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# Sputtering by fast ions based on a sum of impulses

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A simple, unifying description of the sputtering of solids by fast ions is obtained by summing impulses. For both electronic and collisional energy deposition, the scaling of the yield versus energy deposition per unit path length ($dE/dx$) is in agreement with experiment in three different regions of ($dE/dx$), each exhibiting different ejection characteristics: single events, "diffusive spike," and "pressure pulse." The latter is a volume ejection mechanism for which the yield scales as $(dE/dx)^3$ at high ($dE/dx$) when the ion penetration depth is large. This mechanism can account for the observed dependence of the yield of intact biomolecules ejected from the solid state and the ejection angles for the intact molecular ions.

The use of fast ions to produce gas-phase biomolecules from the solid state[1-4] and the studies of ion erosion of ices for astrophysics[5] have led to a large effort to describe mechanisms for molecular ejection from a variety of solids. In spite of this effort certain of the most basic experimental results have not been explained. Here we use a sum of impulses to describe the sputtering by fast ions which penetrate deeply into the sample. For this case we obtain the correct scaling for the sputtering yields produced by fast ions at very high excitation densities, which has been problematic, and show how this relates to ejection processes occurring at low excitation density, thereby providing a comprehensive picture of the sputtering process.

The energy deposited by a fast ion *either* collisionally $[(dE/dx)_n]$ or electronically $[(dE/dx)_e]$ can lead to a cylindrical track[6-8] of energized material in the surface region. The resulting molecular motion causes this material to expand against the "unexcited" material *and* into the vacuum,[2,7-9] Fig. 1(a). Here we describe the ejection resulting from this expansion as due to contributions from radial impulses all along the track, Fig. 1(b). These impulses represent secondary particle cascades for collisional excitation of a solid.[10] For electronic excitation the impulses may be produced by dissociation of molecules,[6,11-13] repulsion of ionized neighbors,[6] or expanding, vibrationally excited large molecules.[9,14]

At low excitation density these impulses overlap only occasionally so that they act independently. If their spatial extent is large enough and energetic enough to eject a particular species, that yield will be linear in $dE/dx$.[6,10-12] On the other hand, at high excitation densities the impulses contribute cooperatively, Fig. 1(b). The description of this cooperation can be complex, particularly in its initial stages, if the material is violently disturbed, as in the "Coulomb explosion" region of a fast ion track[6,15,16] or the center of a dense collision cascade.[10,17] However, when a large region about the track is energized,[18,19] then at some radial extent and time it becomes reasonable to treat the impulses additively. This is the approximation invoked here, in which a sum of impulses is used to describe the sputtering yield at high excitation density. Additivity has been used to interpret the incident angle dependence of electronic sputtering yields[7,8] and as an approximation to so-called "shock-wave" ejection[16] (see Appendix). Whereas the details of the production of the impulses and their evolution will affect the calculated *amount* of ejected material, we show here that the geometry of the problem and the nature of the ejection process determine the scaling of the yield with $dE/dx$. The individual impulses are described by a local energy density, $\varepsilon$, *and its gradient,* $(-\nabla\varepsilon)$, the volume force, and they are assumed to distribute their energy and momentum according to a simple transport law. Ejection of material from the solid then occurs in response to the local energy density at the surface (e.g., as in sublimation) *or* in response to the local volume force, providing a directed ejection process. Assuming the energy propagates according to[7,8]

$$\nabla[\kappa\nabla\varepsilon(\mathbf{r}_i,t)]-\varepsilon/\tau=\partial\varepsilon/\partial t\ , \tag{1}$$

where $\tau$ accounts for any dissipation. To allow additivity the parameter $\kappa$, the diffusivity, is assumed constant over the time and spatial region of interest. (The conclusions will be similar for $\kappa$ not constant.) For a spherical impulse,

$$\varepsilon(r_i,t)=\frac{\Delta E_i}{(\pi\bar{r}^2)^{3/2}}\exp(-r_i^2/\bar{r}^2)\exp(-t/\tau)\ , \tag{2}$$

where $(-\nabla\varepsilon)$ represents the radial volume force moving outward and spreading in time, Fig. 1(c). Here $r_i$ is the radial distance from the center of the impulse and the mean-square radius is $(3\bar{r}^2/2)$, where $\bar{r}^2=r_0^2+4\kappa t$, with effective radius, $r_0$, and energy $\Delta E_i$ at $t=0$. In the Appendix, the results for impulses which propagate without

