dynamical processes are those caused by the impact. Preliminary findings on the Ag₁₉/Pd(100) system at E_{i2} for a substrate made of 1400 Pd atoms with a thermostat acting on the bottom layer to maintain zero temperature have already appeared in the literature.¹² Here our investigation is pursued and completed by considering both collision energies E_{i1} and E_{i2} and a larger substrate. Throughout our calculations a thermostat is set at $T = 160$ K on the lower active layer. Our purpose is to compare the structural changes induced by two different initial conditions and better assess the reliability of the atomic scale description adopted to interpret the experimental data.

2. Model and Computations

In our simulations the embedded atom (EAM) potentials of ref 9 have been modified as described in ref 4 to make them more appropriate to model energetic collisions. We refer to our early work on atomic Ag collisions on Pd(100) for a detailed description of the changes introduced and a discussion of their adequacy to model energetic impacts.⁴

Our system consists of a single slab made of six layers, modeling the (001) surface of Pd and submitted to periodic boundary conditions. The computational cell thereby constructed is defined by the vectors a_x 20a[100], a_y 20a[010], where a is the Pd lattice constant. This leads to a unit cell containing 4800 Pd atoms. As initial arrangement for the Ag₁₉ cluster, we took a six-capped icosahedral structure. Several initial configurations for Ag₁₉ are then produced by heating the clusters to temperatures between $T = 1000$ K and $T = 1500$ K. For each collision, one cluster configuration is first selected and then relaxed at $T = 0$ K. The bottom layer of the substrate is kept fixed, while a dynamical thermostat, based on velocity rescaling, is applied every 10^{-14} s to the layer above it to reset its temperature to $T = 160$ K. This value, higher than the lowest considered in the experiment ($T = 80$ K), yields conditions of frozen mobility at thermal equilibrium and compensates for the

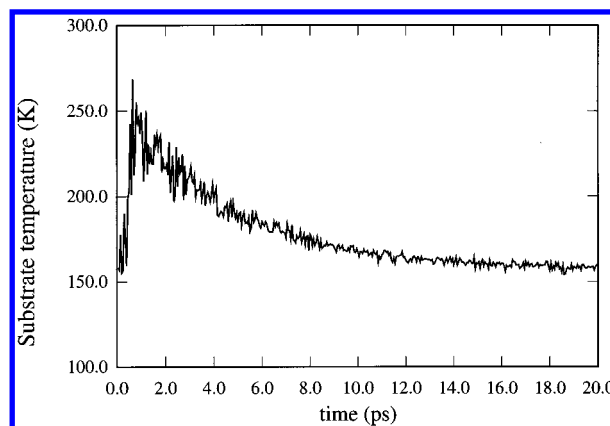


Figure 1. Behavior of the substrate kinetic energy (expressed in units of temperature) as resulting from the impact on the uppermost layer of the Pd(100) substrate of a Ag₁₉ cluster at kinetic energy equal to 95 eV. A thermostat set to $T = 160$ K is applied to the lower moving layer.

larger diffusion barrier of the model (0.6 eV) with respect to experiments (0.37 eV).¹³ The calculated barrier would lead, on an experimental time scale, to mobility activated at $T \sim 250$ K, while atomic diffusion occurs experimentally for $T > 175$ K.

At time $t = 0$, the Ag₁₉ cluster begins to move down from its initial position, with its center of mass located at 20 Å above the uppermost Pd layer. The center of mass of the Ag cluster is given initial coordinates chosen randomly inside the surface unit cell. The impact of Ag₁₉ on Pd(100) occurs with a total kinetic energy along the [001] direction equal to $E_{i1} = 20$ eV and $E_{i2} = 95$ eV. An angle $\theta = 15^\circ$ with respect to the surface normal is introduced in conformity with the experimental setup. Accordingly the total initial kinetic energies are equal to 21.44 eV (E_{i1}) and 101.84 eV (E_{i2}). For each impact energy 100 collisions are produced. It is instructive to consider the temporal behavior of the substrate instantaneous kinetic energy, expressed in units of temperature, during the impact (see Figure 1, which refers to a collision at E_{i2}). In principle, intervals as large as 20 ps are needed to converge to the value imposed by the application of the thermostat. However, we found that shorter trajectories, ranging between 10 and 15 ps, are sufficient to obtain a configuration representative of the collision outcome.

