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Collisional dynamics of Ag_{19} on Pd(100): a molecular dynamics study

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Abstract. By means of molecular dynamics simulations based on realistic n-body potentials we investigate structural and dynamical features inherent to the energetic collision of a silver cluster (Ag_{19}) on the Pd(100) substrate. Both the system and the impact energy (E_i = 95 eV) adopted have been chosen to parallel an experimental study of size selected Ag cluster deposition on Pd(100). Our results indicate that the experimental cross section obtained via thermal energy atom scattering at the same collision energy is well reproduced by the simulations.The modeling allows to rationalize the collision outcome in terms of defect production and cluster atoms implantation. The adsorbed structures have an heterogenous nature and are mostly two-dimensional.

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I Introduction

Cluster deposition and growth on solid surfaces are intimately related. The first approach allows, when combined with moderately low impact energies, to control the fabrication of adlayers made of peculiar structural units. These can give rise to adsorbed films displaying unique properties, which can be tailored by changing the nature of the systems involved and the accessible experimental parameters such as temperature and coverage. In this respect, size selection and "soft landing" of clusters are a viable alternative to traditional techniques of surface growth, provided the adsorption process and the thermodynamic conditions preserve to a large extent the structural nature of the adsorbed nanostructures. Recently, a series of experiments of size selection and cluster deposition have been performed on the system Ag_n^+/Pd(100) [1, 2] by using thermal energy atom scattering (TEAS). Three colliding systems have been investigated (Ag_1^+, Ag_7^+, Ag_{19}^+) for impact energies equal to E_{i1} = 20 eV and E_{i2} = 95 eV and in the range of temperature 80 K$< T <$ 400 K. In [1, 2], an indirect analysis of surface morphology and dynamical formation of adsorbed islands has been performed in terms of the cluster cross section for diffuse scattering. This quantity is obtained from the attenuation of the helium specular intensity. The information extracted from the data of [1, 2] on the degree of defect production, implantation and cluster fragmentation are consistent with the existence of different regimes, related to the amount of colliding energy per atom, varying from $\sim$ 1 eV/atom (Ag_{19}^+, E_{i1} = 20 eV) to 95 eV (Ag_1^+,E_{i2} = 95 eV).

Molecular dynamics simulations and collision-adapted embedded atom method potentials have proved useful to describe microscopic details of the deposition process [3–12]. At low temperatures this approach is ideally suited to quantify the amount of structural modification induced on both the cluster and the substrate by the impact. Indeed, since relevant mobility is suppressed by kinetic constraints, the time interval spanned by the simulations (a few ps) becomes adequate to describe the relaxation process which follows the collision. The results recently obtained in the case of Ag_1^+ [12] and Ag_7^+ [11] can be summarized as follows. Simulation and experiments are in good agreement when Ag atoms collide at energies E_{i1} = 20 eV and E_{i2} = 95 eV on the Pd(100) substrate. Indeed, for both impact energies the TEAS values of the cross sections measured at T = 80 K in the case of Ag_1^+ on Pd(100) are very similar to those calculated, i.e. Σ_{exp} = 24.9 $\sigma_{Pd(100)}$, Σ = 32 $\sigma_{Pd(100)}$ for E_{i1}, Σ_{exp} = 53 $\sigma_{Pd(100)}$, Σ = 61.2 $\sigma_{Pd(100)}$ for E_{i2}. Here the cross sections Σ are given in units of the surface unit cell $\sigma_{Pd(100)}$ = 7.56Å^2 (see [13]). It should be recalled that the average classical cross section can be obtained from the geometrical overlap of simple cross sections centered at each defect on the surface (adatom, substitutional impurity, vacancy) [14]. These latter are easily quantified at the end of the simulations, which are performed consistently with the requirement of zero initial and final temperature of the whole system, i.e. the collision begins with both cluster and substrate fully relaxed and mutually isolated and ends when the positions in the whole system do not show appreciable changes upon further integration of the equations of motion. In the case of Ag_7 the cross sections extracted from the calculations agree with the experimental ones only for E_{i2} = 95 eV, thereby indicating a possible deficiency of the modeling to correctly reproduce cluster fragmentation when the impact energies are lower than $\sim$ 10 eV/atom. In the simulations the deposited clusters are neutral, a choice that appears legitimate in view of the fact that in the experimen-

tal setup the size selected charged clusters are neutralized just after the impact.

