THEORETICAL ASPECTS OF CLUSTER FORMATION BY keV BOMBARDMENT OF RARE-GAS SOLIDS

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The mechanism of energy dissipation in argon crystals bombarded by 100 and 500 eV Ar^+ has been examined using classical dynamics. The study indicates that very high yields may be expected and that large molecular Ar clusters, Ar_n, may form via recombination in the near surface region. The results are compared qualitatively to recent matrix-isolation SIMS experiments on a variety of inert-gas solids.

1. Introduction

Rare-gas solids provide unique matrices for trapping a variety of reactive atoms and molecules. In recent studies it has also been found that the secondary ion mass spectra (SIMS) of compounds stabilized in solid Ar, Kr and Xe yield important structural information about the isolated material [1–3]. In these experiments, the rare-gas solid is bombarded with a 0.5–5 keV primary ion, often Ar^+. The information about the matrix-isolated species is then obtained from the mass spectrum of the material ejected from the solid. The mechanism of energy dissipation of the primary ion and subsequent ejection of material has not been explored for rare-gas solids but has been investigated in detail for a variety of ion-bombarded metals such as Ni [4] and Cu [5] using well-established classical dynamics techniques. These techniques have also been employed to establish a generalized theory of the molecular cluster ejection process on chemically reacted metal surfaces [6,7]. It is not clear, however, whether these concepts are applicable to rare-gas solids where cohesive energies are more than an order of magnitude smaller.

The SIMS spectra of solid Ar is characterized by an intense Ar^+ peak and a variety of Ar_n^+ cluster ions [2]. The largest clusters are characterized by $n \leqslant 25$ as limited only by the mass range of the detector. Their relative intensities are found to decrease nearly exponentially with increasing n. In addition, the kinetic energy distribution of ejected Ar^+ ions is extremely narrow (0–12 eV) relative to those distributions found from metals [5]. It is important to understand these observations if matrix-isolation SIMS is to become a viable technique. In this work, then, we examine the mechanism of energy dissipation in ion-bombarded Ar crystals and compare the results of classical dynamics calculations to those obtained on metals.

The results show that very large yields may be expected and that in contrast to metals, a significant fraction of the atoms may originate from the second or third layer. Large clusters of Ar_n have been observed in the calculations. The atoms in the cluster need not consist of atoms that were originally contiguous in the lattice, although many of them are ejected from highly localized regions of the solid. In general, we believe our model calculations yield a realistic picture of the energy dissipation in crystalline Ar and should aid in the interpretation of matrix-isolated SIMS spectra.

2. Description of the calculation

The basic scheme for computing the dynamics of

the bombarding particle and the Ar substrate has been described in a recent series of articles [4–7]. Briefly, the positions and momenta of all the particles are developed in time by integrating Hamilton's equations of motion. The final positions and momenta of the ejected particles can then be used to determine yields, energy and angle distributions, and possible cluster formation.

The infinite solid is modeled by a finite microcrystallite, in this case consisting of a face-centered-cubic array of Ar atoms. The size of the crystallite is chosen so that further increases in the number of atoms do not substantially alter the predicted observables. Because solid Ar has an extremely small heat of sublimation (0.08 eV), a crystallite of 7 layers with ≈180 atoms per layer (fig. 1a) (a total of 1265 atoms) is needed to contain the processes involved when a primary particle bombards the surface with only 100 eV. The calculation of one Ar impact on this crystal requires ≈50 times more computer time than a similar calculation on a 250 atom Ni microcrystallite. Due to this difficulty, only 21 Ar impacts have been determined for each set of calculations. This number is too small to produce statistically reliable quantitative results so our analysis is restricted to a mechanistic investigation of the ejection of Ar atoms and clusters. For all calculations, the Ar^+ ion is incident at an angle of 45° from the surface normal along a ⟨100⟩ azimuth of the (001) crystal face and is given a kinetic energy of 100 or 500 eV. For the latter case, the crystal is not large enough to contain all the action, although the calculations do allow for a qualitative indication of the effect of primary ion energy on the process.

