ELECTRONIC MECHANISMS FOR SPUTTERING OF CONDENSED-GAS SOLIDS BY ENERGETIC IONS

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The sputtering of condensed gas films by ions with energies $>$ 10 keV/amu is controlled by the electronic energy loss of the ions. The sputtering yields are large, from 0.1 to $10^3$ or more molecules lost per incident ion, and they are predominately quadratically dependent on the electronic energy loss. The sputtering mechanisms that may be effective depend on the radial distribution of the initial ionization and excitation, the Coulomb energy in the separated charge distribution, the relaxation of the charge cloud to form a neutral plasma and the transfer of energy from the electronic to the nuclear system. The formation of mobile fragments in condensed molecular gas films and their activated diffusion are also features of the process. These factors that lead to loss of heavy particles from the surface of the films are considered in some detail.

1. Introduction

Recent experiments on sputtering of condensed gases [1,2], UF$_4$ [3] and alkali-halides [4], and desorption in organic solids [5] have focused attention on the conversion of electronic excitation energy into heavy particle motion in a solid. This is a problem of general interest in materials, but the effects are particularly pronounced in condensed gases because of their low binding energies. In these materials a low temperature, temperature independent sputtering regime was found in which the sputtering yield was determined by the energy deposited in electronic excitation and ionization. At higher temperatures the yield was also correlated with electronic energy deposition but here the sputtering yield was temperature dependent, as in the sputtering of alkali halides [4], and is thought to be due to diffusion and subsequent ejection of damage fragments [1]. These data are discussed in a companion paper in this issue [6]. In the present paper we consider the mechanisms for both the low-temperature erosion, which requires direct conversion of electronic excitation energy into nuclear motion, and the high-temperature release and ejection of the target material.

Along the track of a fast incident particle motion of the target atoms may be produced by a cascade of collisions resulting from a single hard collision of the incident particle with a target atom. This is known to account for only a small fraction of the energy lost by fast ions but accounts for all the nuclear motion leading to sputtering in most metals and semi-conductors [7]. For all solids it is the ultimate fate of nearly all the energy deposited electronically to be converted into random nuclear motion (heat). A small fraction is stored as defects in the solid and another small fraction of this energy is lost to escaping electrons, photons and heavy particles. The ejection of heavy particles (sputtering) depends upon the energy density (in space and time) which is converted into nuclear motion near the surface. If the electronic excitation diffuses rapidly away from the track of the incident particle (where the excitation was initially produced) compared with the rate at which it is converted to nuclear motion the energy density may be too low to allow the nuclei to overcome the surface binding energy. This is the case for metals and most semi-conductors. Even if the electronic energy remains localized, however, un-
less it is converted to nuclear motion rapidly compared with the rate at which thermal diffusion spreads and thus reduces the nuclear energy density, that density may still be too small for effective ejection of heavy particles from the surface. However, in insulating materials such as the condensed gases and alkali halides, which have low surface (molecular) binding energies, experiments show that many atoms (molecules) do receive sufficient energy to leave the surface. Even in some high surface binding energy insulators such as quartz and mica, high enough electronic excitation density produces sufficient nuclear motion to lead to the formation of defects and etchable tracks [8]. The result of this motion is the production of displacements along the track, and therefore, as pointed out by Stieger and Noggle [9], Haff [10] and Brown et al. [11] such materials might also be expected to “sputter electronically”. We first discuss the deposition in the target material of the incident ion’s energy and then outline the possible mechanisms for energizing heavy particle motion. Sputtering results are then reviewed and subsequently analyzed by considering thermal transients in the material. Individual processes for the conversion of electronic excitation energy into heavy particle motion are then examined, and the probability of sputtering by such processes is estimated. In section 7 the effect of the charge state of the incident ion is considered and in the appendix a review of useful cross section information is given.

2. Electronic energy deposited by charged particles

The distribution of energy deposited electronically in a material by a passing charged particle can be divided into close and distant collisions using Bohr’s adiabatic criterion [12]. Close collisions involve a direct electronic impulse to the target electrons producing, in some cases, excitations but primarily ionizations and accompanying secondary electrons. The more energetic secondaries are often referred to as delta rays. Such collisions occur at distances \( r \ll v/\omega \equiv r_0 \) from the charged particle path (track), where \( v \) is the incident particle velocity and \( \hbar \omega \) is the electronic binding energy. Part of the energy thus deposited is stored as the potential energy in an electron—

hole pair. Much of the excess kinetic energy of the delta rays is deposited in further ionization and excitation at distances \( r \gg r_0 \). Energy is also deposited at distances \( r \gtrsim r_0 \) by collective, dipole excitations and ionizations of the atomic charge cloud. In metals and low band-gap materials such excitations are often referred to as plasmons. The energy deposited in these “distant” collisions is roughly one half the total for fast incident ions, \( v \gg v_0 \), where \( v_0 \) is the mean speed of the outer shell electrons. The relative amounts of energy deposited in excitation vs. ionization is fairly constant for \( v \gg v_0 \) (~0.1) but increases at lower energies. The fraction of ionizations of inner shell to outer shell electrons is less than about 0.1 in a material such as \( \text{H}_2\text{O} \) for incident light ions at the highest velocities considered here (1.5 MeV/amu) but falls off very rapidly with decreasing energy to \(<10^{-4}\) at the lowest energies (10 keV/amu). This is of some interest as inner shell excitations are known to lead to atomic displacements [13] and ejection [14].

At low energies (\( v < v_0 \)), excitations and ionizations require close collisions, and dipole effects become less important. However, an electron-gas description of the total energy loss, in which the electron gas is polarized by the incident ion, is also frequently used at these energies [15]. In an atomistic picture the energy loss due to distortion of the charge cloud can be described as charge sharing between the incident ion and the target atoms. In gases this is referred to as the charge exchange cycle. The contributions to the stopping power for protons in \( \text{H}_2\text{O} \) gas [16] are shown in fig. 1. In a solid the relaxation of the distortion of the target charge cloud can extend over a number of atomic sites and produces collective electronic motion in the media [17]. (For additional discussion on the cross sections see appendix.)

The fraction of the total electronic energy deposited, both by the incident ion and by the secondary electrons, within the radius \( r_0 \) is 0.6–0.75 at large \( v \) and increases to unity as \( v \to 0 \) or as the number of energetic secondary electrons decreases [17]. Since \( r_0 \) is proportional to \( v \), the electronic energy density around the track of the ion is larger, and may be much larger, on the low velocity side of the stopping power maximum than at an equal stopping power on the high velocity side.
3. The production of heavy particle motion

The collision time of a 100 keV proton is $\sim 10^{-17}$ s and the mean time between collisions that give rise to electronic excitation or ionization is $\sim 10^{-16}$ s. Energetic secondary electrons (those with kinetic energies greater than the ionization energy of the solid) lose most of their energy in times $\sim 10^{-15}$ s, this energy going principally to further excitation and ionization. On the average between one and two additional ionizations per initial ionization are produced. After this cascade of ionizations a substantial fraction (half) of the energy lost by the primary ion is stored in the potential energy of the hole-electron (ion-electron) pairs and in the electric field of separated charges. Most of the remainder is still contained in the kinetic energy of secondary and tertiary electrons incapable of further excitation or ionization. Almost none is yet in the energy of motion of the nuclei. Below we examine the processes contributing to energy transfer to the nuclei and the time scales involved.

