Fragmentation and recombination of copper dimers deposited on an Ar film

M. Ratner, W. Harbich, and S. Fedrigo

Institut de Physique Expérimentale, Ecole Polytechnique Fédérale de Lausanne, PHB-Ecublens, CH-1015 Lausanne, Switzerland

The collision between a copper dimer and an Ar film is investigated by molecular-dynamics simulations. A dimer fragmentation rate of 24% is found for an impact kinetic energy of 25 eV per atom, in agreement with previous experimental results. Temporary dissociation of the dimer followed by a reaggregation is observed in 14% of the cases. The collision induces a fast superheating of the Ar film around the impact point followed by a liquefaction. The cooling rate of the copper dimer is found to be one order lower than the cooling rate of the Ar film in the impact area. [S0163-1829(99)01239-4]

I. INTRODUCTION

Basic and technological interest in the physical properties of nanostructured materials has stimulated the development of many imaginative techniques in order to produce such materials. Among them, the deposition of size-controlled particles on a well-defined surface has been targeted by several groups.[1] The successful deposition of small size selected metal clusters into weakly interacting supports with low fragmentation gave access to new cluster information via analysis techniques which are today in general impossible to apply in gas-phase experiments because of particle density arguments. For example, Raman spectroscopy of Si_6 and Si_7 clusters embedded in N_2 matrices allowed the determination of their geometrical structures.[2] However, the deposition of small particles on a bare metal surface at hyperthermal kinetic energies E_k leads to strong fragmentation and implantation.[3] Recently it has been shown experimentally that the addition of a thin Ar layer on top of the surface, as suggested by previous molecular-dynamic simulations,[4] allowed to deposit small clusters on a metal surface without any damage for an impact energy E_k of 2.8 eV per atom.[5] The experimental fragmentation rate of Ag_2 when colliding with a rare gas surface was found to be unexpectedly low for kinetic energies much higher than the dimer binding energy.[6] For example, more than 30% of silver dimers were still found intact after being deposited at 100 eV of kinetic energy in Ar films. It has been suggested that this could be partially explained considering reaggregation due to the high diffusivity of the fragments in the locally overheated rare-gas film.[6]

In this paper we report the results of a molecular-dynamic study of a copper dimer impact with an Ar surface at kinetic energies per atom E_k ranging between 1 and 30 eV. In the case of $E_k = 25$ eV the trajectories are obtained for 23 different initial nonequivalent geometrical configurations allowing an estimation of the fragmentation rate. Cu_2 has been chosen in place of Ag_2 because, to our knowledge, no workable Ag-Ar potential exists, while a Cu-Ar pair potential has been recently proposed and used.[7] Based on the fact that the binding energies of Cu_2 and Ag_2 are similar, respectively, 2.08 eV (Ref. 8) and 1.66 eV,[9] we assume that the fragmentation rates obtained from the simulation can be compared to the Ag_2 experimental fragmentation rate. The simulation con-

firms that the proposed fragmentation-recombination process can happen. However, the low occurrence of this process indicates that it is not likely the main explanation for the low observed fragmentation.

II. MODEL

The system is modeled by two-body potentials. The Ar-Ar Lennard-Jones potential parameters are $\varepsilon = 0.0104$ eV and $\sigma = 3.4$ Å. The pairwise interaction potential between Cu and Ar is described by the analytical expression given by Cheng and Landmann.[7] The four parameters modified Morse function,[10,11] fitted on the experimental equilibrium, vibrational, and rotational constants $D_e = 2.08$ eV,[8] $r_e = 2.219$ Å, $\omega_e = 266.5$ cm^{-1}, $\omega_e x_e = 1.04$ cm^{-1}, $B_e = 0.1088$ cm^{-1}, $\alpha_e = 6.2 \times 10^{-4}$ cm^{-1},[12] represents the Cu-Cu energy. The cutoff distances are 8.7 Å for the Ar-Ar interaction and 12.3 Å for the Ar-Cu and Cu-Cu interactions. The Ar slab is made of 20^3 unit cells arranged in a cubic box with $X, Y,$ and Z directions along the [100], [010], and [001] crystallographic axes, respectively. Periodic boundary conditions are implemented only in the X and Y directions. The bottom surface interacts with an additional three-layer-thick frozen Ar slab. Equation of motions are solved via the velocity version of the Verlet algorithm[13] in the microcanonical ensemble with a time step $dt = 1.4 \times 10^{-15}$ s. dt is reduced by a factor of 10 during the first picoseconds when high energies and velocities are involved. Before starting the collision, the slab is relaxed in order to reach a temperature of 10 K, while Cu_2 is at the equilibrium with no rotation.

