CLASSICAL DYNAMICS DESCRIPTION OF LOW ENERGY CASCADES IN SOLIDS: ATOMIC EJECTION FROM SOLID ARGON

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Energetic (∼ eV) atoms, produced by the repulsive decay of electronic states excited by photons, fast ions or electrons can lead to sputtering (desorption) from an insulating solid. Here a classical dynamics program is used to describe the dispersion of the kinetic energy of such atoms and the likelihood that this energy leads to atomic ejection. Yields of ejected atoms versus depth of excitation were calculated for an argon-like solid (fcc) in which one atom is started at a given depth in the solid with a kinetic energy in the range 0.3-3.0 eV and with a random initial direction of motion. The calculated yields averaged over depth and the energy spectra of both the recoils and the ejected atoms are presented. These compare surprisingly well with the standard collision cascade results even though the energy transfer is not by binary elastic collisions. That is, the initially energized atom collides simultaneously with a number of nearest neighbours and subsequent kinetic energy transport from a depth to the surface occurs predominately by successive collisions along the nearest neighbor (110) directions with dissipation to the lattice at each collision. Therefore, the relationship between the energy transfer processes in the simulation and that in the standard binary collision cascade model of energy transport is examined.

1. Introduction

In this paper, we examine the sputtering (desorption) from an argon-like solid caused by deposition within the near-surface region of kinetic energy from a few tenths of an eV to a few eV. Such energy deposition events can occur as a result of non-radiative relaxation following electronic excitations of the solid by incident ions [1], photons [2] and electrons [3]. Therefore, a detailed description of dissipation of this energy is important for interpreting data on desorption induced by electronic transitions.
In this classical dynamics simulation study we examine the energy transfer process from an energized atom to recoil atoms some of which may be ejected from the surface. In previous calculations by Garrison and Johnson [4], the ejection yield was found to depend nearly linearly on the primary energy, similar to the binary collision cascade [5] result. Also, the kinetic energy spectrum of the ejected atoms was approximately equivalent to a binary collision cascade distribution [6]. This was somewhat surprising since the calculations were performed in a crystalline solid and it is clear that at least one of the conditions for the applicability of the standard collision cascade model, that collisions must be binary, is violated. That is, the initially energized atom collides simultaneously with several neighboring atoms for most of the initial directions. Another condition of the standard collision cascade description, that the initial energy be large compared to the bulk cohesive energy, is also not well preserved for the lower energy primaries and recoils tracked in these simulations. Therefore, in order to better understand atom ejection from weakly bonded lattices we analyze the production of recoils in the classical dynamics simulations and compare the results to the standard cascade theory.

Sputtering of surface atoms can occur when energized atoms in a deeper layer initiate a sequence of collisions along crystal axes. This process, often referred to as a “focused” collision sequence [7], has been used to describe the desorption of halogens from alkali halides [8]. More recently, the idea of a mini-cascade of collisions (random or “focused”) has been used by a number of authors [9–12] as a way to explain electronic sputtering and desorption from van der Waals solids. Therefore, we attempt to establish a stronger theoretical basis for the description of the cascade of energy transfer events initiated in weakly bonded solids by an energized atom. The simulation described here is done for initial kinetic energies that correspond, roughly, to the energies released from the repulsive decay of excited dimers typically produced in the electronic excitation of solids [1,2]. The calculations were performed for an argon-like solid, but the results apply to other atomic solids since the dependence of the yield on the energy of the primary excitation roughly scales with the bulk cohesive energy [4,9]. After describing the calculation, we present results for the number of atoms ejected (yield) versus depth and energy of an initial “excitation” as well as the yield integrated over depth for each excitation energy. Understanding these results requires calculating details of the energy transport in the van der Waals solid due to atoms with energies in the interval of tenths of an eV to a few eV and calculating the kinetic energy distribution of the recoils. We compare these calculations to predictions from the binary collision cascade theory and to an estimate made assuming the predominance of “focused” collisions. The relationship between these models is discussed both in the text and the appendices.
2. Model

The crystal studied consists of atoms arranged in a face-centered-cubic array and the interaction between the atoms is assumed to be pairwise [13]. In the calculations a Morse potential [14], which roughly describes solid argon, is primarily used for the pair interaction. However, calculations are also made using a Lennard-Jones potential [15] and a more accurate potential by Aziz and Chen [16] for solid argon in order to understand the sensitivity of the results to the nature of the potential. These potentials and their parameters are given in fig. 1 at the internuclear separations of interest here. The pair interactions are terminated at the distance $R = 10.2 \text{ Å}$, which includes the interactions with up to the seventh nearest neighbors for a lattice constant of 5.31 Å or nearest neighbor distance 3.75 Å. At these distances the assumed pair potentials are only very rough approximations of the interactions. The cutoff used here gives a bulk cohesive energy (sublimation energy) $\Delta H_s = U_h = 0.073 \text{ eV}$ for the Morse potential, $U_h = 0.081 \text{ eV}$ for Lennard-Jones potential, and $U_h = 0.089 \text{ eV}$ for the more accurate potential given by Aziz and Chen [16], ignoring the zero point vibrational energy ($\sim 0.01 \text{ eV}$). The actual sublimation energy of solid argon is 0.088 eV. The potential energy of an atom on (100) surface is calculated to be 0.049, 0.054, and 0.059 eV for each of the