One way of transferring energy from the electronic system to nuclear motion is available to low energy electrons that can no longer ionize: phonon generation. The individual phonons involve small energy loss increments for the electron, $10^{-2}$ to $10^{-1}$ eV. Thus the electrons require times $\sim 10^{-12}$ s to lose their kinetic energy in this way. Individual transfers are too small to provide for escape of heavy particles from the surface binding forces. However, if the transferred energy is confined for long enough to establish quasi thermodynamic equilibrium, individual heavy particles may be capable of escape. This can occur because a Maxwell-Boltzmann energy distribution includes some particles sufficiently energetic to escape the surface even if the average energy per particle is much lower. The time for establishing quasi-equilibrium, however, is much longer than the mean, thermal collision time since many collisions among the complete ensemble of atoms (molecules) in the confinement is required. (Of course, thermodynamic models are often useful approximations to the energy disposal in a material even if equilibrium is not established.) The relatively slow rate at which energy flows into heavy particle motion through free electron generation of phonons requires long confinement times for this energy if a high transient temperature is to be established. This will be discussed further in section 5.

A second possible route for energizing heavy particles is through electric fields produced by the displacement of charge in the ionization process. The energetic secondary electrons come to the end

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of their paths at larger radial distances from the primary particle track than the positive ions which were their original partners. The net result is a negatively charged shell surrounding a positive core. Very large electric fields may briefly exist, tending to break the intermolecular bonds, displacing and energizing the molecules in a "Coulomb explosion". Far from the surface these fields and forces are radial and the Coulomb explosion has been advanced as the mechanism for etchable track damage in insulators [8]. Near the surface the fields and forces on both the negative and positive species have an outward component that may produce ejection of heavy particles from the solid [9–11].

The time to accelerate a heavy particle (for example an H$_2$O molecule) over a lattice spacing to an energy equal to the binding energy of an H$_2$O molecule in its solid (0.55 eV) is $\sim 3 \times 10^{-13}$ s and requires electric fields $\sim 10^3$ V/cm. Such fields will be rapidly reduced by polarization of the bound electrons. For example, at a frequency $\sim 10^{16}$ s$^{-1}$ the dielectric constant of water ice changes from $\epsilon \sim 1.0$ to $\sim 1.72$ corresponding to polarization of the bound electrons and at about $10^{-13}$ s$^{-1}$ from $\epsilon \sim 1.72$ to $\sim 3.2$ due to bond distortion. Molecular reorientation (which gives the large static dielectric constant for H$_2$O) occurs at much lower frequencies [18].

Even more important than the response of bound charge is the response of the free electrons of the system – either those normally present in the material or those created in the ionization cascade. They may move to neutralize the fields before the heavy particles have been significantly accelerated. In metals, the density of free electrons is so large and they are so mobile that the electric field is screened in $10^{-15}$ s or less. In typical semiconductors the diffusion coefficient of electrons is such ($D_e \approx 10$ cm$^2$/s) that the electrons of a 20 Å radius negative shell will return to neutralize the positive core in times $\sim 10^{-14}$ s. There can be no significant energizing of heavy particles in such short transient electric fields. In insulators the situation may be different. If $D_e \approx 10^{-2}$ cm$^2$/s, the relaxation time of the negative shell will lengthen to $\geq 4 \times 10^{-13}$ s, comparable to the time required to energize heavy particles in the transient electric field. In rare gas solids $D_e$ is still large [19] and energizing heavy particles through the Coulomb field seems unlikely. For condensed molecular gas solids the electrons may be strongly localized, producing immobile negative ions or trapped electrons [20,21] and the possibility of energizing heavy particles. The fraction of electrons which are trapped in crystalline ice is rather small, but for alkaline ices it may be $\sim 0.5$ [22]. Only in a case in which the electronic binding energies are larger than the intermolecular bond energies of the solid can such a condition be expected to occur. For H$_2$O the electronic binding energy is $\sim 10$ eV; the intermolecular bond strength is 0.55 eV. The trapping must be extremely rapid, however, to localize the electrons before they have moved to neutralize the field and fast trapping is improbable for electrons that have substantial kinetic energies.

The positive charge mobility also limits the maintenance of charge separation. In condensed gas solids the exchange of a bound electron occurs in $\tau_e \sim 10^{-14}$ s. This corresponds to a 20 Å diffusion in $\sim 10^{-12}$–$10^{-13}$ s. Positive ion mobility in ice [18] is of the order 0.01–0.1 cm$^2$ V$^{-1}$ s$^{-1}$ which for fields $\sim 10^3$ V/cm over 20 Å yields a relaxation time $\sim 10^{-12}$ s. Primarily based on the low probability of fast ($<10^{-13}$ s) trapping of electrons, the cooperative electric field of separated charge seems quite unlikely to be sufficiently persistent to energize heavy particles for escape from the surface.

A third route for transfer of electronic excitation to heavy particle motion is prominent for free molecules. In collisions of fast electrons or ions with molecules, vibrational excitation (i.e. nuclear motion) is primarily a by-product of electronic excitation [23]. As the electronic transitions produced occur rapidly, on the order of the collision time ($\sim 10^{-17}$ s for 100 keV protons), the nuclei of the target can be treated as being stationary during such a transition. Because the final-state electronic distribution is often rather different from that of the initial state, the nuclei "relax" into a new vibrational state or dissociate due to the enhanced Coulomb repulsion. This is simply an expression of the well-known Franck-Condon principle in molecular spectroscopy and applies equally well to transitions produced by fast ions, electrons or photons [23]. This relaxation is favored because the lifetimes of radiative transitions are long ($\sim 10^{-9}$ s) compared to the nuclear acceleration times; that is, the photon field is weakly connected relative to Coulomb repulsion. The same is true for electron–ion recombination in gases in which
the slow electron can be thought of as forming a temporary "quasi-bound" state in the Coulomb field and "decaying" either by photons ($\sim 10^{-9}$ s), a two electron, non-radiative process, or Coulomb repulsion (23). In gas phase reactions, such dissociative recombinations occur in $\tau_e = (\tilde{r}_+^2 \lambda_e / \alpha_e)$ where $\tilde{r}_+$ is the radius of the positive ionization region, ($\sim 10$ Å), $\alpha_e$ is the recombination rate constant, $\lambda_e$ is the mean distance between ionization events along the primary ion track: $\lambda_e = W / (dE/dx)_e$ where $W$ is the average energy expended per ionization and $(dE/dx)_e$ is the linear energy loss to electronic processes. We define $\xi = n^{-1}(dE/dx) = \xi \times 10^{-15}$ eV cm$^2$ where $n$ is the number density of the material. For $W = 30$ eV, $n = 3 \times 10^{22}$ /cm$^3$ and $\alpha_e$, for ice, $= 10^{-8}$ cm$^3$/s [24]; $\lambda_e \sim 100$ (Å)/\xi and $\tau_e \sim 10^{-12}$/\xi. For $\xi > 10$ this time becomes quite short compared with characteristic cooling times of a hot track and recombination of electrons with ions in the core of the track may be an important means by which electronic energy is rapidly transferred to nuclear motion.