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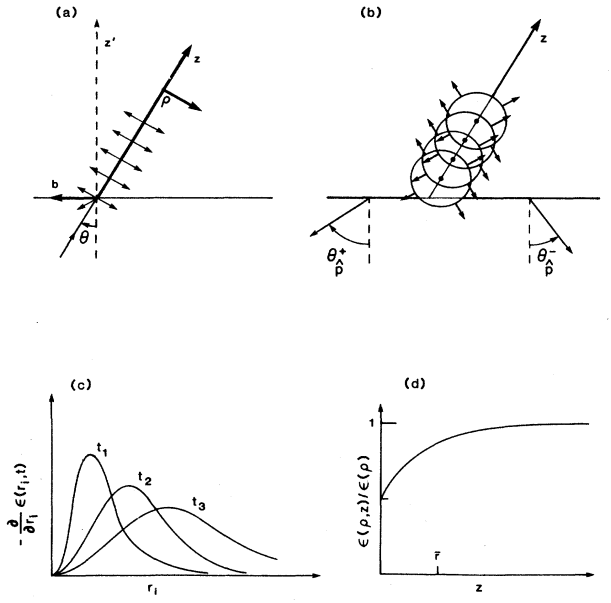


FIG. 1. Track of impulses: (a) Small vectors indicate expansion around track of ion incident at angle $\theta$ along $z$ direction, $\rho$ is radial distance from track, $b$ is radial along surface distance from penetration point; (b) expansion represented by summed spherical impulses, $\theta_{\hat{p}}^{\pm}$ are directions of net momentum for outside track core; (c) radial volume force of an impulse vs time; (d) summed energy density in Eq. (3) along the track divided by the value at large $z$, $\epsilon(\rho)$.

spreading are given.

When these impulses are widely separated in space or time they act individually. Increasing the excitation density, the impulses ovelap. The sum of the impulses gives a total energy density in the track,[7,8]

$$\varepsilon(\rho,z,t)=\int_0^{\infty}\varepsilon(r_i,t)\frac{dz_i}{\lambda}$$
$$=\varepsilon(\rho,t)[1+\mathrm{erf}(z/\bar{r})]/2\ . \tag{3a}$$

Here $\lambda^{-1}$ is the number of impulses produced per unit path length along the track; $z_i$ and $z$ are measured along the track and $\rho$ perpendicular, Fig. 1(a); $\mathrm{erf}(x)=2\pi^{-1/2}\int_0^x \exp(-y)dy$; and

$$\varepsilon(\rho,t)=(dE/dx)_{\mathrm{eff}}\frac{1}{\pi\bar{r}^2}\exp(-\rho^2/\bar{r}^2)\exp(-t/\tau)\ , \tag{3b}$$

which is the value of $\varepsilon$ at large $z$, where $(dE/dx)_{\mathrm{eff}}\equiv\Delta E_i/\lambda$. The summed impulses are used to describe two different types of sputtering, one in response to the energy density and the other to the net volume force. These will be considered for normal incidence [$\theta=0$ in Fig. 1(a)], assuming $(dE/dx)_{\mathrm{eff}}$ is proportional to $dE/dx$ for each process.

If the energy density of the cylindrical track is sufficiently large at the surface, small molecules may exit individually from the solid. This occurs when the local agitation of the lattice can lead to ejection, often referred to as "thermal spike" sputtering. (Here we use "diffusive spike.") For this process the yield can be written[6,19,20]

$$Y=\int dt\int d^2\rho\,\Phi(\varepsilon(\rho,0,t)/n_M U)\ , \tag{4}$$

where $\Phi$ is the local flux of molecules from the surface determined by $\varepsilon$, $n_M$ is the molecular number density, and $U$ is the cohesive energy per molecule. When $(dE/dx)_{\mathrm{eff}}\gg\pi r_0^2 n_M U$ and $r\to\infty$, then for the $\varepsilon$ in Eq. (3a) we showed,[7,8] $Y\propto(dE/dx)_{\mathrm{eff}}^2$. Such a dependence of the yield on the deposited energy density has been established experimentally[11,21,22] for electronic sputtering of low-temperature, condensed-gas solids at excitation densities which roughly satisfy $[n_M^{-1/3}(dE/dx)_{\mathrm{eff}}/U\gtrsim 1]$.