A word of caution is in order concerning our choice of modeling the collision of a small cluster on a finite-size substrate via periodic boundary conditions. As recently stressed in the literature,¹⁵ the treatment of boundary conditions to model cluster collisions on surfaces requires special care, since pressure waves generated by the impact and reflected at the boundary can dramatically affect the long-term predictions of the simulations. As an analysis of the results of ref 15 indicates, these effects have to be properly considered whenever the long-time behavior of a strongly disturbed system is under study, and they appear to be particularly serious for clusters containing more than 100 atoms at relatively high collision energy (10 eV/atom). It is worth recalling that the focus of our work is to rationalize the collision outcome for smaller cluster sizes (19 atoms) at lower impact energies (not larger than 5 eV/atom). This is achieved by calculating the population of defects created by the impact at substrate temperatures that pertain to the regime of nonactivated thermal mobility, i.e., a regime intrinsically unrelated to the long-time behavior of the system. Given these objectives and the conditions of our simulations, which are very close to those typical of a low-energy, “soft landing” deposition inducing minimal disturbances on the substrate, we are confident

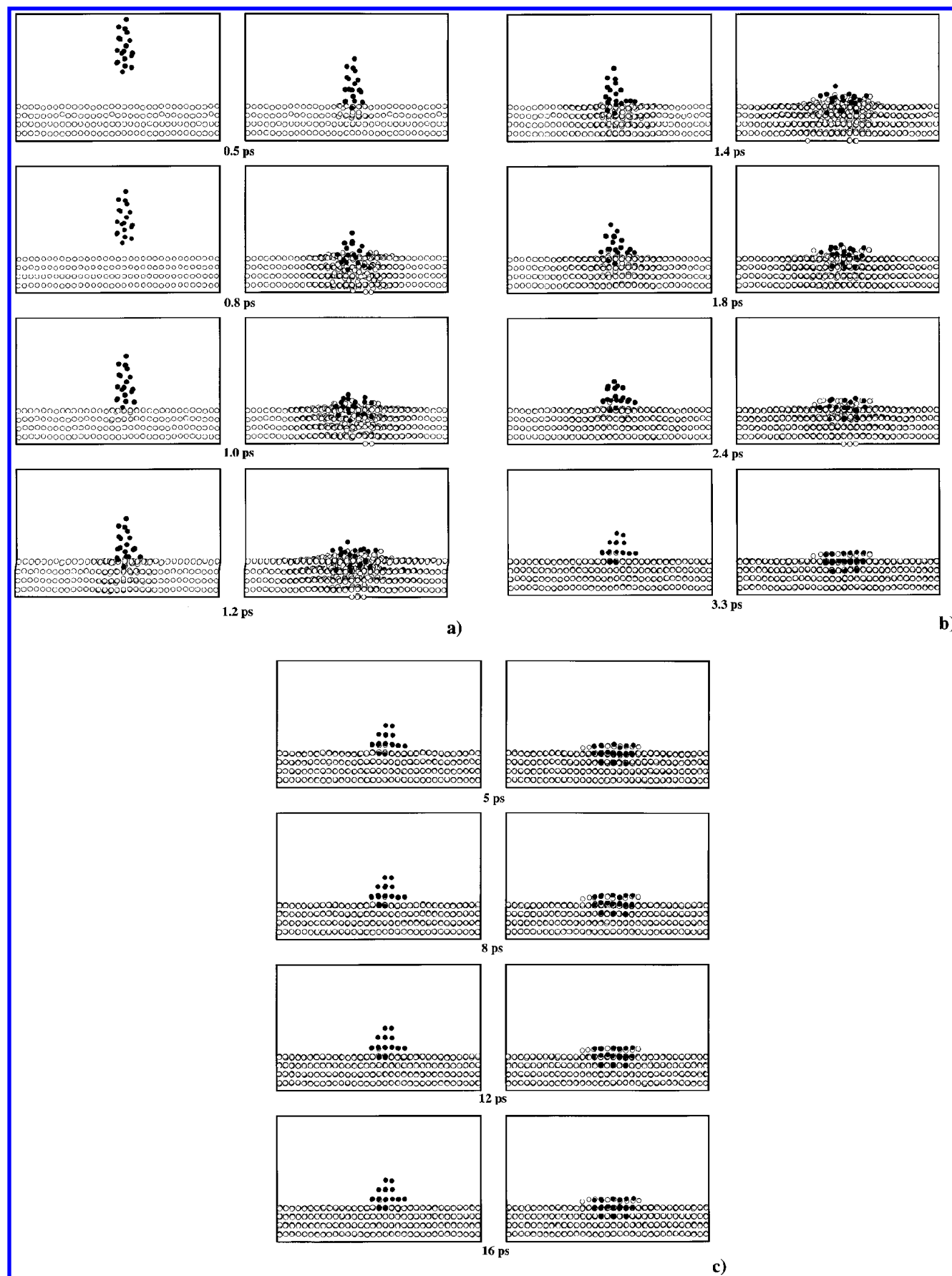


Figure 2. Snapshots showing the deposition of Ag_{19} on $\text{Pd}(100)$ (lateral view). On the left, impact energy equal to 20 eV; on the right, impact energy equal to 95 eV. The indicated times are taken with respect to the beginning of the deposition, with the cluster center of mass located 20 Å above the uppermost Pd layer. Filled circles represent Ag atoms, and empty circles represent Pd atoms. For each panel, only the Pd atoms belonging originally to the first four layers are shown.

that the use of periodic boundary conditions is sufficiently accurate to provide a realistic picture of impact process. This statement is not only consistent with the suggestions of ref 15 relative to the applicability of the method presented in that same paper but also with the results obtained in the case of atomic collisions at energies equal to 20 and 95 eV and discussed in ref 4. In that case the data obtained for the cross sections were found to be essentially independent of the system size for $N_s > 200$ (N_s being the number of atoms on each substrate layer) and on the particular boundary condition employed (lower substrate layer fixed or mobile).