![Fig. 1. Potential curves used in simulation. Solid curve: Morse potential [13] $D_e \exp\{-\beta'(R - R_o)\}[\exp\{-\beta'(R - R_o)\} - 2]$. $D_e = 0.0114 \text{ eV}, \beta' = 1.425/\text{Å}, R_o = 4.04 \text{ Å};$ short dash–long dash curve: Lennard-Jones potential [14] $4\epsilon[(R/o)/R]^{12} - (R/o)/R)^6]$. $\epsilon = 0.01031 \text{ eV}, R_o = 3.4 \text{ Å};$ dashed curve: more accurate potential due to Aziz and Chen [15].](image-url)
surfaces respectively, about 2/3 of the corresponding bulk cohesive energy. In ref. [4] the cutoff is \( R = 6.38 \) Å, which includes only the interactions up to the second nearest neighbors and gives a bulk cohesive energy of 0.061 eV. Although an accurate bulk cohesive energy is important in simulating the ejection of surface species, the repulsive part of the interaction is also very important for describing the transport of kinetic energy. The Lennard-Jones potential in fig. 1 is seen to more closely represent the attraction between molecules around equilibrium separation of the Aziz and Chen potential, whereas the Morse potential gives a closer description of the repulsive interaction in the important (\( \sim \) eV) energy range.

We simulated the motion of the system of argon atoms using a classical dynamics procedure, in which the equations of motion are integrated by a fourth order predictor-corrector method [17] described in appendix A. In starting the program the atoms are given a small component of thermal motion. To determine the sputtering yields, both the position and the momentum of each atom are checked at the end of each run of the program. If an atom is farther from the original surface of the solid than the interaction termination distance (10.2 Å) then we assume that it is sputtered. In addition, any "surface" atom more than \( \sim 5 \) Å from the original surface having an energy greater than its binding energy and momentum outward was also assumed sputtered. This allowed shorter run times. The runs are typically terminated at the physical time of about \( 2 \times 10^{-12} \) s. To make sure that we included every ejected atom, runs were extended \( \sim 3 \) times in some cases. The calculations are made for five initial kinetic energies, \( E_i = 0.3, 0.7, 1.0, 2.0, 3.0 \) eV, which are given to one of the atoms in the model crystallite as a kinetic energy impulse. The angular directions are chosen in such a way that equal solid angle elements get equal probability. Utilizing the symmetry of the fcc lattice enough directions are chosen so that the fluctuations are small. Typically six monolayers with an equivalent number of rows and columns are used with free boundaries; i.e. edge atoms are exposed to free space. When particles were energized in deeper layers care was taken to examine the effect of the artificial boundaries other than the surface by adding additional atoms and/or using periodic boundary conditions on all sides except the true surface.

3. Results

3.1. Yields versus depth and energy of excitation

We show in figs. 2a and 2b sputtering yields from the (100) surface versus depth of energized particles calculated using the Morse potential for the five different energies, where the yield is the average number of atoms ejected from the surface for a single energizing event. Results for (111) surface were
Fig. 2. Yields from (100) face versus layer of initially energized atom (○) (ref. [4]) and (△) represent calculations using Morse potential (a) $E_i = 3$ eV, 1 eV, 0.3 eV. (b) $E_i = 2$ eV, 0.7 eV. performed for the 2 eV case and are about 80% of the results in fig. 2. Also shown are calculations from ref. [4]. It is seen from the figure that the two results have a similar dependence on the excitation energy but are somewhat different in magnitude, with our yields being smaller. Although the potentials used in the two cases are not identical, the differences in magnitude are primarily due to the differences in the cutoff of the interaction potential. Basically, the effect of the longer cutoff is to increase the cohesive energy. In the case of the surface atoms, when the cutoff is shorter, a low energy atom can escape to a force-free region which would otherwise still exert an attractive force, pulling the atom back to the solid surface. We tested this for the 3.0 eV initial excitation. The decreases in the yields in going from cutoffs at 6.38 Å to 10.2 Å are 0.36, 0.20, 0.10, 0.18, 0.06, 0.08 from first through sixth layer. As to
the bulk atoms, the shorter cutoff reduces the pulling force on a fast moving atom, hence makes the energy transfer in the collision more efficient.

It is worth noting that because each atom interacts with many other atoms the energy lost by a fast surface atom in overcoming the binding along the normal is about twice the potential energy of the surface atom [18], while the energy for the slowest particle to escape is slightly higher. This is often called the surface binding energy [19–21]. For the Morse potential this energy is about 0.11 eV. It is higher for the slower atoms because of the larger lattice deformation caused in the process of ejection, opposite to the assumptions of Oliva et al. [22]. Similarly, to eject a surface atom along ⟨110⟩ direction, which is the nearest neighbor direction, the effective barrier is about 0.15 eV ≈ 2Uₜₙ. If the atom is energized by being struck from below, these energies are smaller (≈ 1.5Uₜₙ).

In order to examine the effect of the potential on these calculations, we show in fig. 3 the yields calculated using the Lennard-Jones, Morse, and Aziz and Chen potentials. It is seen that for similar repulsive potentials the yields
from the surface layer increase as the binding decreases. In addition, it is seen in fig. 3 that including the zero point energy increases the yields by about 10\%, roughly corresponding to the reduction in binding. For the Lennard-Jones potential in fig. 3 the surface yields are smaller but the yields from the deeper layers are larger. That is, the steeper potentials are more efficient in transferring kinetic energy giving a longer range of energy propagation. Therefore, an accurate repulsive interaction is required for these energy impulses.