There are a growing number of examples of dissociative-type deexcitations in solids. In the larger band gap semiconductors in which the electronic recombination energy exceeds the energy required to displace an atom, defects are formed or atoms are stimulated to diffuse [25]. Defects are similarly formed in the alkali halides by electronic excitation [26]. Still another example of the changes in the electron cloud resulting in nuclear motion in a solid is the creation of an inner shell ionization in one atom of a conglomerate (molecule or solid). Such an ionization may be followed by an Auger transition which further depletes the electronic charge cloud leading to atomic dissociation and the formation of defects [13] or, if it occurs near the surface, to desorption, [14].

4. Summary of experimental results

The stopping power dependence of the sputtering yield for a number of condensed gas solids bombarded by light ions is discussed in a companion paper in this issue [6]. The low temperature results clearly indicate a strong non-linear dependence on the electronic component of the stopping power, $(dE/dx)_e$, which dominates the energy loss at the incident ion energies of interest. Because sputtering is a surface phenomenon and charge equilibrium is not fully established in the sputtering layer one would expect the incident charge state to affect the yield, a point which will be discussed in section 7. Based on yields for which the incident ion charge is very nearly equal to the equilibrium charge-state, the dependence for light ions appears to go approximately as $(dE/dX)_e$ over a broad range of energies and for a number of materials. At low velocities for He$^+$ ions there are significant enhancements observed over and above this square law dependence. These may be due partly to non-equilibrium charge state effects, but they may also be due to changes in the spatial density of the electronic excitations and ionizations as the radial size of the particle track decreases with decreasing ion velocity below the peak in the electronic stopping power. The high temperature yields show a strong temperature dependence characteristic of activated processes such as diffusion of damage products when the irradiated material is a molecular solid.

5. Thermal spikes

Sputtering yields that are non-linear with the electronic excitation suggest that cooperative energizing processes occur. Such processes can lead to the formation of a thermal spike in the material after the passage of the ion. Brown et al. [27] considered this for H$^+$ and He$^+$ erosion of H$_2$O assuming the electron-ion recombination energy in the ionization track is the heat source. Seiberling et al. [28] considered the Coulomb repulsion energy as a heat source to describe the data for UF$_4$ erosion. Other heat sources can also be considered: phonon generation by low energy electrons, transfer of electronic excitation into vibrational excitation via secondary electrons or energy release in chemical reactions. In the energy region where elastic nuclear energy loss dominates, energy is put directly into nuclear motion and high density cascades are often treated as thermal spikes [29]. From any of these heat sources sputtering is thought of as being produced by molecular evaporation at the intersection of the "hot" track with the surface during the short duration of the thermal transient.

Johnson and Evatt [30] have shown that the sputtering yield, $S$, from a thermalized cylindrical
region which decays in time has the general form,

\[
S = \left( \frac{dE}{dx} \right)_h \left[ \frac{1}{(KT)(CT)} \frac{P(T)}{\sqrt{(2\pi M kT)}} \right]_{T=L} \times I(L/T_0).
\]  

(1)

In eq. (1) \((dE/dx)_h\) is the electronic energy deposited per unit path length and converted into heat. The term in brackets is evaluated at temperature \(T = L\), where \(L = U/k\), \(U\) is the surface binding energy, \(k\) is the Boltzmann constant, \(K\) is the thermal conductivity, \(C\) is the heat capacity; \(P(T)\) is the equilibrium vapor pressure, and \(M\) is the mass of a molecule. The quantity \(I(L/T_0)\) depends on the track radius, and hence on the maximum initial spike temperature, \(T_0\), and on the non-linearity of the thermal diffusivity [30]. \(I\) is independent of ion energy if \(T_0 \gg L\) or if the square of the track radius is proportional to \((dE/dx)_h\) [31,27,28]. This expression depends in a more sensitive way on \(U\) (via \(L\)) than the collision cascade expressions of ref. 7.

For convenience we evaluate eq. (1) with the parameters for a high temperature gas [32], \(C = (3/2)nk\), \(P = nkT\), (where \(n\) is the molecular density) and \(K = (k/\bar{a}_D)/2kT/M\) (where \(\bar{a}_D\) is a molecular diffusion cross section). If the radius of the spike is assumed to be sufficiently small (so that \(L/T_0 \ll 1\)), eq. (1) becomes

\[
S \approx 0.011 \frac{\bar{a}_D}{U^2} n^2 (f_h)^2, \tag{2}
\]

where \(f_h\) is the fraction of the electronic energy loss \(\xi\) which is deposited as heat.

Using existing experimental data and assuming the measured sputtering yields go as \((dE/dx)^2\), values of \(f_h\) have been determined as given in table 1. As pointed out by Brown et al. [27], and as can be seen from table 1, \(f_h\) is small at high ion energies. For the parameters chosen, this fraction appears to consistently be of the order of 0.2 for the light ions on a number of condensed gases [2]. Although the agreement among rather different systems is encouraging, the physical relevance of this fraction can only be determined by examining the energizing processes carefully.

In fig. 2 we calculate \(f_h\) as a function of energy from data for He\(^+\) on H\(_2\)O assuming equilibrium stopping powers for He\(^+\) ions. If a thermal spike is operative, it is seen that the fraction of the deposited energy involved increases at low velocity. This is consistent with a decreasing track radius and a larger fraction of the energy in primary excitation and ionization. Taking account of the non-equilibrium charge state of the incident He\(^+\)

![Fig. 2. Fraction of ion energy spent as heat to describe measured yields for He\(^+\) in H\(_2\)O using eq. (2) with the data in ref. 27. (1/w) is the gas value [34]; although both I and W change for the solid, the ratio should not change dramatically.)](image)