Since Ar has a closed-shell electronic configura-

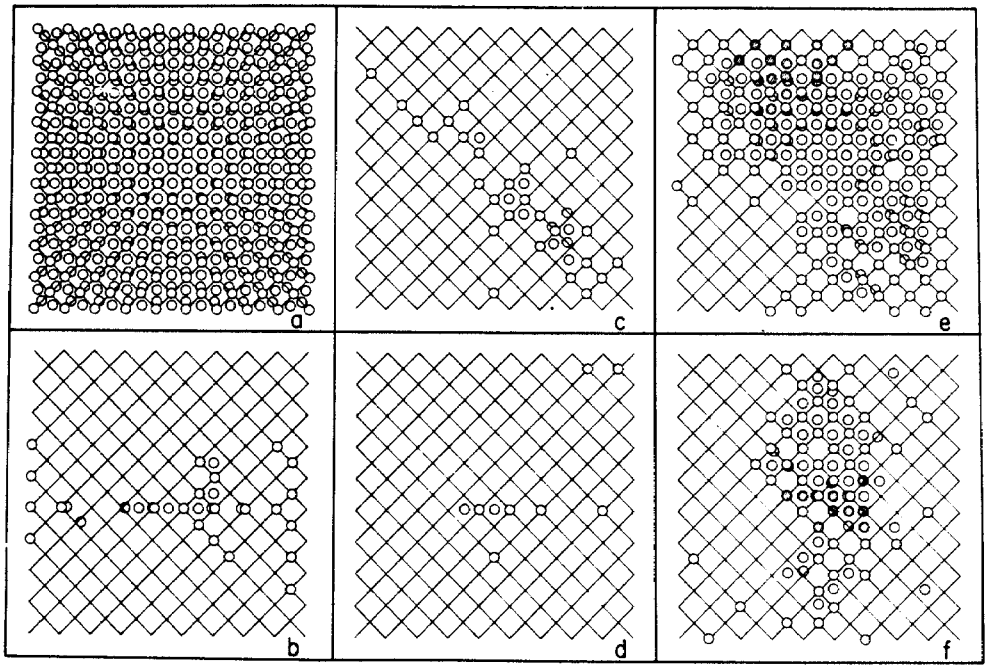

Fig. 1. View of crystal from above the surface. (a) Three layers of full crystal with slight perspective. The viewer is looking directly at the center of the crystal. The grid lines connect first-layer atoms only. Second-layer atoms are in the open spaces. Third-layer atoms peak out behind the first-layer ones and have grid lines crossing them. The primary ion is incident from the left at a polar angle of 45°. The primary ion impact points are near the center of the crystal. (b) Original positions of atoms that ejected from 500 eV ion impact along a plane of symmetry. A total of 37 atoms eject from this impact. In all cases only atoms that eject from the third layer of the crystal and above are shown. (c) Original positions of atoms that ejected from a 100 eV ion impact. A total of 43 atoms eject from this impact. (d) Same impact point as shown in (b) except that the primary ion has 100 eV of energy. A total of 10 atoms eject from this impact. (e) Original positions of atoms that eject from a 500 eV ion impact. The shaded atoms comprise an Ar_{25} cluster. A total of 250 atoms eject from this impact. (f) Original positions of atoms that eject from a 100 eV ion impact. The shaded atoms comprise an Ar_{12} cluster. A total of 98 atoms eject from this impact.

tion the interaction among the atoms in the solid can be reasonably approximated by a pairwise additive form [8]. For the short-range repulsive interaction a Born–Mayer or exponential function fit to values determined by ab initio electronic structure techniques [8,9] is used for the potential. This interaction has the form

$$V(R) = 3400 \exp(-3.27R), \quad R < 2.20 \text{ Å}, \qquad (1)$$

where R is the separation distance between two Ar atoms in Å and the potential $V(R)$ is in eV. Considerable effort has been expended to develop the long-range attractive interaction between two Ar atoms, with many different function forms and sets of parameters being tested [8]. Since the processes examined in this study involve collision energies from tenths to tens of eV, the differences among the various forms should not be as important as for the examination of extremely low-energy processes. Thus the Morse potential [10] has been chosen as follows:

$$V(R) = 0.0114 \exp[-1.425\,(R - 4.04)] \times \{\exp[-1.425(R - 4.04)] - 2\}, \quad 2.92 \leqslant R \leqslant 6.38 \text{ Å}, \qquad (2)$$

where the potential is given in eV. For R between 2.20 and 2.92 Å cubic spline is used to smoothly connect the two forms in eqs. (1) and (2). For R greater than 6.38 Å the potential is set equal to zero. The lattice constant of fcc Ar is 5.311 Å.