In this paper we pursue the numerical investigations undertaken in connection with the "soft landing" experiments described in [1, 2] by focusing on the collisional dynamics of the Ag_{19}/Pd(100) system. As a part of a larger study which is in progress and involves not only the consideration of different impact energies but also the inclusion of temperature effects in the behavior of the cross sections, we present here results for the impact of Ag_{19} carrying an initial energy E_i equal to 95 eV. Our purpose is twofold. On the one hand, we are interested in characterizing the processes of atomic rearrangement, defect formation and implantation, in analogy with the analysis of [11, 12]. On the other hand, our calculated cross section for E_i = 5 eV/atom will allow us to check and better define the lower bound of reliability of the atomic-scale description with respect to the values of the impact energy.

II Model and computations

In our simulations the embedded atom (EAM) potentials of [15] have been modified to make them more appropriate to model energetic collisions. To this purpose a Molière potential [16] is adopted at short distances (up to 0.9 Å) in the repulsive two body part, while the origanl EAM otential is restored, via a matching polynomial, at distances beyond 1.9 Å. The Ag–Ag repulsive potential is further modified by adding an exponential, rapidly decreasing interaction described by parameters fitted to the cohesive energy and average equilibrium distance of the Ag_7 ground state structure. This latter has been obtained via quantum chemical configuration-interaction calculations as reported in [17]. It is worth recalling that the EAM scheme is not suitable to calculate accurately the structure of isolated clusters, because of its intrinsic inadequacy to treat undercoordinated systems. In the context of cluster-substrate collision the EAM approach appears to be somewhat more legitimate, and it has been widely used in the literature [3–12].

Our system consists of a single slab made of seven layers, modeling the (001) surface of Pd and submitted to periodic boundary conditions. The surface Wigner-Seitz cell thereby constructed is defined by the vectors $\mathbf{a}_x$ = 10a[100], $\mathbf{a}_y$ = 10a[010], where **a** is the Pd lattice constant. This leads to a unit cell containing 1400 Pd atoms. At time t = 0 the Ag_{19} cluster begins to move down from its initial position, corresponding to a Z coordinate of the center of mass lying at $\sim$ 15 Å above the uppermost Pd(100) plane. As initial arrangement for the Ag_{19} cluster we took a six-capped icosahedral structure. A set of initial configurations for the collision process is then produced by running repeated MD annealing cycles at temperatures ranging in between T = 1000 K and T = 1500 K. Before each simulation of the collision, both the cluster and the slab are relaxed to T = 0 K. As a consequence, initial cluster structures are highly disordered and bear little resemblance to the one imposed at the beginning.

The impact of Ag_{19} on Pd(100) occurs with a total kinetic energy along the [001] direction equal to E_i = 95 eV. An angle θ = 15° with respect to the surface normal is introduced to mimic the experimental situation of [1]. The system dissipates the incoming kinetic energy via a dynamical thermostat which act on the bottom layer only. This is implemented by resetting to zero the velocities of a given atom whenever the scalar product between its forces and velocities is negative. This constraint does not hamper a local increase of temperature in the impact region but prevents the system from globally heating up due to its limited size. The collision of the cluster with the surface is repeated 50 times, each corresponding to different initial cluster configurations and locations with respect to the substrate. The cluster-substrate interaction is followed during 15 ps, a temporal interval largely sufficient to describe the structural evolution toward the stable configuration at T = 0 K.