In all cases the Cu_2 initial speed is parallel to the Z direction. The initial geometrical configuration is described by four variables. The projection of the Cu_2 center of mass on the Ar surface gives the impact position (X,Y) and (θ,φ) specify the Cu_2 ordination (θ versus the Z axis, φ versus the X axis). The collision at $E_k = 25$ eV is simulated for several different initial geometrical configurations. In that case the impact positions studied are the head on impact with an Ar atom (case A) and an impact between two nearest neighbors (case B). In case A, (θ,φ) cover the sphere by 30° increments while in case B the increment is taken as 30° for θ and 22.5° for φ. Fragmentation rates are obtained by averaging properly on (θ,φ).
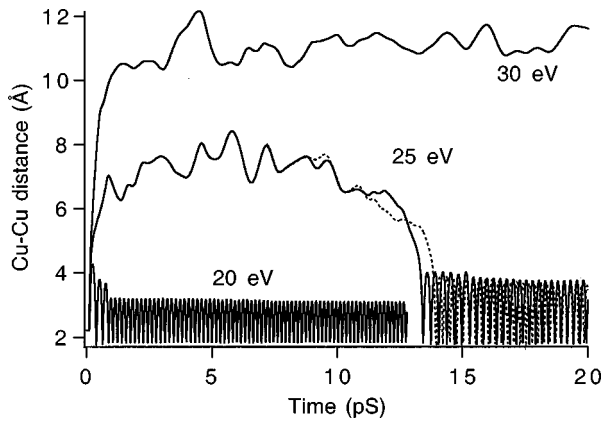
FIG. 1. MD simulations trajectories of the Cu_2 interatomic distance after the impact on an Ar film for three different Cu_2 kinetic energies per atom, $E_k=20$, 25, and 30 eV. The geometrical initial conditions are $\theta=90°$, $\varphi=0°$, and head-on impact. At $E_k=25$ eV the continuous line describes a trajectory obtained for an isolated system while the dotted line trajectory is the result of a simulation with the boundaries of the Ar film slab fixed at 10 K.

III. RESULTS AND DISCUSSION

Figure 1 displays the evolution of the Cu-Cu distance after collisions at $E_k=20$, 25, and 30 eV, case A with $\theta=90°$, $\varphi=0°$, illustrating the three possible outcomes of the process. At $E_k=20$ eV, the copper dimer stays bounded as shown by its oscillating trajectory. At $E_k=25$ eV, dissociation occurs promptly after the impact, the Cu-Cu distance stays larger than 6 Å during nearly 13 ps, then the two fragments recombine, as revealed by the vibrating behavior of the Cu-Cu distance. At $E_k=30$ eV, the dimer fragments and no reaggregation is observed during the simulated time of 30 ps. The Cu-Cu distance stays larger than 10 Å. We cannot strictly exclude the possibility of a reaggregation after the simulation time. However, we believe that after 30 ps the Cu atoms are practically frozen in the film and therefore they have very little chance to recombine (see the discussion concerning the Ar film temperature).

In order to study the effect of the boundary conditions, we have also calculated the trajectory of the copper dimer at $E_k=5$ eV with identical initial geometrical conditions, but maintaining the temperature of the three outer Ar layers at 10 K. Technically, the atom positions and velocities are set every 50 time steps, respectively, to the resting positions and to a random speed corresponding to 10 K of kinetic energy (velocity scaling). Although this is not the most realistic model, it has the merit to mimic the extreme case of perfect 10 K boundaries. The resulting trajectory (also shown in Fig. 1) is very similar to the case of the isolated system. It indicates that the Ar cube size is large enough to avoid the problem of the heat transfer through the boundaries for simulation times in the order of 20 ps. It should be noted that the addition of 50 eV (the impact energy) to the whole system corresponds to an increase of 1.56 meV per Ar atom which is equivalent to only 2% of the cohesive energy.