To check for the formation of clusters, the relative kinetic energy, T_r, plus potential energy, V, from eq. (2) for all pairs of atoms is calculated after the collision cascade has been terminated. If the total energy of the dimer

$$E_{\text{tot}}^{\text{dimer}} = T_r^{\text{dimer}} + V \qquad (3)$$

is negative, then the tested dimer is bound. For many of the impact points several bound dimers are detected. From these the possibility of linked or overlapping dimers is checked. If this condition is found, then

$$E_{\text{tot}}^{\text{cluster}} = T_r^{\text{cluster}} + \sum_{i=1}^{n-1} \sum_{j>i}^{n} V(R_{ij}), \qquad (4)$$

with n being the number of atoms in the cluster, is recalculated for all of the atoms in the linkage to evaluate the possibility of forming a cluster. As in the dimer analysis, if $E_{\text{tot}}^{\text{cluster}}$ for the atoms in the linkage is less than zero then this set of n atoms is considered to be a cluster. This definition of cluster formation using the restriction of linked dimers underestimates the number of aggregates of atoms whose $E_{\text{tot}}^{\text{cluster}}$ is negative. This overly stringent definition has been chosen because the interaction potential for each cluster size is not known and because the possibility of unimolecular dissociation of the cluster on the way to the detector has not been taken into account.

3. Results and discussion

The yields of species calculated to eject from an Ar(001) crystal bombarded by 100 and 500 eV Ar^+ are summarized in table 1. The average number of species ejected per trajectory is not shown due to the relatively small number of trajectories that were deter-

Table 1
Yield of species ejected from an Ar bombarded Ar(100) crystal [a]

energy (eV) of the primary particle [b]	100	500
number of primary Ar impacts	21	21
total number of Ar ejected	1161	1324
number of species ejected		
Ar_1	775	855
Ar_2	63	89
Ar_3	30	29
Ar_4	12	12
Ar_5	1	3
Ar_6	4	6
Ar_7	1	4
Ar_8	1	3
Ar_9	2	2
Ar_{10}	1	–
Ar_{11}	1	–
Ar_{12}	2	1
Ar_{15}	1	–
Ar_{25}	–	1
Ar_2/Ar_1	0.08	0.10

[a] The yields presented here are for neutral species. For direct comparison with SIMS experiments an ionic interaction needs to be included.

[b] The primary particle is initially at a polar angle of 45° with respect to the surface normal in the ⟨100⟩ azimuthal direction.

mined. The calculated Ar yields of ≈55 at 100 eV and ≈65 at 500 eV, however, are more than an order of magnitude larger than those found for Cu(001). The results indicate that these enormous yields are certainly a reasonable consequence of the collision dynamics so that concepts such as "thermal spikes" or "thermal sputtering" are not necessary to explain such yield enhancements for this case.

The damage created in the lattice is calculated to be quite extensive as has been reported earlier for copper. This effect is illustrated in fig. 1 where the schematic diagram in fig. 1a shows a three-dimensional drawing of the first three layers of the microcrystallite. Subsequent representations in figs. 1b–1f depict the original location of particles that are found to eject for five different trajectories. In fig. 1b, for example, a 500 eV Ar^+ ion is incident along the symmetry line in the ⟨100⟩ azimuth. There are 37 particles found to eject at distances of up to 25 Å from the impact point. In addition, there are a significant number of atoms which eject off the symmetry line indicating the importance of using three-dimensional microcrystallites to obtain a full picture of the particle ejection process. It is even possible, as shown in fig. 1c to induce collisions that eject particles along a diagonal line consisting of close-packed atoms, some of which are behind the impact point of the 45° incident Ar^+ ion. There is a large variability of the yield with impact parameter. The trajectory shown in fig. 1d yields only 10 atoms even though the average yield for all impact points is over 50.

It is of interest to examine the layer from which the Ar atom is found to eject. This is particularly important information for matrix-isolation SIMS since it restricts the region of the Ar crystal where trapped molecules are expected to eject. The results, as shown in table 2, clearly illustrate that nearly all of the action arises from the first two or three layers of the crystal. This observation is in contrast to that found from ion-bombarded Cu(001) where 95% of the particles originate from the first layer [5]. On the other hand, the results rule out models which require Ar atoms to eject from 5 to 10 layers below the surface.

The mechanism of cluster formation in these systems is of particular interest since molecular cluster ions containing up to 25 atoms have been observed by SIMS. Two examples of trajectories which result in large cluster species are given in figs. 1e and 1f. In fig. 1e, 500 eV Ar^+ ion bombardment results in the ejection of 250 atoms. Such high action is found to occur rather infrequently, but when it does happen, the ejecting atoms are in a favorable position to form large clusters. In this case, the atoms noted in fig. 1e have formed an Ar_{25} species. The mechanism of formation is very similar to that found for Cu multimers in that the atoms that form the cluster arise from a fairly localized region of the surface although they need not be contiguous. The concept of recombination discussed previously [7] is clearly applicable to this situation. In this mechanism, even though the atoms in the cluster originate from a fairly localized region of the crystal, the collision processes which give rise to the ejection of the various constituent atoms are independent. This is in contrast to the ejection of a molecular species such as benzene where generally one collision ejects the entire 12-atom cluster [11]. For Ar crystals, it does appear, that third- and fourth-layer atoms may be involved in cluster formation. In fig. 1e, for example, eight atoms in the cluster arise from the third layer and three (not shown) arise from the fourth layer. Similar conclusions are drawn by examining the trajectory shown in fig. 1f where the Ar_{12} cluster consists of two first-layer atoms, four second-layer atoms, five third-layer atoms and one fourth-layer atom. Note in this situation that none of the first-layer atoms above third-layer atoms that eject and form part of the cluster are found to form part of the cluster. In three of the cases, the first-layer atom is not even found to eject. In both of the examples shown in figs. 1e and 1f, then, it is clear that these large species do not form by direct fragmentation of the Ar lattice.