3. Results

An illustration of two collision processes corresponding to the impact energies E_{i1} and E_{i2} for the same initial configuration is given in Figure 2a,b,c. The different snapshots allow one to follow the structural changes induced by the energetic deposition and their evolution with time. Without loss of generality we selected here an example in which the cluster has shape quite elongated in the [001] direction.

In the early phase of approach ($0 < t < 1$ ps in the case of E_{i1} and $0 < t < 0.5$ ps in the case of E_{i2}), the cluster moves toward the substrate with little structural modification. An overall observation of the sequences reveals that the rapid establishment of a stationary morphology, which requires not more than ~ 3 ps, is common to both collision energies. However the degree of induced disorder is markedly different in the two cases. For E_{i1} we observe a transitory regime characterized by the adjustment of the cluster to the substrate, with a moderate involvement of the neighboring Pd atoms. Penetration of the Ag atoms into the substrate is limited to short displacements between the first and the second layer. A few exchanges occur among Pd atoms belonging to different layers. The cluster arranges in three adlayers, with a few replacement sequences occurring between Pd and Ag atoms. Therefore it appears that an impact energy per atom $E_{i1}/N \sim 1$ eV, substantially smaller than the cluster cohesive energy (2.2 eV), cannot induce a transition from a three-dimensional to a two-dimensional adsorbed structure, which is the most stable arrangement of Ag₁₉ on Pd(100).

A different picture emerges from the analysis of the snapshots relative to the collision at E_{i2} . Shortly after the first contact with the substrate ($t = 0.5$ ps, Figure 2a), several Pd atoms move away from their initial positions, giving rise to a transient disordered structure involving all active layers. Topological order is recovered at $t = 3.3$ ps (Figure 2b), while chemical disorder establishes in the two upmost substrate layers and in the adsorbate, which contains Pd and Ag atoms. For both collision energies no relevant changes are observed in the structure of the adsorbate–substrate system at longer times ($t > 3.3$ ps, Figure 2c). The system adjusts to the thermal conditions imposed by small atomic displacements around the stable equilibrium sites.