III Results

A typical collision of the Ag cluster on the Pd(100) substrate is illustrated in Fig. 1a, Fig. 2a and Fig. 1b, Fig. 2b, projected on the (100) plane and on the surface (001) plane respectively. In this particular example, the cluster veloc-

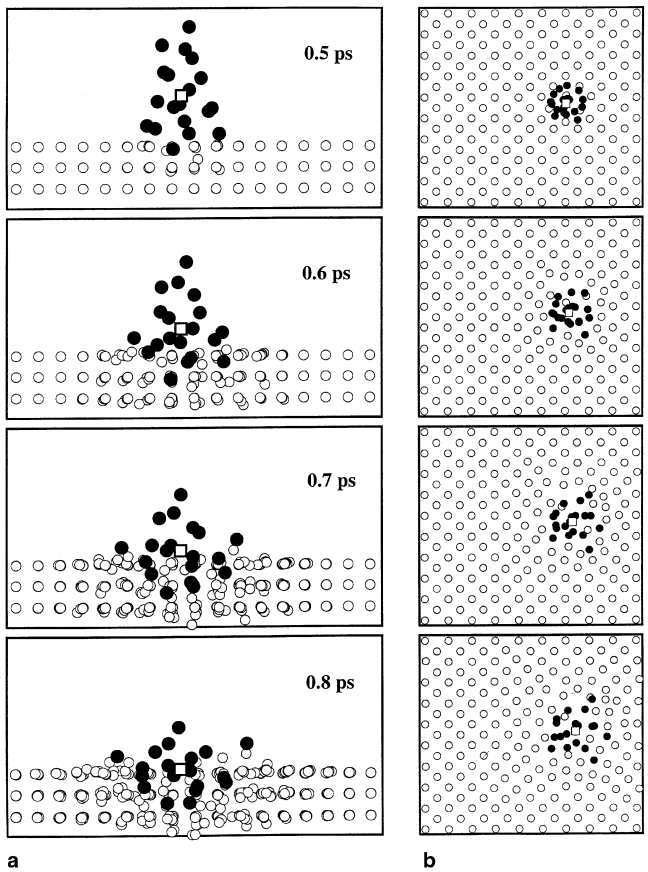

Fig. 1a, b. Early stages of the impact of Ag_{19} on Pd(10). An angle of incidence of 15° is introduced with respect to the surface normal. The total kinetic energy is 95 eV in the perpendicular direction. *Filled circles* represent Ag atoms and *empty circles* represent Pd atoms. The *open square* is the position of the cluster center of mass. In **a** three layers of Pd atoms are shown, and the coordinates are projected onto the (100) plane. In **b** the coordinates are projected onto the surface (001) plane and only the uppermost original Pd atoms are shown

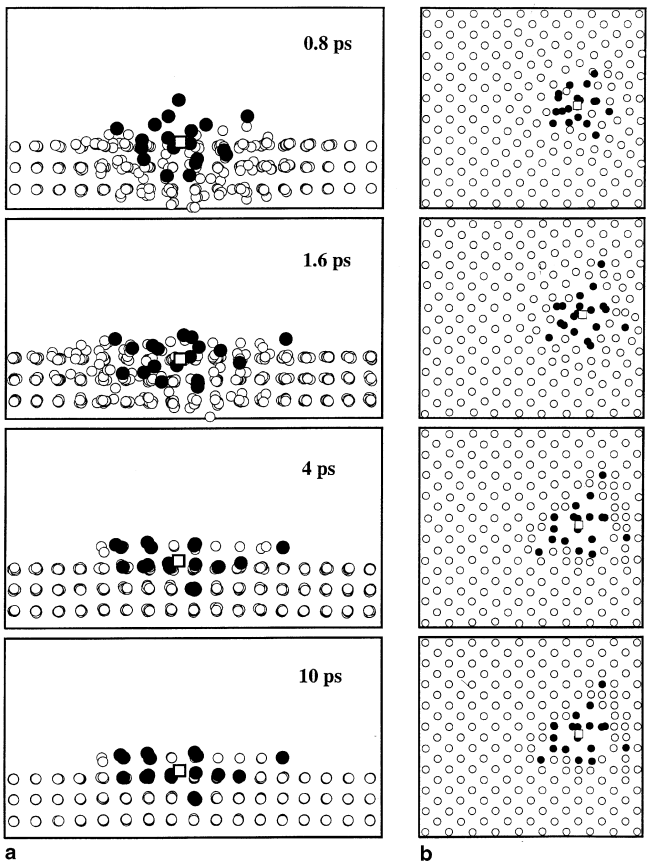

Fig. 2a, b. Late stages of the impact of Ag_{19} on Pd(100). The symbols are the same as in Fig. 1