What is typically neglected is that the energy density exhibits a gradient radially and towards the surface, Fig. (1d), which gives a net volume force, Fig. (1a), to the near-surface material. This "pressure pulse," described by $-\nabla\varepsilon$, can dislodge a volume of material from the rest of the solid if the net impulse is large enough. The net momentum, $\mathbf{p}$, given to a molecular volume, $n_M^{-1}$, in the time $t_e$ is obtained from

$$\left[\frac{\Delta M\mathbf{v}}{\Delta V}\right]=\beta\int_0^{t_e}(-\nabla\varepsilon)dt\equiv n_M\mathbf{p}\ . \tag{5}$$

The proportionality "constant" $\beta$ is, for example, $(C_p/C_v)-1$ for a gas. We assume a volume is ejected when the normal component of the momentum transfer, $(\mathbf{p})_n$, for molecules at the edge of the volume, exceeds some critical value,[16,23] $p_c$. Substituting Eq. (3) into Eq. (5) we find

$$p_c=\left[\frac{\beta}{4\pi\kappa n_M}\left[\frac{dE}{dx}\right]_{\mathrm{eff}}\right]\frac{1}{r_c}(r_c,t_e,r_0,\tau)\ , \tag{6a}$$

where $r_c$ is the radius $[r=(\rho^2+z^2)^{1/2}]$ into the solid at which the injection criterion is satisfied. $F$ is a function which are large $t_e$ and large $\tau$ equals one. In that case the radial extent of the ejected volume is simply

$$r_c=\frac{\beta}{4\pi\kappa n_M p_c}\left[\frac{dE}{dx}\right]_{\mathrm{eff}}\propto\frac{1}{n_M 2/3}\frac{1}{U}\left[\frac{dE}{dx}\right]_{\mathrm{eff}}\ . \tag{6b}$$

The quantities in the denominator were rewritten using the material cohesive energy in order to obtain the expression on the right. That is, $p_c\propto(2MU)^{1/2}$, where $M$ is the molecular mass, and $\kappa\propto\bar{v}\Delta\bar{L}$, a characteristic speed [e.g., $(2U/M)^{1/2}$] times a characteristic length (e.g., proportional to molecular spacing). The sputtering yield is the half sphere of ejected material[16,23] obtained using Eq. (6b),

$$Y\approx n_M\frac{2\pi}{3}r_c^3\approx\frac{C}{n_M}\left[\frac{1}{U}\left[\frac{dE}{dx}\right]_{\mathrm{eff}}\right]^3\ . \tag{7}$$

An identical result is obtained for impulses which do not spread (see Appendix), so that $C$ is a dimensionless parameter to be determined by the details of the transport and escape processes. Therefore, the scaling for the sputtering yield in this high $(dE/dx)$ regime is also seen

to be remarkably simple and is insensitive to the nature of the transport process depending primarily on the track geometry.

A yield which has a dependence on $dE/dx$, like that in Eq. (7), was measured by Hedin *et al.*[24] for whole (intact) leucine molecules ejected from a leucine sample by MeV heavy ions with fixed initial "track radius." Because this was the first, and is still the only, measurement of intact ejection of large neutrals, it was not clear that their observed dependence on $(dE/dx)_e$ had any generality. Recently a classical dynamics simulation of a track of expanding large molecules also indicated such a dependence in the calculated ejecta.[9] The origin of this cubic dependence, the pressure pulse ejection of a volume of material, is now established via Eq. (7).

There is additional experimental evidence for the dependence in Eq. (7). Thompson *et al.*[17] showed that the measured *collisional* sputtering yield was roughly proportional to $(dE/dx)_n^3$ at very high $(dE/dx)_n$, although the changing penetration depths complicated the interpretation. The results for the *electronic* sputtering yield[25] of Eu from $Eu_2O_3$ also varied nearly as $(dE/dx)_e^3$ even though the initial track radius was not constant. Similarly, at very high $(dE/dx)_e$ low-temperature water ice sputtering yields varied faster than quadratically on $(dE/dx)_e$.[15,26] Finally, in the linearized pressure pulse description, the *area* on the surface of the ejected volume varies as $(dE/dx)_e^2$. This dependence is consistent with yields from ice measured at very high excitation density for thin samples for which ejecta come from all depths.[27] Based on Eq. (7), the foregoing results give a consistent picture of the ejection process at very high $dE/dx$ for both collisional and electronic sputtering of small *or* large molecules.