### Table 1

<table>
<thead>
<tr>
<th>Gas</th>
<th>Ref.</th>
<th>(U) (eV)</th>
<th>(\epsilon)</th>
<th>(n \times 10^{-22}) (cm(^{-3}))</th>
<th>(W) (eV/ion pair) *</th>
<th>(A_{ee})</th>
<th>(f_h)</th>
<th>(A_c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar</td>
<td>[2]</td>
<td>0.083</td>
<td>1.67</td>
<td>2.6</td>
<td>26.4</td>
<td>12 \times 10(^{-3})</td>
<td>0.17</td>
<td>1 \times 10(^{-1})</td>
</tr>
<tr>
<td>CO(_2)</td>
<td>[6]</td>
<td>0.27</td>
<td>1.7</td>
<td>2.3</td>
<td>34.2</td>
<td>7.7 \times 10(^{-3})</td>
<td>0.19</td>
<td>3 \times 10(^{-3})</td>
</tr>
<tr>
<td>SO(_2)</td>
<td>[33]</td>
<td>0.38</td>
<td>1.99</td>
<td>1.4</td>
<td>32.4</td>
<td>1.6 \times 10(^{-3})</td>
<td>0.17</td>
<td>7 \times 10(^{-4})</td>
</tr>
<tr>
<td>H(_2)O</td>
<td>[1,27,31]</td>
<td>0.55</td>
<td>3.2</td>
<td>3.3</td>
<td>30.0</td>
<td>3.1 \times 10(^{-3})</td>
<td>0.2</td>
<td>2 \times 10(^{-1})</td>
</tr>
</tbody>
</table>

\(n^{-1}(dE/dx)_h = \xi = \tilde{\xi} \times 10^{-15} \text{ eV cm}^2\)

Experiment: \(S_{ee} = A_{ee} \tilde{\xi}^2\) (assumed form)

Thermal: \(S_{ee} = 0.011(\bar{a}_D/U^2)n^2(f_h)^2\) \((\bar{a}_D = 2n^{-2/3}, \bar{a}_D \sim 3.6 \text{ Å}^2\) for argon) from eq. (2)

Ionization: \(S_{ee} = (1/\epsilon)n/\bar{a}_D U k/\epsilon W^2\) \(\tilde{\xi} = A_c \tilde{\xi}^2\) from eq. (5)

\* Gas values [34].
ion (section 7) the calculated $f_\nu$ will be slightly larger at high energy and smaller at low energy than in fig. 2.

The validity of this thermal model depends on the formation of a cylindrically heated region. A spherical thermal spike formed by a localized energy input $E_s$ in a material with a binding energy $U$ will produce free particle motion over a distance \[ \overline{\Delta Z} \sim 0.02 (E_s/U)^{5/3} (\tilde{a}_d n^{1/3}) \] or a mini-cascade of low energy molecules (atoms) with an extent \[ \overline{\Delta Z} \sim \frac{3}{2\pi^2} (n\tilde{a}_d)^{-1} (E_s/U) \] which is the sputter depth for hard sphere collisions [7]. A cylindrical region will be formed if the spacing between the individual thermal deposition sources, $\lambda_h$, is much less than $\overline{\Delta Z}$, and the electronic to thermal conversion time is much less than the thermal dissipation time for the heated regions ($\sim 10^{-12}$ s). For the purpose of this estimate we assume $\lambda_h$ corresponds to ionization sites, $\lambda_i^{-1} = (dE/dx)_i/W, W = 30$ eV. (In all cases we have used the gas estimates of $W$; in liquid $H_2O, W \sim 20$ eV.) Therefore, the minimum stopping power required for the cylindrical approximation is $\xi = n^{-1} (dE/dx)_e > 10^{-14}$ eV cm$^2$. For $H^+$ and $He^+$ on $H_2O, \xi$ ranges from $6 \times 10^{-15}$ to $8 \times 10^{-14}$ eV cm$^2$ and therefore a spike may indeed be appropriate for describing the $He^+$ data if the energy is deposited rapidly. Seiberling et al. [28] have pointed out that the phase change at the boundary of the heated region may form a thermal trap which slows the dissipation of thermal energy, increasing the likelihood of forming a cylindrical spike. If a cylindrically heated region does not occur then the thermal sputtering yield is \[ S = \frac{\overline{\Delta Z}/\lambda_h}{U} \] where $\lambda_h \approx E_s (dE/dx)_h^{-1}$, with $E_s$ the local electronic energy deposited as heat. At very low incident ion energies ($\sim 10$ keV/amu) and heavier ions such as oxygen a thermal spike created by nuclear elastic collisions [32] may contribute significantly to the yield.

6. Ionization spike

As discussed in section 3, if charge separation is maintained for times as long as $3 \times 10^{-13}$ s, the ions along the track may be displaced by the high electric field, with resulting ejection of heavy particles from the surface of the material. This is the same process proposed by Fleischer, Price, and Walker [8] for formation of etchable tracks in certain insulators. The electric force on an ion pushing it in the $Z$ direction toward the surface in cylindrically symmetric positive core and negative sheath geometry is \( \mathcal{A}/(e/\lambda_1)^2 \), where $e/\lambda_1$ is the charge per unit length along the track, $e$ is the high frequency dielectric constant (here the frequency of interest is $\sim 10^{13}$/s) and $\mathcal{A}$ is a number the order of 1 that varies slowly with the radial dimensions of the charge separation. The sputtering yield then has the form [10,27]

\[ S = A \frac{\overline{\Delta Z}/\lambda_h}{U} \left[ \frac{e}{\lambda_1} \right]^2, \] (5)

where $U$ is the surface binding energy and $\lambda_1 = (n\tilde{a}_d)^{-1}$ is the mean free path for an atom or molecule. Since $e/\lambda_1$ is proportional to the electronic energy deposition per unit path length, $(dE/dx)_e$, according to eq. (5), $S$ is proportional to $(dE/dx)_e^2$ as in the experiments.

For energetic protons where $(dE/dx)_e$ is low, and hence the average distance between charges along the track is large compared with the radius of the track ($\sim 20$ Å), treated the geometry of the electric field as a cylinder is a poor approximation. In this case the ejection probability can be written as a product of the probability of a positive ion being produced within $\overline{\Delta Z}_s$ of the surface, $[1 - \exp(-\overline{\Delta Z}_s/\lambda_1)]$, times the probability another ion will be produced close enough to it to provide sufficient repulsion for the first ion to overcome the surface energy barrier, $[1 - \exp(-\overline{\Delta Z}_{12}/\lambda_1)]$, where $\overline{\Delta Z}_{12} = e^2/eU$. When $\lambda_1$ is large this yield is identical to that in eq. (5) using eq. (3b). In table 1 we compare the calculated and measured yields for light ions and within the uncertainty of the parameters reasonable results are obtained except for argon.