Table 2
Percentage contribution of each layer to the total yield and cluster yield

Layer number	Energy of the primary particle			
	100 eV		500 eV	
	total yield	cluster yield	total yield	cluster yield
1	61	48	57	46
2	23	34	25	31
3	9	12	12	18
≥4	7	6	6	6

As the energy of the primary ion increases there is a greater propensity for the ejected atoms to be aggregated in clusters. This is reflected in the Ar_2/Ar ratio as shown in table 1. This observation is in qualitative agreement with recent experiments where solid argon was bombarded by He^+ ions at 500 and 2000 eV. In this case the Ar_2^+/Ar^+ went from ≈0.01 to ≈0.1 as the energy was increased [2].

The kinetic energy distribution of the ejected Ar atoms is of interest from a mechanistic standpoint. The peak in the energy distribution curve is characteristic of the surface binding energy of Ar in the crystal and the presence of a high-energy tail is indicative of a collision cascade, rather than of a thermal, process. The calculated energy distribution for Ar is given in fig. 2a. The peak in the curve occurs at only 0.06 eV and the width is extremely narrow – on the order of 0.1 eV. From fig. 2b, however, the presence of the high-energy tail is clearly observable.

There are no experimental results which are directly comparable to our calculations, although the distributions of Ar^+ have been measured using a quadrupole mass spectrometer equipped with a Bessel box energy analyzer [2]. In these experiments, the energy distributions were found to exhibit a full-width at half-maximum of ≈6 eV as well as the expected high-energy tail characteristic of a collision cascade process. Although this energy spectrum is quite narrow relative to those obtained from metals, it is still considerably broader than the calculated spectra. There are several possible explanations for this deviation including charging, bandwidth of the analyzer and differences between ion and neutral trajectories [12]. Ideally, it would be of interest to directly measure the distributions of the neutrals, perhaps using Doppler-shifted laser fluorescence [13] or multiphoton ionization techniques [14], to obtain a direct comparison with our predictions.

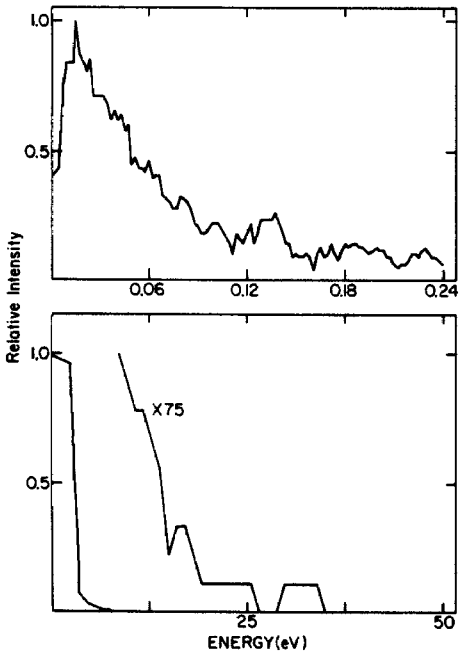

Fig. 2. Calculated argon energy distribution. (a) Low-energy regime. The resolution is 0.01 eV. (b) High-energy tail. The resolution is 5 eV.

4. Conclusions

The results of this study have raised several important points. First, it has been demonstrated that extremely high yields may be obtained from certain systems using the classical dynamics approach. For the case of solid argon, the reason for these high yields is simply that the very small cohesive energy in the solid allows a large number of low-energy atoms to eject. This approach should now be useful to examine anomalously high sputtering rates in other systems such as ice [15]. Secondly, we have demonstrated that it is possible to produce very large clusters via the recombination mechanism. This mechanism should be applicable to other situations where very large clusters have been observed [16] without having to conclude that they form via direct lattice fragmentation. Finally, the results for crystalline Ar should provide a qualitative basis for understanding the mechanism of energy dissipation in matrix-isolation SIMS experiments.

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