The model described here also predicts the direction of the momentum impulse, hence the exit angles. For large $t_e$, large $\tau$, and for $\rho$ larger than $r_0$, the momentum impulse can be written [either Eqs. (5) and (6b) or Eqs. (A2) and (A4)] as

$$\mathbf{p}=p_c r_c\left[-\frac{\hat{z}}{r}+\frac{\hat{\rho}}{\rho}\left[1+\frac{z}{r}\right]\right]. \tag{8}$$

For molecules on the surface and $b>r_0$ (or $>n_M^{-1/3}$) this gives a momentum at an angle to the *surface normal of*

$$\theta_{\hat{\mathbf{p}}}^{\pm}=\frac{\pi}{4}\pm\frac{\theta}{2}, \tag{9}$$

Fig. 1(b), where $\theta$ is the incident angle. Since the molecules in the ejected volume evolve collisionally as they expand away from the surface,[28] a distribution of angles around these values will be found and the effect of surface binding should be included. Recently, Ens *et al.*[29] showed that the promptly ejected, whole molecular ions of leucine exhibit an angular distribution indicative of such a "pressure pulse." For normal incidence, $\theta=0°$, the yield was found to peak at $\sim 50°$ off the normal, close to $\theta_{\hat{\mathbf{p}}}=45°$ predicted above. For $\theta=45°$, their $\theta_{\hat{\mathbf{p}}}^{-}$ peak in Fig. 1(b) shifted to roughly 90° to the *incident ion* direction. This is consistent with but somewhat larger than the $\sim 68°$ given by Eq. (9).

The foregoing model also gives the average momentum of the ejecta, which, because of the binding, is equal to $p_c/2$, i.e., the mean energy is proportional to $U$ as in all sputter processes. For the ejection of intact molecular ions, which come from the surface layer within a radius $R_i$ of the track,[18,19] the mean momentum, $\sim p_c[(2r_c/R_i)-1]$ if $R_i$ is much larger than the damage radius, is larger than that for intact neutrals in agreement with measurement. The dependence of the yield on incident angle, $\theta$, is also predicted. For the quadratic, diffusive spike regime this was shown to be $(\cos\theta)^{-1.6}$ at small $\theta$,[7,8] and for the cubic, pressure pulse regime it will have a similar dependence.[16] However, in these two sputtering regimes the *exit angle* distribution of the ejecta should differ markedly. In the diffusive spike regime it should not depend very strongly on $\theta$, exhibiting a rough cosine dependence about the surface normal, modified by collisions.[28] In the pressure pulse regime, ejecta from the core ($<r_0$) will exhibit a component back along the "track"[29–31] whereas material from $r>r_0$ will exhibit an angle away from the track as in Eq. (9).

In this paper we used a sum of impulses to describe the sputtering of molecules over a broad range of $dE/dx$. At low excitation density $[1\gtrsim n_M^{-1/3}\,(dE/dx)_{\text{eff}}/U]$ individual impulses can act to eject species if these impulses are sufficiently energetic over an areal extent comparable to their size.[6,19] Single event ejection regions of $(dE/dx)$ have been established for collision cascade[10] and electronic sputtering of atoms and certain small molecules.[8,11,12]

When the impulses occur close together in space and time they can act cooperatively. Therefore at low $dE/dx$, ejection of "large" or tightly bound species will depend on the statistical occurrences of a number of closely spaced events,[19] resulting in a rapid dependence of the yield on $dE/dx$.[18,19,22] Increasing $dE/dx$, the impulses will eventually always act cooperatively to eject large species or to cause additional ejection of small species by a more efficient use of the energy. For the latter case the local energy density parametrizes the motion leading to ejection, giving the diffusive spike regime of sputtering, which is quadratic in $dE/dx$ when the penetration depth is large. Such a dependence is well documented for ejection from small molecule, low-temperature, condensed-gas solids.[11,21,22]