When the charge density in the track becomes quite large, in addition to direct ejections from the surface the Coulomb repulsion may serve as a cylindrical heat source as pointed out by Seiberling et al. [28]. Since the energy in the Coulomb field goes as $(dE/dx)_e^2$, the thermal yield, which is quadratic in the heat source as in eq. (1) and (2), would be highly non-linear $\sim (dE/dx)_e^4$. Such a process, however, would be strongly space charge
limited, otherwise the Coulomb energy stored in the electric field would exceed the input energy \((dE/dx)_c\). Treating the initial positive and negative ion charge distributions as gaussians with widths \(r_+\) and \(r_-\), respectively, then at high ionization density the Coulomb energy stored in the cylindrical spike per unit length is:

\[
\left[ \frac{dE}{dx} \right]_c = \frac{1}{c} \left( \frac{e}{\Lambda_i} \right)^2 \ln \left( \frac{r_+^2 + r_-^2}{2r_+ \cdot r_-} \right).
\]  

(6a)

In addition to this space charge energy, there is the potential energy of ionization which is proportional to the numbers of ions. Per unit path length it is

\[
\left( \frac{dE}{dx} \right)_i \approx I/\Lambda_i,
\]  

(6b)

where \(I\) is the average ionization energy. The sum of these contributions cannot exceed \((dE/dx)_c\), that is,

\[
\left( \frac{dE}{dx} \right)_c \geq \left( \frac{dE}{dx} \right)_c + \left( \frac{dE}{dx} \right)_i.
\]  

(6c)

Ignoring any electron kinetic energy, the energy transferred to phonons and that retained in intramolecular vibrations, the equality sign in (6c) applies. At large \((dE/dx)_c\) the logarithmic radial function in (6a) must decrease with increasing \((dE/dx)_c\) in such a way that \((dE/dx)_c\) is proportional to \((dE/dx)_c\) - not to its square. The space charge limitations on (6a) will be such as to reduce \(r_-\), the radial extent of the negative charge. Secondary electrons will be unable to move as far from the positive core of the track as they would at lower ionization density. The transition from quadratic to linear behavior occurs in the region \(\xi \sim 100\), (the maximum value of \(\xi\) for He\(^+\) in H\(_2\)O is \(\sim 75\)).

It is important to consider the disposition of the Coulomb energy of eq. 6a if the electrons are not immobilized in traps so as to provide an electric field capable of energizing ions. If the electrons remain free (and hence mobile) the Coulomb energy is transferred to the kinetic energy of the electrons as they return to neutralize the positive core of the track. If the hot electrons cool slowly they may only partially shield the nuclei. Further, this energy can be transferred to the nuclei through electron-phonon interactions or perhaps through plasma modes at the extremely high densities which will exist in the core of the track.

7. Particle charge state effect

The comparison between the sputter yield and the stopping power is generally made using equilibrium stopping powers; that is, stopping powers measured or estimated for a material with a thickness such that the fraction of beam particles in any charge state has reached a constant before the particles have lost a significant fraction of their energy. As sputtering is a surface phenomenon the sputtering layer thickness may be significantly smaller than the beam equilibration depth. If that is the case, the sputter yield should then be more usefully compared to the stopping power of the incident ion rather than the equilibrium stopping power, taking account of the change in the former through the depth that is contributing to sputtering.

In fig. 3 is given the equilibrium charge state fractions for H\(_2\)O on H\(_2\)O [35]. It is seen that He\(^+\) is the dominate ion only over an energy range \(~120\) keV to \(~600\) keV, whereas the He\(^++\) erosion data of Brown et al. [27] and Bottiger et al. [36] extend over an energy range of 10 keV to 2 MeV. This is in contradistinction to the H\(^+\) erosion data (10 keV to 1.5 MeV) for which H\(^+\) is the dominant ion over the range (\(\sim 40\) keV).

As noted in section 4 the sputter yields of H\(_2\)O ice for He\(^+\) ions at energies below the stopping power maximum are well above the yields for H\(^+\) ions if they are compared at equivalent equilibrium stopping powers [1]. The yield for He\(^+\) ions at energies above the stopping power maximum are low in a similar comparison with H\(^+\) results. A small difference has also been observed

Fig. 3. Equilibrium charge states of helium (He\(^0\), He\(^+\), He\(^++\)) (solid lines) and hydrogen (H, H\(^+\)) (dashed lines) vs energy. From ref. 35.
in the sputter yield of H$_2$O ice by H$^+$ at the same
equilibrium stopping power above and below the
maximum, the low energy yield being higher.

To measure the effects of the projectile charge
state on S, we measured the erosion rates of H$_2$O
ice for 1.5 MeV He and C ions in two different
charge states [37]. The singly-ionized beam from
the Van de Graaf was passed through a 1200 Å
carbon foil to modify the charge state. By compar-
ing the total number of incoming particles
(measured by backscattering) to the integrated
beam current, the charge state of the He and C
ions on exiting the foil were determined to be
$+1.95 \pm 0.05$ and $+3.2 \pm 0.3$, respectively, close
to the predicted equilibrium values. Using the
modified beam to erode water ice, the yield mea-
sured about 30% greater than the yield for incident
He$^+$. The He ions lost about 50 keV to the foil,
but this results in too slight a change in $dE/dx$ to
account for a measurable change in S. Therefore,
the enhanced erosion rate of the more highly-
charged particle is related to the increased energy
loss near the film surface. The higher value for the
yield brings the high energy helium results into
good agreement with the results for hydrogen.

For the 1.5 MeV carbon ions, however, nearly
identical erosion rates were measured for both the
$+1$ and the approximately $+3$ beams [37]. Ini-
tially, one would expect a larger charge state effect
for C than for He since the deviation of the
singly-ionized C beam from its equilibrium state is
greater. However, as the erosion rates for carbon
are more than an order of magnitude greater than
those for helium and the velocity is below the
stopping power maximum, the C ions probably
reach charge-state equilibrium well within the
sputtered layer in either charge state. Substantial
charge-state effects have been observed for F$^{++}$ on
H$_2$O at and above the stopping power maximum
[38].

The rate at which the charge state changes with
depth, the electronic stopping power of different
charge states and the depth contributing to
sputtering all enter the problem. They are ex-
amined below for the case of He$^+$ and H$^+$ on an
H$_2$O frost [37]. The charge state fractions are calculated from rate equations of the form [39]

$$ \frac{1}{n} \frac{df_{He^+}}{dz} = \left[-\left[\sigma_{He^+ - He^+} + \sigma_{He^+ - H^+}\right]f_{He^+} + \left[\sigma_{He^+ - H^+}\right]f_{He^+} \right] $$

which depend on removal or stripping cross sec-
tions ($\sigma$) and capture or charge exchange cross
sections ($\sigma^e$) in the material with number density
$n$, $z$ being a measure of depth. Using cross sections
for He estimated from the data of Allison [39] and
for H from Dagnac et al. [40] and Toburen et al.
[41], the equilibrium of $f_{He^+}$ and $f_{H^+}$ with depth
is shown for a few energies in fig. 4. It is seen that
H$^+$ equilibrates at a shallower depth than He$^+$,
primarily due to the large charge exchange cross
section. The proton fraction reaches $e^{-1}$ of its
total charge in about 3 monolayers while He$^+$
achieves the same level of equilibration in about 6
monolayers, or much more for the largest energies
shown. At high energies the equilibrium is very
slow as both the stripping and charge exchange
cross sections are small. In fact, above the maxi-
mum in the sum, $\sigma^e + \sigma^c$, which occurs well below
the stopping maximum, the equilibration depth
increases with energy. As incident H$^+$ is close to
the equilibrium fraction over most of the energy
range of interest and equilibrates, at low energies,
relatively close to the surface only a small excess in
sputter yield at low energy is to be expected by
referring to equilibrium stopping powers, in agree-
ment with observations. However, for incident
helium this is not the case and a further evaluation
has been made.