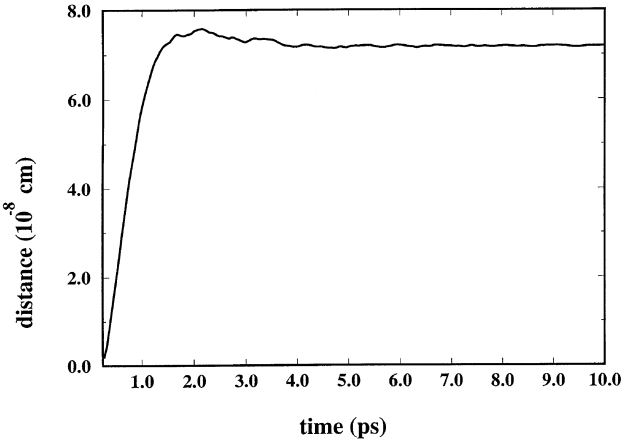

Fig. 3. Temporal evolution of the average distance R_{cl} (calculated with respect to the surface (001) plane) between the positions of the cluster atoms at time t and their positions at time $t = 0$. We recall that at time $t = 0$ the Ag_{19} cluster begins to move down from its inital position, corresponding to a Z coordinate of the center of mass lying at ~ 15 Å above the uppermost Pd(100)plane

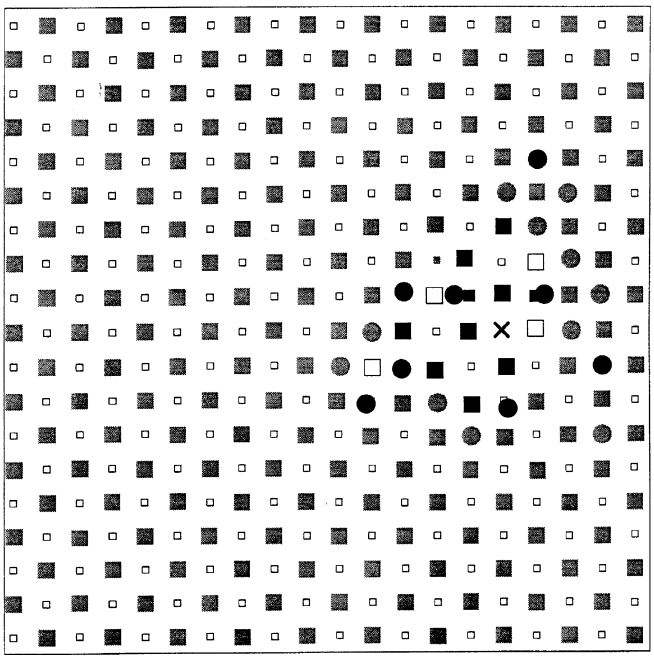

Fig. 4. Final location of cluster and substrate atoms, in the collision illustrated in the text. *Filled symbols*: Ag atoms. *Grey symbols*: Pd atoms originally in the first layer. *White symbols*: Pd atoms originally in the second layer. For both Ag and Pd, circles represent adatoms, *big squares* represent atoms in the first layer, *small squares* atoms in the second layer. The cross corresponds to the position of the only Pd atom which moved up from the third to the second layer

ity is directed along the [010] direction with respect to the (001) surface plane. Within the first picosecond the cluster undergoes an abrupt transition from a three-dimensional to a two-dimensional arrangement, giving rise to important intermixing, especially in the first layer. The spreading out of the incoming Ag atoms on the surface (001) plane can be easily observed by following the sequence of snapshots in Figs. 1b and 2b, where only the cluster atoms and those originally belonging to the uppermost layer are represented. The loss of any reminiscent three-dimensional character which occurs in between $t = 0.8$ ps and $t = 1.6$ ps (see the two upper snapshots in Fig. 2) proves that a non-negligible fraction of the incoming energy is able to promote in-plane movements. This leads to a highly non compact form of the adsorbate, in agreement with the analysis of [2]. Negligeable changes are detected for times larger than 4 ps, as shown in Fig. 2.