An insight into the extent of lateral aggregation in the two different situations can be gained by considering Figure 3, which gives a view of the impact plane just before the achievement of the stationary state. In-plane movements have occurred only for E_{i2} , while the structure of the cluster remains highly compact at E_{i1} . For this particular example the calculated effective cluster cross sections per atom are $4.4\sigma_{\text{Pd}(100)}(E_{i1})$ and $7.1\sigma_{\text{Pd}(100)}(E_{i1})$. These results reflect the different coordination of the Ag atoms and Pd impurities on the surface. In particular the value of the effective cluster cross section at E_{i1} lies close to the lowest obtainable for a cluster of 19 atoms on the Pd(100) substrate ($4.1\sigma_{\text{Pd}(100)}$).

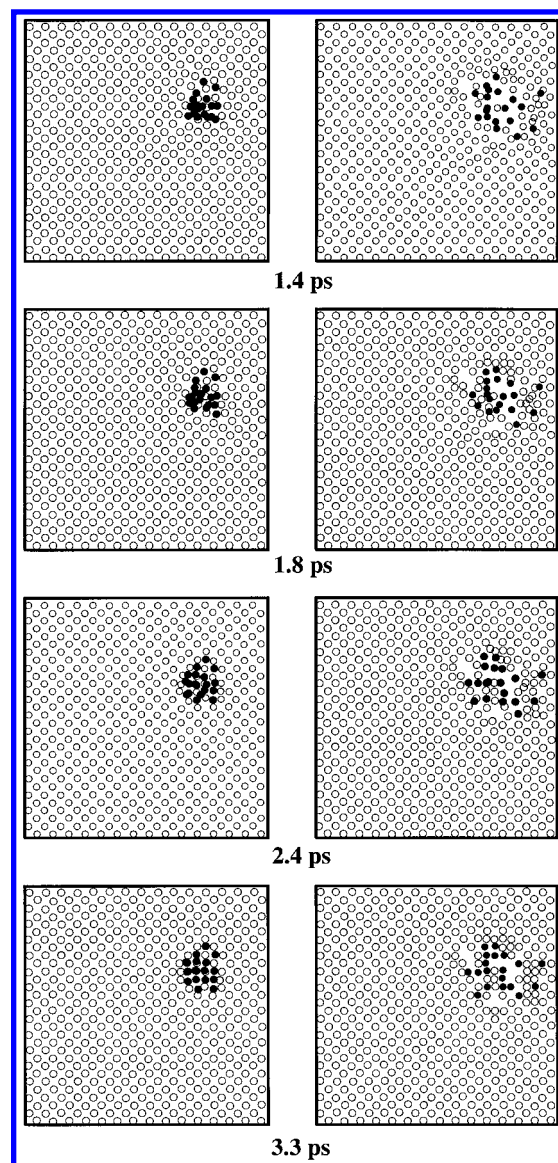


Figure 3. Snapshots showing the deposition of Ag₁₉ on Pd(100) (top view). The selected time interval is $1.4 \text{ ps} < t < 3.3 \text{ ps}$ from the beginning of the deposition. For clarity only the Pd atoms belonging originally to the uppermost layer are shown. On the left, impact energy equal to 20 eV; on the right, impact energy equal to 95 eV.

The simulations provide a picture of the collision process consistent with the existence of two different regimes, a first occurring on a short-time scale and involving enhanced motion in the region of the impact and a second corresponding to thermalization of a chemically disordered structure with little atomic movements. This is also demonstrated by the time evolution of the average distance R_{cl} between the cluster atomic positions at time t and their values at the beginning of the simulation (Figure 4). The initial transitory regime, which features a steep increase of R_{cl} , is indicative of an enhanced, transient mobility of the cluster atoms. This first part is followed by oscillations of R_{cl} around its average value, more pronounced in the case of E_{i1} , as a consequence of the low coordination of the cluster atoms forming the second and third adlayers and not directly bounded to the substrate atoms.