We have estimated the partial stopping power
for the pure He$^+$ component of the beam, $\xi_{He^+}$,
from the equilibrium stopping power. At high
energies we assume that $\xi_{He^+}$ is about four times
the value for incident protons. At low energies we
assume that $\xi_{He^+}$ and equals the equilibrium

\[
\begin{align*}
1 \frac{df_{He^+}}{d\zeta} &= \left[-\left[\sigma_{He^+ - He^+} + \sigma_{He^+ - H^+}\right]f_{He^+} + \left[\sigma_{He^+ - H^+}\right]f_{He^+}\right] \\
&= \frac{1}{n} \frac{df_{He^+}}{dz}
\end{align*}
\]

Fig. 4. Equilibration vs depth for He$^+$ (solid lines) and H$^+$
(dashed lines) in an H$_2$O gas. Energies indicated in keV.

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value at 1 keV. Using the tables of Ziegler [42] and the Bragg additivity rule to obtain an equilibrium stopping cross section with the charge state fractions in fig. 3, the partial stopping powers in fig. 5 are obtained. At 10 keV the results are uncertain as the estimate depends on small differences between the equilibrium ξ and ξ_{He}^o. Harberger et al. [43] have calculated partial stopping powers in the binary encounter approximation, BEA. At high velocities these are roughly a factor of two too small, as the BEA neglects dipole excitations (see appendix). With this in mind the ratio of ξ_{He}^+ to ξ_{He}^- is not inconsistent with their BEA results. At low energies the BEA is reasonably accurate for describing excitation and ionization energy losses for incident screened particles [44]. However, the total energy loss must include contributions from the charge-exchange cycle (stripping and excitation of the incident neutrals) and neutralization of the ions (fig. 1). In the absence of these contributions the BEA ratio of ξ_{He}^-/ξ_{He}^+ is ~1.6 at 10 keV. As the charge exchange effect will increase the ion stopping power more than the neutral stopping at the lower energies, due to the tightly bound electrons on He, the BEA ratio is not unreasonable and will be used at 10 keV.

The stopping power relevant to sputtering is an appropriately weighted average of the partial stopping powers (fig. 5) over the depth distributions of the charge state fractions (fig. 4) in the sputtering layer. More simply we display in fig. 5 the average stopping power at a depth of 4 monolayers in H_2O as a function of the initial energy of He^+ incident ions. At this depth the stopping power is seen to be significantly different than the equilibrium stopping power: by about a factor of 1.3 higher at low energies and a factor of 1.7 lower at high energies. Using such averaged stopping powers would make the data at high and low velocities much more consistent. However, the high energy factor would predict a sputtering yield discrepancy of 2.9 (on a (dE/dx)^2 basis) rather than 1.3 as measured in the carbon foil experiment. The result indicates that the depth contributing to sputtering is much larger than 4 monolayers. On the other hand, a deeper contributing layer applied to the factor between equilibrium and incident He^+ stopping powers at low energies leads to a correction much too small to bring the measured high yields into line with the H^+ results. This strongly suggests that ionization density increases, arising from smaller track radii, contribute in a dominant way to the excess sputtering yield at low energies.

8. Chemical reactions and thermal diffusion

The production of reacting species in a solid can result in material erosion due to the energy released in the reaction. If the reacting species are produced close together or are mobile in the material then such processes are likely. Further, if the exothermicity of the reaction is significantly greater than the material binding energy and if the reaction occurs near the surface then the reaction products themselves may escape. Alternatively such reactions can locally heat the material causing thermal ejection of neighboring molecules or atoms. This was one of the heat sources listed in section 5.

As the molecular binding energies are small for condensed gases, typical gas phase reaction energies are generally enough to eject matter (e.g. OH + OH + M → H_2O_2 + M + 2.12 eV). Reactions in solids are not as well understood as in gases and liquids but it is well-known that new species are observed in irradiated ice. For example, in about 10^{-14} s the reaction H_2O^+ + H_2O → H_3O^+ + OH occurs with high probability in water ice and, further, peroxyces have been observed in irradiated ice [20,24].

We consider briefly two types of reactions and estimate their contributions to sputtering: first a reaction involving two species produced at different sites along a single particle track. For this case,
if the production density is low the yield is simply,
\[ S = c \frac{\Delta Z_s}{\lambda_1} \cdot \frac{\bar{r}_i}{\lambda_2} g(T, \phi). \]  
(8)

where \( \Delta Z_s \) is the sputter (escape) depth, \( \bar{r}_i \) is the reaction radius and \( \lambda_1^{-1} \) and \( \lambda_2^{-1} \) are the numbers of the two species produced per unit path length. The factor \( c \approx 1 \) if the species are of the same type (e.g. OH + OH) and \( \sim 2 \) if they are different. The function \( g(T, \phi) \) expresses the fact that the reaction may well depend on background temperature \( T \) because of a reaction or diffusion barrier and on the total particle fluence \( \phi \) because of accumulation of competing reaction sites. An exothermic reaction produces atomic motion, in the form of a thermal spike or mini-cascade (eq. (3)), giving a sputter yield quadratic in the electronic stopping power (through \( \lambda_1^{-1} \) and \( \lambda_2^{-1} \)). “Two-hit” processes are familiar in radiation biology and radiation chemistry [45].

In a recombination reaction (electron-ion, ion-ion, etc.) on the other hand, even though two species are involved, since they are created in a single hit of the incident ion,
\[ S = \frac{\Delta Z_s}{\lambda_1} \cdot f(T, \phi), \]  
(9)

where \( f(T, \phi) \) is a recombination probability. This type of reaction also produces atomic motion but it gives a sputter yield linear in the electronic stopping power unless proximity of the recombination events is such as to produce a cylindrical spike (section 5).

The reacting species must overcome energy and spatial barriers requiring thermal activation. Such activation can occur in the transiently heated track region [46] which we described when discussing sublimation by a thermal spike. The yields produced by transient heating are nonlinear but not necessarily quadratic in \( (dE/dx) \). Further, the transient decay time must be long compared to the diffusion and reaction times of the interacting species if this process is to be important.

Thermal activation and diffusion may also occur after decay of the transient due to the background temperature of the material. The temperature dependence of \( S \) for \( D_2O \) which is dominated by \( D_3 \) and \( O_2 \) release [6] is such a case. Observations of temperature dependent sputtering yields in \( H_2O \) [1,6] \( CO_2 \) [6,47] and \( SO_2 \) [6,33], but not in argon [2] clearly point to the formation and diffusion of reaction products in the molecular solids. Erosion of the material may be due, in such cases, not to the ejection of products from the surface but rather to simple diffusion of weakly bonded products from the interior to the surface where they can escape over a small energy barrier.