3.2. Integrated yields and energy spectra

In fig. 4, we give the calculated yields integrated over depth, \( z \).

\[
\Delta z = \int Y(z) \, dz = \sum_k Y_k / l.
\]  

(1a)

where \( Y_k \) is the average yield for an excitation in the \( k \)th layer and \( l \) is the layer spacing (half the lattice constant). Equal probability of initial excitation per unit depth is assumed in eq. (1a) and random orientation of the initial momentum direction. We plot the result versus \((E_i - U_b)/U_b\) in fig. 4 in order to give the result in terms of tabulated quantities and it can be compared to

![Graph](image)

Fig. 4. Integrated yield \( \Delta z \), for Morse potential (●) divided by layer separation \( l \) plotted versus \((E_i - U_b)/U_b\). (●) Similar result for Aziz and Chen potential and (△) for Lennard-Jones. Bars indicate uncertainty in calculated yield due to angular mesh, extrapolations to deeper layers for the higher \( E_i \), particularly for Lennard-Jones potentials.
Fig. 5. Average differential yield of sputtered atom energies, \( E \). Histogram for \( E_0 = 3 \) eV located randomly in each layer. Line, the collision cascade energy spectra (Thompson spectra \( (2U_h E)/(E + U_h)^2 \)) normalized to the simulated yield (which is about half that expected from ref. [18] (appendix B)).

The usual collision cascade expression. It is seen that the simulation points are roughly linear in this quantity. Writing

\[
\frac{\Delta z}{l} = c \left( \frac{E_i - U_h}{U_h} \right),
\]

we obtain \( c = 0.17 \). This is close to the result in ref. [4]. (In that paper the smaller, “surface” binding energy, \( U \), was used instead of \( U_h \).) The constant \( c \) found here is half that typically used in the binary collision description of the cascade [19] summarized in appendix B. Also shown in fig. 4 are values for the Lennard-Jones and Aziz and Chen potentials at 2 eV. As \( E_i \) is scaled to the cohesive energy for each potential, the differences in \( \Delta z \) seen indicate a slight dependence on the repulsive potential.

In fig. 5 we give the total energy spectrum of the ejected species for an initial energy of 3 eV averaged over depth using the Morse potential. Also shown is a plot of the Thompson energy distribution [6] of sputtered atoms \( (E/(E + U_h)^2) \) normalized to the 3 eV total yield. There is reasonable agreement between these, as pointed out by Garrison and Johnson [4]. Below we describe the energy transfer processes leading to these results.

### 3.3. Energy transfer

The sputtered atoms are almost exclusively surface atoms [4]. The nature of the energy transfer from below the surface is closely related to the crystal
structure of the solid argon. Each argon atom has 12 nearest neighbors, all of which are along \( \langle 110 \rangle \) directions. Depending on the direction of motion of the energized atom it strikes 1 to 4 nearest neighbors in the first collision. These atoms receive most of the initial kinetic energy. Of the order of 70\% is carried away as kinetic energy along the \( \langle 110 \rangle \) directions, with a fraction going into the potential energy. In fig. 6 it is seen that for \( E_i = 1 \) eV the distribution of energy among these first recoil atoms, \( E_1 \), depends on \( \alpha \), the angle between the momentum direction of the initially energized atom (primary) and the \( \langle 110 \rangle \) axis in which a particular recoil atom resides. The upper curve is for the Lennard-Jones potential and the lower curve is for the Morse potential. It is seen that the Lennard-Jones potential has a higher energy transfer efficiency, again emphasizing that, at these collision energies, the nature of the repulsive interaction is important.

According to fig. 6 (drawn lines), the energy transfer to a first recoil is roughly proportional to \( \cos^2 \alpha \) for the large energy transfers, as the projection of the momentum of the primary along the \( \langle 110 \rangle \) axes determines the momentum impulse to a first recoil. The first recoil energy can be written as

\[
E_1 \approx E_i \beta (\cos^2 \alpha - b).
\]

where \( \beta \) and \( b \) depend slowly on \( \alpha \), \( E_i \) and the potential. In a binary, hard-sphere collision [23] \( \beta = \xi^2 \) and \( b = 1 - \xi^{-2} \) where \( \xi = D/2 \tilde{a} \) (appendix B). Here \( D \) is the nearest neighbor distance (\( D = \sqrt{2} l \)) and \( \tilde{a} \) is the effective hard-sphere radius. (For close-packed spheres \( \xi = 1 \) so that the fractional
energy transfer is \( \cos^2 \alpha \). Calculating the momentum transfer (diffusion) cross section \([24]\) (i.e. \( \delta_d = \pi(2a)^2 \) appendix B) we obtain \( \xi \approx 1.35, 1.38 \) for the Lennard-Jones and Morse potentials for a 1 eV collision and \( b \approx 0.45, 0.47 \) values close to those for the lines in fig. 6. In addition, the bulk cohesive forces and the non-binary nature of the interaction reduce the effective energy transfer.