For large species the volume ejection mechanism dominates. That is, at very high $dE/dx$ the impulses act cooperatively forming a pressure pulse which gives an overall outward and radial momentum to a volume of material at the surface.[2] This has been treated as a shock phenomenon[16,23] (see Appendix), which might contribute at very early times. Here we show that the primary characteristics of total yields in this regime can be simply described as the outward expansion of the material driven by the *net* impulse from track. For the linearized pressure pulse with cylindrical geometry described here the yield scales as $(dE/dx)^3$ and the momentum of the ejecta is correlated with the track direction. This scaling is a result of the track geometry and was shown to be consistent with a number of experimental observations. This mechanism acts in all materials but it is of particular interest for large species such as biomolecules. As the ejec-

tion of large, intact species requires a number of impulses, and as the local energy density is detrimental to their survival, the yields should not exhibit either the linear or the diffusive spike, $(dE/dx)^2$ dependence. However, the pressure pulse, $(dE/dx)^3$-dependent, ejection of a *volume of material* provides a favorable ejection process. This dependence will persist down to some "threshold"[19] at which $r_c \approx r_0$. Below this the yield will go to zero at a rate determined by the molecular size.[18,19,22] The analytic models used here describe the scaling of the very high $dE/dx$ ejection process and show its relationship to the other ejection processes.

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## APPENDIX

The results in Eqs. (7) and (9) are also obtained using impulses which *do not spread* (delta functions). (This model, as presented, cannot describe the diffusive spike regime). The volume force for each contributing spherical impulse can be written for *no dissipation*

$$d\mathbf{f}_i = F_0 \delta(r_i - \bar{v}t - r_0) \frac{\mathbf{r}_i}{r_i^3} \frac{dz_i}{\lambda} , \tag{A1}$$

where $\lambda^{-1}$ is the number of such sources per unit length, of extent $dz_i$. The effect travels outward at a speed $\bar{v}$ characteristic of the transport process. The net momentum for a line of sources [viz., Eq. (5)] is

$$\mathbf{p} \equiv n_M^{-1} \left[ \frac{\Delta M \mathbf{v}}{\Delta v} \right] = n_M^{-1} \int_0^{t_e} \int d\mathbf{f}_i dt . \tag{A2}$$

For normal incidence the normal component is

$$(\mathbf{p})_n \equiv n_M^{-1} \left[ \frac{\Delta M \mathbf{v}}{\Delta V} \right] n = \frac{F_0}{\bar{v}\lambda n_M} \frac{1}{r_c} \quad \text{for } r_c > r_0, \quad t_e \to \infty . \tag{A3}$$

Therefore, the escape criterion is satisfied for

$$r_c = \frac{F_0}{p_c \bar{v} \lambda n_M} . \tag{A4}$$

In the shock model of Bitensky and Parilis[16] the quantity given here as $F_0/\lambda$ was assumed to be proportional to $(dE/dx)^{1/2}$, based on the radial spread of the energy to some critical threshold energy for shock formation.[23] Although invoking shock wave formation is inconsistent with treating the impulses as linearly additive, their results may apply to the inner region $(r < r_0)$ in our discussion. This would give a "shocked" region smaller than that affected by the linearized pressure pulse described here.

The impulsive source distribution in Eq. (A1) should scale as $dE/dx$, via $\lambda^{-1}$. [In Ref. 16 it scales as $(dE/dx)^{1/2}$]. For example, if the track expansion is initiated by expanded molecules[14] then

$$F_0/\lambda \approx (\Delta E_{\text{ex}}/\Delta R)/L ,$$

where $L$ is a molecular size and $\Delta E_{\text{ex}}$ is the impulsive energy associated with a radial expansion $\Delta R$ per molecule. This can be written as $\sim (dE/dx)_{\text{eff}}/\Delta R$, and the results in Eqs. (6b) and (7) are obtained if $p_c \bar{v} \propto U$. (Similar arguments can be made for the other initiating processes.) Therefore, only the determination of $C$ in Eq. (7) depends on the assumptions about the energy transport. In the picture presented here the diffusivity, $\kappa$, in Eq. (6b) is replaced by $\bar{v}\Delta R$.

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