If more than one activation process is involved the observed yields can be fitted to the form
\[ S = S_0 + \sum_j S_j \exp(-\Delta E_j/KT), \]  
(10)

which is the sum of contributions from eq. (8) and (9), where \( \Delta E_j \) is the activation energy for the \( j \)th process. In CO\(_2\) two steps are observed in \( S \) at about 40 K and 50 K which imply activation energies corresponding to Van der Waals type binding energies (~0.01–0.02 eV), (e.g. \( O_2 \) or CO molecules in \( CO_2 \)). For \( SO_2 \) an activation energy \( \Delta E \approx 0.056 \) eV is obtained and for \( H_2O \) \( \Delta E \) varies from about ~0.05 eV for low temperatures to ~0.30 eV at high temperatures (>125 K). The lower activations energies correspond roughly to those expected for diffusion of radicals and higher energy roughly to that for migration of trapped electrons [20].

In the case of \( CO_2 \), the steps in \( S \) are clearly related to the production of stored molecular fragments since irradiation at low temperature, followed by heating, results in additional release of material not due to further irradiation, as shown in table 2. In \( CO_2 \) a thickness dependence of the temperature dependent yield was also observed, suggesting at the highest temperatures the migrating species have diffused out from the full thickness of the material. Assuming the later, the num-

<table>
<thead>
<tr>
<th>Fluence ((10^{14} \text{ions/cm}^2))</th>
<th>Yield (^*) ((10 \text{K})) (\text{molecules/ion})</th>
<th>Increase in yield (^*) ((T \rightarrow 47 \text{K})) (\text{molecules/ion})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.6</td>
<td>39</td>
<td>250</td>
</tr>
<tr>
<td>3.2</td>
<td>47</td>
<td>122</td>
</tr>
<tr>
<td>5.6</td>
<td>65</td>
<td>50</td>
</tr>
</tbody>
</table>

\(^*\) Uncertainty in yields due to reproducibility is about 20%.
number of species created per unit path length by an incident 1.5 MeV He⁺ ion either directly or by subsequent reactions in the irradiated region is (0.5 /Å). Further, this effect saturates with increasing fluence, indicating that either reactions between neighboring tracks reduce the yield or the amount of unaffected material decreases. At \( T = 50 \) K the measured radius of influence for the temperature dependent yield is of the order of 5 Å.

The temperature dependent part of the yield will be linear in \((dE/dx)_e\), eq. (9), if it involves diffusion leading to recombination or diffusion of a radiation product which can be produced by a single excitation [1]. However, if two reacting species are required the dependence will be like that described in eq. (8) with \( g \propto \exp (-\Delta E/KT) \). This appears to be the situation for CO₂ for which \( S \propto (dE/dx)_e^2 \) at 77 K [6].

9. Relaxation of energy from vibrational and electronic states

Secondary electrons with energies below the lowest electronic level lose most of their energy in molecular condensed gas solids to vibrational excitation (~10% of the total energy loss). If these electrons remain mobile they can produce additional vibrational excitation on return to the track under the influence of the Coulomb field. The molecules have vibrational levels, weakly coupled to the lattice phonons, which are greater than or close in energy to the surface binding energy (e.g. H₂O, \( U = 0.55 \) eV, \( v_1 = 0.453 \) eV, \( v_2 = 0.198 \) eV and \( v_3 = 0.466 \) eV; O₂, \( U = 0.091 \) eV, \( v = 0.193 \) eV). Although the vibrational energy of a molecule may exceed the surface binding energy, the weak coupling with the lattice suggests that vibrational relaxation will produce a number of low energy phonons but will be inefficient in delivering energy increments large enough to produce ejection. This situation could change if the vibrational excitation density is high, resulting in a local increase in effective temperature.

In condensed gas solids roughly 10% (fig. 1) of the energy lost by a fast ion is deposited directly into well defined electronic bound excited states. These states have energies much larger than \( U \) and are populated in the track region. An additional 30–40% of the energy lost by a fast ion is stored in electron–ion pairs. This latter energy is also available in the track region if the electrons are mobile so they can return to neutralize the track core. In such a material, then, a neutral plasma with hot electrons (heated by the Coulomb field during neutralization) is produced in the core region containing ~40–50% of the total energy deposited. This energy becomes available as heat on cooling of the electrons and recombination of the electrons and ions as discussed earlier.

In condensed gas solids (or molecular clusters) single electron–ion recombination occurs in two steps. First a weakly bound excited state (exciton) is formed very rapidly (\( \alpha \sim 10^{-6} \)–10⁻⁷ cm²/s). These states relax to lower lying electronic states by electronic to nuclear energy transfer (as described in section 2, with lattice distortion and phonon production) in ~10⁻¹³ s, releasing a fraction (~20%) of the stored ionization energy. The decay of the deep lying states, however, is slow in low temperature solids, as the ground state potential surface is not degenerate with the excited state surface near the latter’s equilibrium point. Hence luminescence (~10⁻⁹ s), generally accompanied by lattice relaxation, will compete favorably with exciton relaxation to the ground state at low temperatures [48,49]. If 20% of the full recombination energy becomes available then the sputter yield of eq. (9) for a 1.5 MeV proton would be \( S \sim 0.05 \) (\( E_i \sim 2 \) eV, \( \lambda_i^{-1} = n\xi/W, W = 30 \) eV, \( W \sim 1 \)), the same order of magnitude as the observed \( S \sim 0.1 \) for H₂O ice. This amount of energy is also consistent with table 2 in which approximately 20% conversion of electronic energy to heat, \( f_s \), was found to be required to account for the slope of \( S \) vs \( \xi^2 \) for the several gases studied.

The nature of the electronic relaxation process can change dramatically if the excitation or electron–ion density is high. In this situation the wave functions of the free electrons overlap significantly, interfering with localization of the electron on a single center. This may produce a number of effects. Electron “neutralization” will occur with high probability to a repulsive state between neighboring positive centers which energetically distorts the lattice allowing relaxation of at least one electron to the ground state. The yield for ejection by such events is now non-linear in \((dE/dx)_e\) requiring at least two closely spaced ions [e.g. eq (8)]. Using a reaction radius \( r_t \sim \pi^{-1/3} \), \( g = 1, E_i = 10 \) eV, and \( \lambda_i \) as above, then for a 1.5 MeV proton \( S \sim 0.1 \) similar to the experimental
result. (Note: this is roughly equivalent to the estimate in eq. (5) in the limit of large $\lambda_{\alpha}$.) For the case above, in which the electron density is high, recombination directly to a low lying state or the ground state may be initiated by electron–electron collisions. Such an Auger recombination is dominant at high densities in semiconductors [50]. The recombination energy is deposited in further heating of the electrons and is subsequently converted to nuclear motion by phonon generation, as discussed earlier. The rate of energy transfer depends strongly on the plasma density. Such a density dependence is present in the result shown in fig. 2. In the low energy region ($v < v_0$) where the track radius is smaller than at high energies, the full recombination energy is required to be rapidly deposited as heat to account for the observed erosion yield.