The simulations show that collision sequences are produced along the nearest neighbor axes. To study this we tested various initial energies and directions and recorded the maximum kinetic energies of the recoils. Independent of the direction of the primary, a first recoil transfers most of its acquired kinetic energy to the next atom on the \( \langle 110 \rangle \) axis determined by the initially energized atom. The second recoil then transfers most of its kinetic energy to the next atom on this axis and so on, giving a sequence of collisions along the axis, often called a “focused” collision sequence \([23]\). Using a Morse potential and several values of initial energy \( E_i \), the fractional energy transfer at each stage of collisions is given in fig. 7. It is also roughly independent of different initial energies used. The lower curve is the fraction of the kinetic energy of a primary which appears as the kinetic energy of a first recoil when the direction of the primary momentum is along a \( \langle 110 \rangle \) axis (i.e. \( \cos^2 \alpha = 1 \) in fig. 6). This is plotted versus the energy of the primary. The upper curve is the corresponding transfer from a recoil to a subsequent recoil. It is seen that the recoil energy transfer is \( \geq 50\% \) for the full energy range of interest and it is above 70\% for energies larger than 0.3 eV. Because of this high efficiency of energy transfer, collision sequences are important in the transport of energy from the bulk to the surface atoms. It is also seen from fig. 7 that the efficiency of energy transfer from recoil to recoil is higher than from a primary to a recoil.
as more kinetic energy is spent in the latter case in the deformation of the crystal, which is largely maintained in subsequent collisions. The decreases in both curves seen at low energy are due to the binding forces. For the upper curve the energy difference \( E_{\chi_{-1}} - E_{\chi} \) between subsequent recoils is roughly a constant (\( \sim 0.12 \) eV) above \( 0.6 \) eV.

The question remains as to how the collision sequences are started when the process is initiated with the momentum of the primary in an arbitrary direction. From fig. 6 we see that for an initial momentum orientation of the primary such that \( \cos^2 \alpha \leq 0.5 \), i.e. \( \alpha \geq 45^\circ \), the fraction of energy transferred to a first recoil is small, less than 10% of the initial energy. For \( \alpha \leq 45^\circ \) the impulse given to a first recoil is significant and its direction is also within 45° of the \( \langle 110 \rangle \) axis, as long as the primary does not cross the \( (100) \) plane. This guarantees that the parallel component of momentum of a recoil receiving a significant energy transfer is greater than its perpendicular component. This preferential momentum transfer along the nearest neighbor axis initiates a collision sequence. (This is consistent with the “focusing” criterion of Thompson [23], \( \xi < 2 \) for small angle binary collisions of hard spheres, i.e. \( \xi D > 4a \) (appendix B), a condition fulfilled even for the highest energy used in our simulation. Energies ten eV or more are required to violate this for the potentials used.)

As the initial energy increases, primaries can cross the \( (100) \) plane and off-axis energy transfers by recoils occur more frequently. When analyzing our simulation data, we found that the first recoils could sometimes transfer energy to an atom not in the initial \( \langle 110 \rangle \) direction. As this transfer is small it affects the ejection yields only when the initially energized atom is near the surface and the energy is relatively high. We find such an effect only for 2.0 and 3.0 eV initial energies, accounting for at most 25% of the yield for the 3.0 eV case.

3.4. Energy spectra of recoils

Since the binary collision model makes definite predictions about the energy spectra of the recoils in the solid this quantity was calculated. For a primary of energy \( E_i = 1.0 \) eV, any recoil of maximum kinetic energy greater than 0.075 eV is recorded during the collision process, until no atom in the solid has maximum kinetic energy greater than 0.075 eV is found. This is to insure that any recoil energetic enough to cause sputtering is included. The corresponding spectra of maximum recoil kinetic energies from this simulation are given in fig. 8 calculated using the Morse potential. The binary collision cascade prediction [5,19] in a gas gives the number of recoils with energy greater than \( \bar{E} \) produced by a primary of energy \( E \), as

\[
N(E) \approx \frac{6}{\pi^2} \frac{E_i}{E}, \quad E \ll E_i, \tag{3a}
\]
To account for atomic displacement in a solid and/or energy lost to the lattice, Sigmund [5] writes

\[ N(E) \approx \frac{6}{\pi^2} \frac{E_i}{E + 2W}, \quad E \ll E_i, \tag{3b} \]

where \(W\) is a "displacement energy" often taken to be the bulk cohesive energy [5]. These expressions correspond to recoil spectra of the form

\[ \left| \frac{dN}{dE} \right| \approx \frac{6}{\pi^2} \frac{E_i}{(E + 2W)^2}, \tag{3c} \]

with \(W = 0\) for eq. (3a). The result in eq. (3c) with \(W = 0\) is seen in fig. 8 (long dash–short dash curve) to be remarkably similar both in absolute size and dependence on \(E\) to the simulation spectrum except at the lowest energies.

As the atoms are not displaced significantly in the simulation, ignoring \(W\) in the comparison in fig. 8 may be reasonable. (The inclusion of a small "displacement" energy, \(W \approx 0.01\) eV, can further improve the agreement in the low energy region.) The similarity of the binary collision cascade and simulation recoil spectra is consistent with the agreement in shape of the exiting atom energy spectrum for the simulation and the Thompson spectra seen in...
fig. 5. However, as energy dissipation clearly occurs in the simulation (viz. fig. 7) the agreement in absolute size for the choice of potential leading to the constant in eq. (3a) is fortuitous. In addition the binary collision cascade expression for $(dN/dE)$ and the simulations each describe a different evolution of events (appendix C).