The enhanced motion observed during the first stage of the impact reflects the spreading of the cluster on the substrate and is directly related to the elevated cluster instantaneous internal kinetic energies that are attained (Figure 5). Such internal kinetic energies are the kinetic energies of the cluster atoms

TABLE 1: Average Number of Ag and Pd Atoms on the Higher Layers and on the Adlayers, Average Number of Vacancies, and Total Cross Section Σ_{cal} , the Latter Given in Units of the Surface Unit Cell $\sigma_{\text{Pd}(100)} = 7.56 \text{ \AA}^2$ ^a

	E_{i1}	E_{i2}
Ag atoms in the third (highest) adlayer	0.26	0.00
Ag atoms in the second adlayer	3.85	0.04
Ag atoms in the first adlayer	11.22	8.68
Ag in the first (highest) substrate layer	3.55	6.96
Ag in the second layer	0.11	3.00
Ag in the third layer	0.00	0.32
Pd atoms in the first adlayer	3.66	11.48
vacancies in the first substrate layer	0.00	0.76
vacancies in the second substrate layer	0.00	0.4
vacancies in the third substrate layer	0.00	0.04
Σ_{cal}	$(84 \pm 3)\sigma_{\text{Pd}(100)}$	$(127 \pm 5)\sigma_{\text{Pd}(100)}$
Σ_{exp}	$(115 \pm 10)\sigma_{\text{Pd}(100)}$	$(140 \pm 10)\sigma_{\text{Pd}(100)}$

^a Σ_{exp} is the experimental cross section, in the same units as Σ_{cal} . E_{i1} and E_{i2} are equal to 20 eV and 95 eV, respectively.

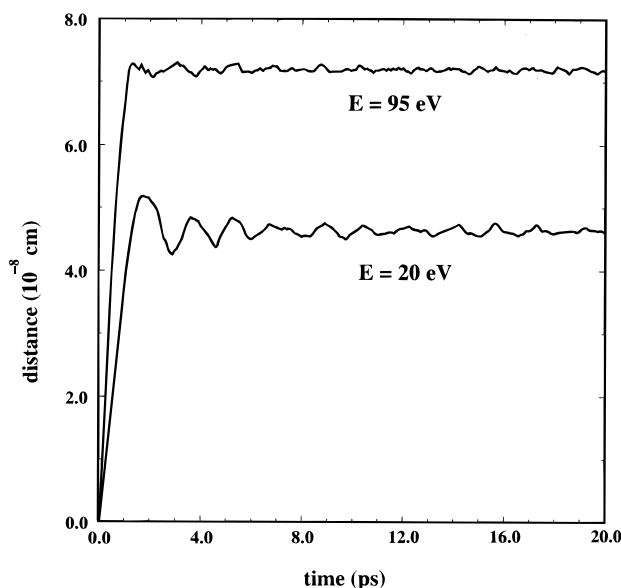


Figure 4. Temporal evolution of the average distance R_{cl} (calculated with respect to the surface (001) plane) between the positions of the cluster atoms at time t and their positions at time $t = 0$.

calculated with respect to the movement of their center of mass. They are representative of thermal motion that develops owing to the conversion of the translational kinetic energy into an internal one. Accordingly, in Figure 5 we find it convenient to express the internal kinetic energies in units of temperature. As shown in Figure 5, the typical times of energy transfer toward the substrate appear to be similar (~ 4 ps) for both E_{i1} and E_{i2} .

The average occurrences of Ag atoms implanted or adsorbed on the Pd(100) substrate and Pd substitutional impurities and vacancies are given in Table 1. As a first observation, we notice that the Ag atoms are distributed over five layers for both impact energies. In the case of E_{i2} the adsorbates created have a predominant two-dimensional character. More than half of the adsorbed atoms are Pd atoms, which were residing initially in equal proportions in the first three substrate layers. This strong intermixing is accompanied by vacancy production, more enhanced in the upper layers. The number of vacancies is consistent with the difference found between the number of Pd substitutional impurities and the number of Ag implanted atoms. Interstitials are absent, in agreement with the results of ref 6 where the behavior of Cu, Al, and Ni cluster/substrate systems was explored for a large set of impact energies. Therefore the impact energy E_{i2} is well-suited to give rise to two-dimensional heterogeneous adsorbed structures, with limited changes in the morphology of the substrate. This latter has undergone only local modifications to its chemical composition.