Another case of the reaggregation process is exemplified in Fig. 2 ($E_k=25$ eV, head on impact, $\theta=60°$ and $\varphi=0°$). The Cu-Cu distance stays larger than 10 Å during the first 5 ps, decreases to around 6.5Å before ending up to reaggregation after 20 ps. The fact that the two copper atoms
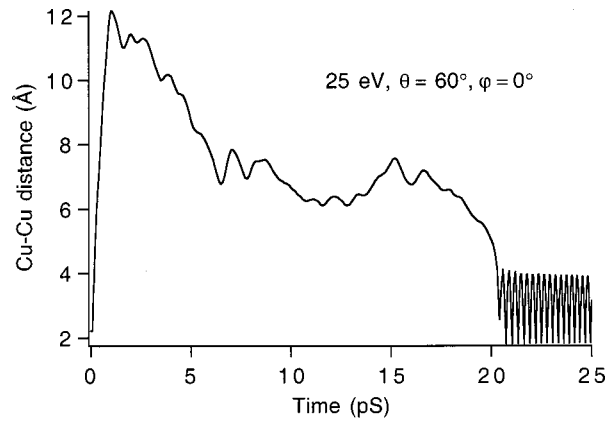

FIG. 2. MD simulations trajectory of the Cu_2 interatomic distance after the impact on an Ar film at $E_k=25$ eV with the geometrical initial conditions $\theta=60°$, $\varphi=0°$, and head-on impact.

separated by 10 Å recombine in this example while they stay apart in the case discussed in Fig. 1 (trajectory obtained for $E_k=30$ eV) suggests that the reaggregation observed is mainly the consequence of Cu atom diffusion in the ''liquid'' Ar in the impact area rather than due to the residual Cu-Cu attractive force.

As mentioned above, at $E_k=25$ eV the simulation was done for 23 different initial configurations which corresponds to 72 different sets of (θ,φ). Taking into account the adequate weight factor (Jacobian), a total fragmentation yield of approximately 24% can be extracted from this calculation (28% and 20% in the A and B cases, respectively). The experimental fragmentation rate of Ag_2 when deposited in Ar at the same energy is 27% $\pm$ 3%,[6] slightly higher than the value deduced from the calculation. Although this difference could be ascribed to the difference in binding energy and (or) in atomic mass between Cu_2 and Ag_2, its confirmation would require a larger number of simulations with different initial configurations.

The existence of the dissociation-aggregation process proposed earlier is clearly demonstrated; however, it is not the dominant process responsible for the low fragmentation rate observed. From the whole set of calculations done for $E_k=25$ eV we found that nearly 14% of the copper dimers undergo this process, meaning that among the observed soft-landing cases less than a fifth of the Cu_2 deposited experience the fragmentation recombination.