The recoil energy spectrum from the simulation can also be approximated using the results from figs. 6 and 7. We write (appendix C)

$$\frac{dN}{dE} \approx \frac{q}{2} \frac{d\cos \alpha}{dE_1} + \frac{q}{2} \int_{\cos \alpha_m}^{1} \left( \frac{dN}{dE} \right)_f d\cos \alpha$$

(4)

The first term gives the spectrum of first recoils produced by the primary: $(dN/dE)_f$ is the spectrum of a collision sequence (“focused”) along a $\langle 110 \rangle$ axis; $q (=12)$ is the number of chains (nearest neighbors) available; and $\alpha_m$ is the maximum angle with the $\langle 110 \rangle$ axis for the primary to produce a recoil along the axis. The first recoil energy is estimated from eq. (2) using constant values $\beta = 1.2$ and $b = 0.5$ (appendix B), to roughly describe the results in fig. 6 for the Morse potential. For perfect “focusing”

$$\left( \frac{dN}{dE} \right)_f \approx \frac{1}{E_\alpha - E_{\chi+1}}$$

(5)

where $E_{\chi+1}$ and $E_{\chi}$ are successive recoil energies. Based on fig. 7 this is nearly independent of $E_\alpha$. Therefore, a rough approximation to the spectrum which has the essential features of the collision sequence is

$$\frac{dN}{dE} \approx \frac{q}{2} \frac{d\cos \alpha}{dE_1} + \frac{q}{2} \left( \frac{dN}{dE} \right)_f (1 - \cos \alpha_m).$$

(6)

The last factor gives a cut-off at the most energetic first recoil energy. Assuming perfect focusing after the first collision an approximation form for the successive recoils using fig. 6 is $E_\chi - E_{\chi+1} \approx E_c [1 - \exp(-E/2E_c)]$. $E_c \approx 0.12$ eV. The difference is an amount of energy dissipated due to binding forces, which is nearly constant above 0.6 eV and decreases with decreasing $E$ at lower $E$. Using this in eq. (6) gives the dashed curve in fig. 8, which is larger than the simulation at higher energies due to the perfect focusing assumption but smaller at lower energies, because of the cut-off at $\alpha = 45^\circ$ in eq. (2). However, the elements of the recoil spectra in fig. 8 are describable via collision sequences along the $\langle 110 \rangle$ axes.

We show in appendix C that the binary cascade and collision sequence (i.e., eq. (4)) description can be formulated by similar transport equations because an ordered set of events can be established in both cases. Therefore, similarities in the recoil kinetic energy distributions might be expected, as the constant in eq. (3a) was shown to vary only slowly with the potential form [5,18]. For larger values of $E_\alpha$ than those considered here, cascades, involving multiple or binary collisions, develop until the energy degrades while propagating away.
from the excitation. When the energy degrades to \( \leq 10 \text{ eV} \) collision sequences along nearest neighbor axes are initiated.

3.5. Estimate of yield

For a primary energy \( E_i \) in layer \( N \), with its initial momentum forming an angle \( \alpha \) with the nearest neighbor axis in consideration, the surface atom on this axis will have an energy \( E_s( E_i, N, \alpha) \). If the minimum kinetic energy required for an atom struck from below to be ejected from the surface along the nearest neighbor axis is \( U \), then the atom will be sputtered if

\[
U \leq E_s( E_i, N, \alpha).
\]

where the simulation gives that \( U \approx 1.5 U_b \) for the (110) axis. For a fixed \( E_i \) and \( N \), the equal sign holds for some maximum angle \( \alpha_m \)

\[
U = E_s( E_i, N, \alpha_m) .
\]

Inverting the result for \( N(E) \) above and using the approximate expression for \( E_i \) in eq. (2) we can obtain \( \alpha_m \). As long as the angle between the initial momentum of the primary and a nearest neighbor axis is less than the maximum angle \( \alpha_m \), which depends on the energy and the depth of the initial excitation, the surface atom on this axis will be sputtered. The contribution to sputtering from this axis will be equal to the solid angle determined by \( \alpha_m \).

Summing over all contributing axes for all contributing solid angles, \( \Omega \), we have the yield versus depth of excitation

\[
Y(z) = \sum_{i=1}^{q} \int P_i(d\Omega/4\pi) \approx q(1 - \cos \alpha_m)/6,
\]

where

\[
P_i = \begin{cases} 
1, & \alpha \leq \alpha_m, \\
0, & \alpha > \alpha_m. 
\end{cases}
\]

For the (100) face \( q/3 (= 4) \) is the largest number of collision sequences along nearest neighbor axes that a primary can initiate, with the condition that each axis must intercept the surface of the solid in order to contribute to sputtering.