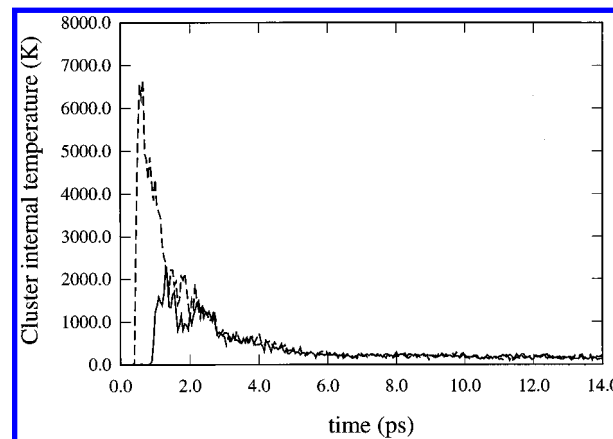


Figure 5. Behavior of the cluster internal kinetic energy (expressed in units of temperature, see text) as a function of time during the deposition at 20 eV (solid line) and 95 eV (dashed line) initial kinetic energy.

In the case of E_{i1} both implantation and intermixing are limited to $\sim 25\%$ of the Ag atoms, a percentage close to that pertaining to the Ag atoms lying above the first, most populated, Ag adlayer. The cluster retains memory of its initial three-dimensional nature by adjusting to the substrate in highly compact forms. The observed behavior is closer to ideal “soft landing”, even though exchanges among atoms of different kind cannot be avoided. In this respect it is worth recalling that a recent molecular dynamics study devoted to zero-energy (i.e. thermal) depositions in the case of clusters has demonstrated that implantation and surface alloying may take place even at $E_i = 0$, depending on the orientation of the substrate and the size of the cluster.¹⁴

Our calculated average value for the total cross section is in good agreement with the experimental data for E_{i2} , while it is significantly lower than the measured one in the case of E_{i1} .² This behavior was already observed in an earlier study of the collisions of Ag₇ on Pd(100)¹¹ and confirms the general tendency of the EAM potentials to yield structures highly compact for impact energies close or inferior to the cluster cohesive energy. As discussed in ref 6 this picture amounts to underestimating the stiffness of the substrate, by giving rise to deposited clusters that wet the substrate upon collision, more than dissociating on it, provided the impact energy is sufficiently low. However, we note that the trends observed in our calculations on Ag₁₉/Pd(100) are more realistic than those obtained in the case of the energetic deposition of the smaller cluster Ag₇. This confirms the semiquantitative character of our approach, which becomes, as expected, more reliable for increasing cluster size.

4. Conclusions

By using a description of the interatomic forces based on *n*-body potentials, we have characterized, at the atomic scale and for times representative of a collision process at low temperatures, the impact of the cluster Ag₁₉ on the Pd(100) substrate. The following conclusions are worth pointing out. On one hand, we have shown that when the collision energies involved are not higher than ~5 eV/atom, the crystalline structure of the substrate is not altered by significant damage, as found by examining the equilibrium morphology attained after a few picoseconds. The final cluster structure is composed of atoms moderately dispersed on the substrate or implanted on it.

On the other hand, this does not necessarily mean that the interface thereby created can reproduce the same conditions of stability and phase separation that are obtained by depositing, via thermal evaporation, atoms on the substrate. Indeed, the kinetics of the collision process induces, even at low impact energies, irreversible modifications of the chemical composition in the upper layers of the adsorbate–substrate system. Our results provide useful indications to experimentalists working in the area of cluster deposition on surfaces, at least in the range of temperatures corresponding to thermally frozen atomic mobility.

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