Using the same potentials, we have also studied the collision of Cu_2 with one Ar atom for a large number of different (θ,φ) angles and a head-on configuration (null impact parameter). The Cu_2 kinetic energy was 50 eV ($E_k=25$ eV) referred to the initially immobile Ar atom. A fragmentation rate higher than 95% is found, independent of whether the Ar atom is allowed to move or not. It clearly confirms that the dense Ar environment in the impact area helps efficiently to confine the two Cu atoms. The ''friction'' applied by the Ar atoms on a particle moving within the Ar slab results in a strong deceleration of the particle. As an example a Cu_2 cluster colliding with an Ar film at $E_k=25$ eV penetrates typically less than 10 Å inside the film before being stopped. The deceleration, which applies to the Cu atoms after the impact when they tend to break their bond by having opposite trajectories, prevents the distance sepa-
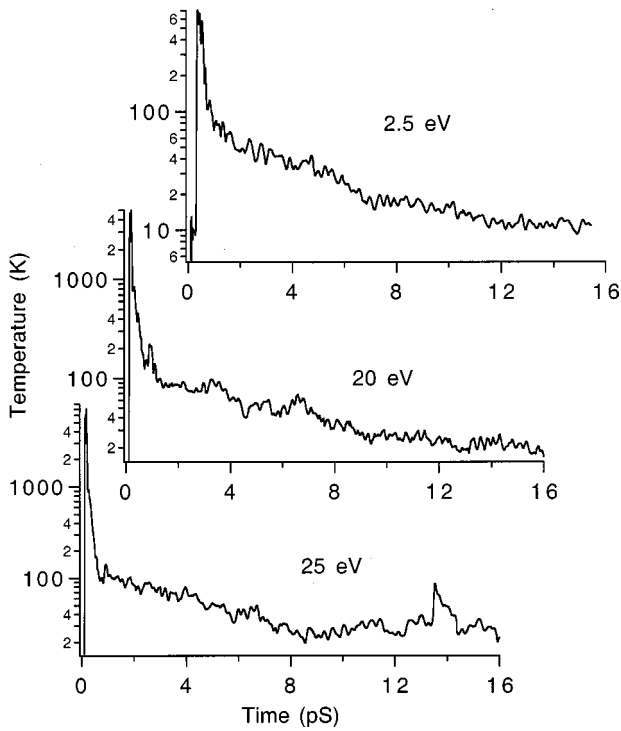
FIG. 3. Temperature of an Ar film during the impact of a copper dimer on this film. The calculated temperatures are presented for three cases of collision energy, $E_k=2.5$, 25, and 30 eV. The temperature in the impact area is estimated by averaging the kinetic energy of the film atoms inside a sphere centered on the Cu_2 center of gravity.
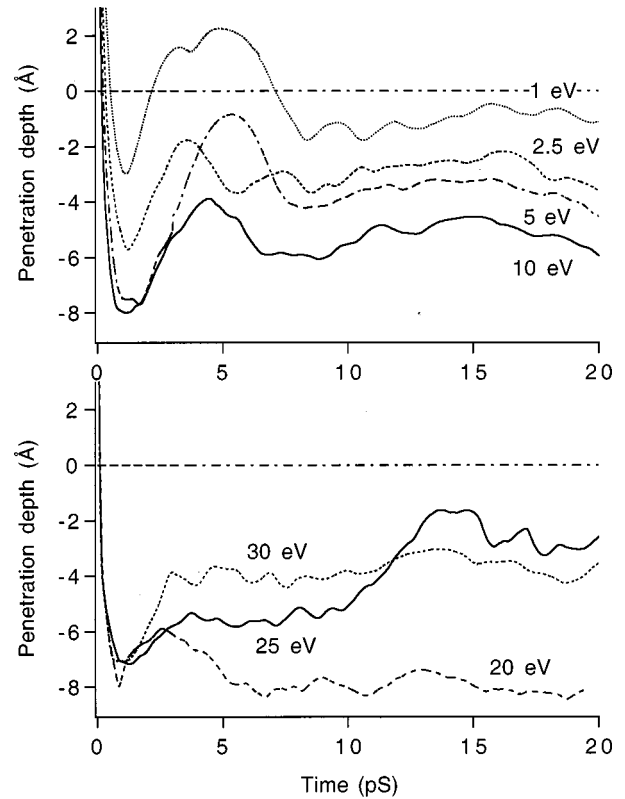

FIG. 4. Penetration depth evolution of a copper dimer into an Ar film when colliding with it. The Cu_2 center of gravity trajectories are calculated for seven different collision energies ranging from 1 to 30 eV per copper atom, initial conditions remaining fixed to $\theta = 90°$, $\varphi = 0°$, and head-on impact.

rating the two Cu fragments to become too large. This process qualitatively explains the low fragmentation observed. It can be included in the large family of the so-called cage effects that were largely studied and used.[14,15]

We define the film temperature T_m near the copper dimer by averaging the kinetic energy of the nearly 50 Ar atoms contained in a 16-Å-diam sphere centered on the Cu_2 center of gravity. Figure 3 displays the evolution of T_m for $E_k = 2.5$, 20, and 25 eV, for a copper dimer initial geometrical configuration of $\theta = 90°$, $\varphi = 0°$ (case A). The evolution of T_m with time can be divided into two regimes; a transient regime comprising very fast heating (in the 0.1-ps scale) followed by fast cooling (typically 1 ps), and then a long-time temperature decay with a time constant of approximately 15 ps. We first consider the case $E_k = 30$ eV. The Ar temperature reaches nearly 5000 K and decreases down to 100 K in less than 1 ps, before starting the long-time decay. Figure 1 shows the corresponding dimer trajectory from which the vibrational energy can be extracted. It raises up to 2 eV and then decreases to 1.1 eV at the beginning of the slow decay. Clearly the equivalent dimer temperature is at least one order higher than T_m at the same time. During the long-time temperature decay (after 1 ps), T_m decreases from 100 to 25 K while approximately 10% of the Cu_2 vibrational energy has been removed. This indicates that the dimer cooling by the surrounding Ar is poorly efficient. In fact, the dimer cooling time constant approaches 200 ps, more than one order larger than the matrix cooling time constant. The evolution of T_m in the two other cases presented in Fig. 3 as well as in the other calculations (similar initial geometrical configuration, E_k

$=1$, 5, 10, and 30 eV) follows a similar trend. At $E_k = 25$ eV, the sudden 50 K temperature increase of T_m nearly 14 ps after the impact is the consequence of the energy gain by the Ar film due to the Cu_2 aggregation (see Fig. 1).