The total yield due to an initial energy \( E_i \) is obtained as in eq. (1a). Calling \( z \approx l(N - 1) \) where \( N \) is the layer number, the contribution to \( \Delta z \) from layers other than the surface layer \( (N = 1) \) is

\[
\Delta z_b = \int_{l}^{\infty} Y(z) \, dz. \tag{9a}
\]

We add to \( \Delta z_b \) the contribution from the surface layer, \( Y_s \), determined in the simulation, which does not involve a collision sequence

\[
\Delta z_s = \Delta z_b + Y_s l. \tag{9b}
\]
This result for $\Delta z_\phi$ is also roughly linear in $E_1$. We find that $\Delta z_\phi / l \approx c' E_1 / U_h$, where $c'$ is roughly constant for $E_1 \gg U$. As $E_1 \approx U \approx 1.5 U_h$, then $\Delta z_\phi / l \approx c E_1 / U_h$, and using the constant $b$ and $\beta$ in eq. (2), $c = 0.11$. This underestimates the yield because of the neglect of low energy particles in describing both $E_1$ and $E_N = E_{N+1} - E_N$.

Because the binary cascade recoil spectrum approximates the simulated recoil spectrum in fig. 8, the yield is more easily estimated using the analytic forms in eqs. (3). Allowing recoils to escape only along $1/3$ of the possible directions ($4 \langle 110 \rangle$ axes for the (100) surface) and only when $E > U$, then by eq. (3a)

$$\Delta z_\phi / l \approx N(U) / 3 \approx 0.14 E_1 / U_h,$$

using $U \approx 1.5 U_h$ and $N(E)$ from eq. (3a). This is close to the simulation value ($c = 0.17$) and this result is independent of the lattice parameters, which was found to be the case in ref. [4]. For the (111) face, only 3 axes cross the surface (1/4 of the directions) giving a yield which has 75% of that for the (100) face. Our simulation gives 80% ($c = 0.14$). (Note: in ref. [4] these were deemed to be the same to within the statistics of the calculation). Therefore, for random orientation the average layer spacing is $l \approx n^{-1/3}$ so the integrated yield is $\Delta z_\phi \approx P_c n^{-1/3}$ with $P_c = c(E_i - U_h)/U_h$ and $c = 0.15$ based on the simulations.

4. Conclusions

A classical dynamics method is used to examine the sputtering (desorption) of atoms from an argon-like solid due to an atom in the bulk suddenly gaining an impulsive energy in the range 0.3–3 eV. Such events are initiated by electronic relaxation processes [1]. These results apply to any low momentum process but not the usual collision cascade regime for which the initially energized particle does not lose all of its momentum in the collision with first neighbors (appendix C). A model crystallite is constructed assuming that the interactions between individual atoms are pairwise additive, using the Morse, Lennard-Jones, and Aziz and Chen potentials. The general trends in the sputtering yields versus layer and integrated yields versus energy deposition are consistent with the work in ref. [4]. However, we expand those calculations and show that the magnitude of the yield versus depth is sensitive to nature of the repulsive interaction and to the range of the interaction included in the calculation.

The production of sputtering from a subsurface event in which an atom is set in motion can be described as follows. The energized atom gives up its energy during a first encounter in which several nearest neighbors are set in motion approximately along the nearest neighbor axes. This initiates collision
sequences along these axes eventually causing the ejection of the surface atoms, if the axes intersect the surface and if the energy is not degraded too severely before it reaches the surface. An estimate of sputtering yield is made based on this description which can be applied to other crystal faces and other crystalline materials.

We also examined the energy transport and dissipation processes for energizing events that are expected to be produced during electronic relaxation in such a solid. The calculated recoil kinetic energy distribution is found to be remarkably similar to the binary collision cascade recoil energy distribution which ignores binding. This is the case even though each atom interacts simultaneously with many atoms, so that the primary atom simultaneously energizes a number of nearest neighbor atoms, and a sequence of “focused” collisions along nearest neighbor axes occurs with some energy dissipation to the lattice. The integrated yield is also similar in form to that of the binary encounter model although the size is different from that obtained using the “standard” parameters. Because of these similarities, we also discuss, in appendix C, the form for a general cascade description of these process. Since the classical dynamics simulation for initial energies much greater than \( U \) can be approximately described as an ordered sequence of events, determined by a scale parameter related to the repulsive potential, a transport equation can be constructed which roughly describes the production of recoils. This equation is similar in form to that used to describe the production of recoils for a binary collision cascade. Therefore, the agreement in nature of the averaged quantities described here is understandable qualitatively. In addition, the binary encounter recoil spectrum may be used to approximate aspects of the sputtering process over the kinetic energy range studied here.

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Appendix A: Calculation

A fourth-order predictor–corrector algorithm of molecular dynamics is used to track the particle motion [25]. The \( n \)th-order predictor–corrector method consists of two steps. In the predictor step the position and momenta and their derivatives of each particle at time \( t + \Delta t \) in the system is computed
from the positions and momenta and their derivatives at time $t$ by Taylor expansion.

$$
\mathbf{r}(t + \Delta t) = \sum_{k=0}^{n} \frac{(\Delta t)^k}{k!} \frac{d^k}{dt^k} \mathbf{r}(t),
$$

(1)

$$
\frac{d^n}{dt^n} \mathbf{r}(t + \Delta t) = \frac{d^n}{dt^n} \mathbf{r}(t);
$$

$$
P(t + \Delta t) = \sum_{k=0}^{n} \frac{(\Delta t)^k}{k!} \frac{d^k}{dt^k} P(t),
$$