A further insight into the different time scales inherent to the collision process is given in Fig. 3, where we represent the time evolution of the average distance R_{cl} (calculated with respect to the surface (001) plane) between the cluster atomic positions at time t and their values at the beginning of the simulation. The enhanced mobility which accompanies the disruption of the three dimensional cluster structure is reflected in a steep increase of R_{cl} over the first 2 ps, corresponding to a diffusion coefficient as high as $5 \cdot 10^{-4}$ cm^2/s. For times larger than ~ 2 ps, R_{cl} decreases slightly, to attain a plateau value at $t \sim 5$ ps.

In Fig. 4 the morphology of the substrate resulting from the impact is elucidated in terms of substitutional defects. The adcluster is formed by 8 Ag atoms and 11 Pd atoms residing initially in the first layer, while 8 of the remaining Ag atoms are found in the first and 3 in the second layer respectively. No vacancies are formed in this particular collision.

The average occurrences of Ag atoms, implanted or adsorbed on the Pd(100) substrate and Pd substitutional impu-

Table 1. Average number of occurrences of Ag and Pd atoms on the higher layers, average number of vacancies and total cross section Σ_{cal}, this latter given in units of the surface unit cell $\sigma_{Pd(100)} = 7.56\,Å^2$. The calculated values of the cross section have been obtained under the hypothesis of geometrical overlap of atomic cross sections centered at each defect on the surface, as discussed in [14]. All values are obtained over 50 collisions at impact energy $E_i = 5$ eV/atom. The number of vacancies refer to the first (uppermost) layer of the substrate. Σ_{exp} is the experimental cross section

Ag atoms lying above the adlayer	0.11
Ag atoms found to form the adlayer	7.54
Ag in the first layer	7.30
Ag in the second layer	3.65
Ag in the third layer	0.41
Pd atoms found to form the adlayer	11.84
Pd atoms lying above the adlayer	0.08
Vacancies	0.60
Σ_{cal}	$(133 \pm 5)\,\sigma_{Pd(100)}$
Σ_{exp}	$(137 \pm 13)\,\sigma_{Pd(100)}$

rities and vacancies is given in Table 1, in terms of averages calculated over 50 different collisions. As a first observation, it is worth noticing that the adsorbates created by the impact have a predominant two-dimensional character, as proved by the limited number of events featuring single Ag or Pd atoms which ended up on the top of the adlayer. The average number of vacancies, which are found essentially only in the first layer is consistent (see Table 1) with the difference between the number of Pd substitutional impurities and the number of Ag implanted atoms. Moreover we found no interstitials, in agreement with the results of [4] where the behavior of Cu, Al and Ni cluster/substrate systems was explored for a large set of impact energies.

Our calculated average value for the total cross section, $\Sigma_{cal} = (133 \pm 5)\,\sigma_{Pd(100)}$ reported also in Table 1 turn out to be in excellent agreement with the experimental finding of [2], $\Sigma_{exp} = (137 \pm 13)\,\sigma_{Pd(100)}$. This result is particularly useful to better define the boundaries of reliability of the atomistic modeling adopted in this work, at least with respect to the possibility of correctly describing the structural changes brought about by the impact. In this work, we showed that our simulations of the impact of A_{19} on Pd(100) via modified embedded atom method potentials provide a description of the surface morphology which compares realistically with experiments for collisions energies as low as 5 eV/atom. In view of the results of [11] indicating an opposite behavior in the case of $E_1 \sim 3$ eV/atom and a smaller cluster, it would be worthwile to further elucidate the issue of model reliability, which is likely to be related to both the impact energies and the size of the clusters involved. Work is in progress along these lines. Furthermore, we are currently investigating the high temperature behavior of the collision produced Ag/Pd(100) system, in terms of most favorable diffusion paths which can lead to the more compact arrangements observed by TEAS.

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