To our knowledge, only Cheng and Landmann considered theoretically the impact of a metal cluster with a rare-gas film.[7] They studied the collision between a copper cluster made of 143 atoms and an Ar liquid film. The cluster temperature and trajectory are given for $E_k = 1.3$ and 5.3 eV. No cluster fragmentation has been revealed by the simulations. The results show that the cluster temperature grows during the deceleration and reaches roughly a maximum when the particle stops. Then the cluster temperature starts to decrease. However, the cluster temperature decay exhibits only one time constant close to 10 ps, which is one order faster than what we have observed in our simulation. This difference in cooling rate can be attributed to the drastic difference in the number of vibrational modes and in the vibrational energies between Cu_2 and Cu_{147}. Clearly the Cu_2 mode with an energy above 200 cm^{-1} hardly couples with the low-energy Ar film modes under 70 cm^{-1}.[16] In opposite, a simple harmonic model indicates that Cu_{147} offers several low-frequency modes in the 50-cm^{-1} range.

The fast initial temperature decay of Cu_2 shown by our simulation (Fig. 1, remark the three first Cu_2 vibrations for $E_k = 20$ eV) as well as the fast initial matrice temperature decay is more difficult to explain. A similar behavior has been observed by Cheng and Landmann when they simu-

lated the impact of Cu_{147} with a bare copper surface and (but less pronounced) with a Xe film with $E_k = 1.3$ and 5.3 eV.[7] When the cluster collides with the Cu surface, its temperature first quickly decays with a time constant of around 0.5 ps, and then undergoes a long-time decay (time constant above 10 ps). In the case of a Xe surface the respective time constants are approximately 25 and 120 ps. The first fast cooling was interpreted as a rapid energy transfer from kinetic to potential energy, the cluster being initially in a superheated state, then consuming the latent heat and ending up in a liquid state. This explanation, which clearly does not hold for an isolated dimer, can be applied to the system formed by the hot film region around the impact point and the copper dimer inside. The origin of the short-time temperature decay of this system is the superheated to liquid-state transformation. Here again the heat transfer between the host and the Ar film is not efficient. During the first picosecond, the Ar temperature decreases by a factor 50 while the Cu_2 energy is reduced by less than a factor 2.

The penetration depth d (Z is the coordinate of the center of gravity) of the dimer into the Ar surface relative to the surface initial position is shown in Fig. 4 for various kinetic energies (head on configuration, $\theta = 90°$, $\varphi = 0°$). The dimer is decelerated by the Ar film until the speed in the Z direction (perpendicularly to the surface) reaches zero. Then the dimer show a reflecting behavior during the next 3 ps before entering in a diffusion regime. The maximum penetration depth (attained nearly after 1.5 ps) increases with the initial kinetic energy for E_k below 10 eV. It stays close to 7 Å for E_k between 20 and 30 eV. The local expansion of the film in the Z direction, which is lower than 2 Å after 20 ps for the highest kinetic energy case is a minor effect relative to the evolution of the penetration depth.

IV. SUMMARY AND CONCLUSIONS

The study of the impact between a Cu_2 molecule and an Ar film at 50 eV of kinetic energy by molecular-dynamics (MD) simulations indicates a fragmentation rate of nearly 24%. This value agrees with the experimental fragmentation rates reported previously for Ag_2 deposition. The simulation shows that for a few cases of initial geometrical configurations, the dimer first fragments, the two copper atoms stay separated by distance as large as 10 Å and then recombine to form a dimer. The occurrence of this effect corresponds to roughly 14% of all the cases. The rather low fragmentation rate observed experimentally when metal dimers are deposited at high kinetic energies in van der Waals films is mainly due to the confining of the dimer atoms by the dense surrounding host through frictional forces during the deceleration of the dimer within the film.

The evolution of the dimer energy as well as the Ar temperature in the impact area shows that both are rapidly superheated before being liquefied in less than 1 ps. Then the dimer and Ar temperature decay much more slowly. In both cooling regimes the heat transfer between the dimer and the film is very poor. This is attributed mainly to the mismatch between the dimer vibrational energy and the solid Ar phonon energies.

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