(2)

$$
\frac{d^n}{dt^n} P(t + \Delta t) = \frac{d^n}{dt^n} P(t).
$$

The differential equations to be solved in our case are Newton’s equations of motion

$$
dt/dt = \mathbf{P}, \quad d\mathbf{P}/dt = \mathbf{F}.
$$

The corrector step is to use the predicted positions and momenta and their derivatives to evaluate the exact $d\mathbf{r}/dt$ and $d\mathbf{P}/dt$ which satisfy Newton’s equations of motion at $t + \Delta t$. The differences between the exact and predicted $d\mathbf{r}/dt$ and $d\mathbf{P}/dt$ are then used to correct the derivatives of all orders using a forward differencing scheme [25]. So at time $t + \Delta t$ we have

$$
\frac{d^k}{dt^k} \mathbf{r}_{\text{corr}} = \frac{d}{dt} \mathbf{r}_{\text{pred}} - \left( \frac{d}{dt} \mathbf{r}_{\text{pred}} - \frac{d}{dt} \mathbf{r} \right) f_k k! (\Delta t)^k.
$$

$$
\frac{d^k}{dt^k} \mathbf{P}_{\text{corr}} = \frac{d}{dt} \mathbf{P}_{\text{pred}} - \left( \frac{d}{dt} \mathbf{P}_{\text{pred}} - \frac{d}{dt} \mathbf{P} \right) f_k k! (\Delta t)^k.
$$

The factors up to $k = 4$ are $f_0^1 = 251/720$, $f_1^1 = 1$, $f_2^1 = 11/12$, $f_3^1 = 1/3$, $f_4^1 = 1/24$. Interested readers are referred to ref. [16].

Appendix B

B.1. Binary collisions – yield

A number of closely related expressions for $\Delta z_s$ have been discussed in the literature [9]. For the binary collision cascade model, Sigmund [19] (eq. (59b)) gives for sputtering by an isotropic point source (in our notation)

$$
\Delta z_s \approx \frac{3}{2\pi^2} \frac{E_i}{U_h} \frac{1}{n \sigma_d}.
$$

(B.1)
when $E_i \gg U_b$. The factor $\delta$ here accounts for a depletion in the effect of mini-cascade due to the presence of the surface and $\bar{\sigma}_d$ is the average transport (diffusion) cross section for the material. In this expression $n$ is the number density of the species which is exiting the surface ($n \approx 2.65 \times 10^{22}$ Ar/cm$^3$). Sigmund assumes $\delta = 1/2$ as the cascade is incomplete at the surface and assigns $\bar{\sigma}_d \approx 3.6$ Å$^2$ for monatomic metals [5,19], so that writing eq. (B.1) in the form of eq. (1b) $c \approx 0.076/\ln \bar{\sigma}_d$ or $c \approx 0.30$. This is much too large for the energy impulses of interest based on the simulation results in fig. 4.

Johnson and Brown [9] used the expression in eq. (B.1) to describe the mini-cascades associated with repulsive relaxation and used $\delta = 1$ to describe rare-gas solids. (Note: for a large cascade $\delta = 0.5$ is probably correct, as the extent of the “cascade” gets small $\delta \rightarrow 1$). In the experiments on molecular condensed gases the unit species leaving was the whole molecule, therefore they used the molecular number density for $n$ and proposed that $\bar{\sigma}_d \propto n^{-2/3}$ for molecular solids. Therefore, if $\delta/\ln \bar{\sigma}_d \approx 1$ then $c \approx 0.15$ [4] in eq. (1b) close to the result here. As the calculated binary cross section, $\bar{\sigma}_d$, is a gradually increasing quantity with decreasing collision energy the effective collision diameter is eventually limited by the lattice size. As the simulations also show that low energy atoms are only ejected from the surface layer a general expression for random crystal orientation should be written as a probability of ejection times the average size of a monolayer, $\Delta z_s = P_c n^{-1/3}$. Now, according to eq. (1b) (see also eq. (10)) the probability of ejection is $P_c \approx c(E - U_b)/U_b$, where $c$ depends only slowly on the potential as seen from fig. 4.

**B.2. Binary collisions – energy transfer**

For binary, hard-sphere collisions of spheres of radius $\bar{a}$ spaced a distance $D$ apart with $\alpha$ the angle between their initial alignment and the direction of motion, the energy transfer to a sphere initially at rest is

$$T = E_i (1 - \xi^2 \sin^2 \alpha), \quad (B.2)$$

where $\xi = D/2\bar{a}$. The angle of scattering $\alpha'$ of the sphere initially at rest relative to the initial axis between the spheres is obtained from

$$\xi \sin \alpha = \sin(\alpha' + \alpha).$$

For small $\alpha$, $\alpha' \approx \alpha(\xi - 1)$. Therefore a collision sequence, “focusing”, is initiated if $\alpha' < \alpha$ or $\xi < 2$, the criterion of Thompson [23]. Close packed spheres, $\xi = 1$, always produce focusing.

The value of $T$ in eq. (B.1) above is modified if simultaneous interactions occur. For close-packed spheres $\xi = 1$, and the impulse given to the initial particle is transferred to four recoils simultaneously. The energy transferred along an axis with an angle $\alpha$ with respect to the initial impulse is $T = E_i \times \cos^2 \alpha/(\cos^2 \gamma + 1)$, where $\gamma$ is the angle between the impulse and the $\langle 100 \rangle$.
axis perpendicular to the initial plane of the recoils. Therefore, simultaneous collisions by the initial particle reduce $T$ (i.e. $E_i$) as do the binding forces.

Appendix C: Recoil spectra

Here we show that the forms used in the text for the recoil spectrum can be written in a manner similar to that for the binary collision cascade model. For ease of notation below we replace $(dN/dE)$ in the text by $F$. The standard cascade expression for the total spectrum of recoiling particles of equal mass, $F_T(E_i, E)$, where $E_i$ is the energy of the initiating particle, is written

$$F_T(E_i, E) = \eta(E_i, E) + \int \eta(E_i, E') F_T(E', E') dE'.$$

(C.1)

$$F_T(E_i, E) = 0, \quad E_i < E.$$

Here $\eta(E_i, E)$ is the number of recoils resulting from the first event, including the scattered primary, having energy between $E$ and $E + dE$. This becomes the binary collision cascade result if

$$\eta(E_i, E) = \frac{1}{\sigma} \left( \frac{d\sigma}{dE}(E_i, E) + \frac{d\sigma}{dE}(E_i, E - E) \right).$$

(C.2a)

where $(d\sigma/dE)$ is the differential cross section for setting a stopped particle in motion and $\sigma$ is the integrated cross section. For a hard-sphere potential $F_T(E_i, E) = 2E_i/E^2, \quad E < E_i$.

Often the partial recoil spectrum, the spectrum of recoil energies of initially stopped particles, is calculated

$$F(E_i, E) = \eta_s(E_i, E) + \int \eta(E_i, E') F(E', E') dE'.$$

(C.3)

Here $\eta_s(E_i, E)$ is the number of recoils set in motion in the first event. For binary encounters this is

$$\eta_s(E_i, E) = \frac{1}{\sigma} \frac{d\sigma}{dE}(E_i, E).$$

(C.2b)

with $\eta$ as before. For hard-sphere collisions, $F(E_i, E) = E_i/E^2, \quad E < E_i$, and for the fastest power-law potential [5.19] $F(E_i, E) = (6/\pi^2)(E_i/E^2)$, which is the result in eq. (3a).

It is important to note that in the calculation of either $F_T$ or $F$ it is possible to obtain a “cascade” spectrum having the “standard” energy dependence (i.e. $E^{-2}$) even if the collisions are not binary. This depends only on the functional dependence of $\eta(E_i, E)$ and $\eta_s(E_i, E)$ and not on the binary nature of the collision.
We can also construct that part of the recoil spectrum produced directly by
the primary only (first generation recoils)

\[ F_p(E_1, E) = \eta_s(E_1, E) + \int P(E_1, E') F_p(E', E) \, dE, \quad (C.4) \]

where \( \eta_s \) is number of stopped particles set in motion by the primary particle of energy \( E_1 \) and \( P(E_1, E) \) is the probability that the primary has energy \( E \) after the first single or multiple collision process. That is, \( \eta(E_1, E) = \eta_s(E_1, E) + P(E_1, E) \), so that for the binary collision cascade (i.e. eq. (C.2a))

\[ P(E_1, E) = \frac{1}{\sigma} \frac{d\sigma}{dE} (E_1, E_1 - E). \quad (C.5) \]

For the hard sphere cross section, \( F_p(E_1, E) = 1/E, E < E_1 \). The primary recoil contribution based on fig. 6 and the discussion in text is \( F_p(E_1, E) = \eta_s(E_1, E) \) and \( F_p(E_1, E) \) in eq. (C.2a) is replaced by \( \frac{dN}{dE} \), used in eq. (4). This would also become singular if the lower recoil energies are treated more carefully than they are when evaluating eq. (6) in the text.

Using \( F_p(E_1, E) \), the total number of stopped particles set in motion is

\[ F(E_1, E) = F_p(E_1, E) + \int F_p(E_1, E') F(E', E) \, dE', \quad (C.6) \]

\[ F(E_1, E) = 0, \quad E_1 < E, \]

which is equivalent to eq. (C.3). If the recoils have a different generation function, \( \eta'_s \), for producing additional recoils (viz. figs. 7), eq. (C.6) can be modified so that \( F \) in the integral is replaced by \( F' \), and an integral equation for \( F' \) is also solved. In this way eq. (C.6) is the equivalent to the expression used in eq. (4). That is \( F(E_1, E) = (dN/dE)_r \), for the collision sequence along a \( \langle 110 \rangle \).

The form in eq. (C.6) above applies to binary or multiple collisions, with or without focusing once \( \eta'_s \) is defined. (It is also equivalent to eq. (C.1) if the primary gives up "all" of its energy in the first recoil production event.) Therefore, the expressions used in the text for "focused" collisions as well as the binary encounter expressions all have a cascade nature as an ordered sequence of events is described. As the energy is simply being divided continuously and repulsive interactions dominate it is probably not surprising that the recoil spectra in fig. 8 are similar. That is, these spectra are not very sensitive to the exact evolution of the cascade as long as many particles are eventually set in motion.

A many-body, classical dynamics calculation, however, is not represented by the above picture because of the interactions with distant as well as close species. However, if energy transfer to nearest neighbors dominates, which apparently it does, then the interaction of the primary with its neighbors can be called the first interaction, even if a number of particles are set in motion,
and subsequent interactions of other species can be ordered, as in the above equations. The difference in $\eta$, and $\eta'$, can, in principle, allow for the energy transfer in an undistorted or distorted lattice so that the events all occur in a background field due to more distant neighbors.

References