10. Summary

Possible erosion (sputtering) mechanisms for condensed gas films excited by fast ions have been considered. There are three principle factors that control the erosion process. The first is the rate at which electrons, produced in primary, secondary or higher order ionization events, return from their largest radii of outward excursion from the ion track to neutralize the positive ions. In general, because electrons ionized to the conduction band cannot be rapidly trapped in states in which they have low mobility, the neutralization is fast compared with the times ($\sim 10^{-13}$ s) required for heavy particles to accelerate in the transient space charge field and escape from the surface (Coulomb ejection). However, if electrons thermalize slowly the screening of the positive ion track may be incomplete for times $> 10^{-13}$ s. The second factor is the rate of transfer of electronic energy from the electron–positive ion plasma that has been formed to the motion of the nuclei. The transfer rate is fast or slow compared with the heat transport away from the track region. If it is fast, a high temperature thermal spike is formed and sublimation can cause material erosion. The third factor is the decay of the bound but highly excited electron–hole system. Even in rare gas solids molecular-type Franck–Condon transitions between electronic states produces nuclear motion [49]. The density of the electron–ion plasma is high; even for the case of 100 keV H$^+$ ions in H$_2$O ice ($\xi = 25$) it is $\sim 10^{21}/$cm$^3$. At this density, Auger type recombination processes keep the plasma hot and transferring energy to the optical phonons of the lattice relatively efficiently.

In molecular solids additional processes may occur. Irradiation of these solids produces reactive species and in some solids electron trapping can occur. The trapped electrons allow the possibility of persistent microscopic fields, with resultant Coulomb ejection if the high frequency dielectric constant is not large. The trapped electrons and other primary radiation products can also react to produce new species which may be ejected at the surface and escape. These erosion processes are therefore temperature dependent and have been observed when eroding H$_2$O and CO$_2$ films.

The charge state of incident ions is important in condensed gas film erosion because the depth required to establish charge-state-equilibrium may be much larger than the depth contributing to the erosion process. Contributing depths may be tens of ångströms. The ion velocity (for equal electronic stopping power) is also important, apparently, through changes in the plasma density along the ion's track, because of changes in the radius of the positive ion core of the track.

A great many aspects of the processes contributing to erosion are still quite incompletely established. The time and spatial scales in which the competing events occur are a challenge to both theory and experiment.

One of us, REJ, would like to acknowledge a number of useful discussions with M. Inokuti, U. Fano and C. Watson.

Appendix

The erosion models discussed in this paper were based on the use of the stopping power. To elucidate the primary processes responsible for the observations, comparisons should also be made using cross sections for events initiated by the incident ion. Toward this end we expand somewhat on our earlier description of these processes and include additional references for cross section data and models. In most cases references and discussion refer to gas phase interactions which may differ significantly for processes occurring in

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condensed gases (e.g. $W \sim 30$ eV for gaseous H$_2$O but $W \sim 20$ eV for liquid).

Whereas the stopping cross section consists at high incident ion energy of roughly equal contributions from dipole and close collision contributions, the ionization cross section is dominated by dipole excitations. Both cross sections exhibit a similar dependence on energy ($\sim \ln(E/E')$) with different values of $E'$, so that the ionization cross section decreases somewhat more rapidly at high energies. The close collision contribution goes as $\sim 1/E$ and determines the behavior of cross sections for non-dipole "forbidden" transitions. The maxima in the excitation cross sections is determined, roughly, by that velocity at which the uncertainty in the energy levels during the collision is of the order of the transition energy, $\Delta E = (v_{\text{max}}^2 \sim \Delta E \cdot \bar{a} / h$, where $\bar{a}$ is an atomic size; e.g., the orbital radius of the electron of interest). This is often referred to as the Massey criterion, which for ionization is roughly equivalent to, $v_{\text{max}} \sim v_0$ as discussed earlier. Since the stopping cross section weights these cross sections by energy transfer, the more energetic processes predominate hence the maximum in the stopping cross section occurs at a velocity greater than $v_0$.

At low energies, if $v < v_0$ but the energy is well above the threshold energy, the close collision, impulse contribution to ionization or excitation cross section increases as $E^2$ or more rapidly. However, low velocity ions produce significant distortion of the electronic charge cloud (viz. the charge exchange cycle). The total stopping cross section therefore is directly related to the electronic drag force on the incident ion and hence goes as $E^{1/2}$. The excitation and ionization cross sections are all system dependent at low velocity and are best described by treating the electrons as being shared by the colliding heavy particles. For those systems for which low energy ionization cross sections are available a dependence on energy which is more nearly linear is reasonable. For excitations, the effective level spacing in the Massey criterion may change significantly in the interaction region, due to distortion of the charge cloud, in which case the cross sections can be large down to quite low energies. The impulse and distortion ("molecular") contributions are clearly seen in inner shell ionization cross sections. For these processes $v_0, \Delta E_i$ and $\bar{a}$ become the mean velocity, removal energy and mean radius of the inner shell electron. Whereas the close collision, impulsive process determines the ionization by light ions, for incident ions with a nuclear charge similar to that of the target atoms, charge sharing will cause the cross sections to remain large down to much lower energies (e.g. keV energies in many systems). In all cases the words large or significant when referring to cross sections are related to the area $\pi a^2$.) This suggests that in considering the differences in erosion yield between the heavy and light ions the role of inner shell processes should be examined. Based on the above discussion, the maximum in the erosion yield of H$_2$O by He$^+$ shows a closer correlation with the ionization cross section than with $(dE/dx)$, based on the above.

Reference material on cross sections

For many systems discussed in the text accurate data is not available over the energy range of interest. Therefore understanding models and using scaling laws based on incident electron data is useful. References are listed once although they may contain information in several categories below.

Cross section and stopping power models
A large number of texts are available; a few are listed below:
R.E. Johnson, An introduction to atomic and molecular collisions (Plenum, New York, 1982).

Stopping power and range data:

Ionization and excitation cross sections and $W$ values – outer shell
C.F. Barnett, J.A. Roy and J.C. Thompson, Atomic and molecular cross sections of interest in controlled thermonuclear

H. Bichsel et al., Average energy required to produce an ion pair ICRU Report 31 (7910 Woodmont Ave., Washington D.C. 20014, 1979).


Ionization and excitation cross sections and $B$ values – inner shell


Charge exchange and stripping cross sections and equilibrium charge states

H. Tawara, Atomic and Nuclear Data Tables 22 (1978) 491.


J.B. Marion and F.C. Young, Nuclear reaction analysis – graphs and tables (North-Holland, Amsterdam, 1968).


Spatial deposition of energy


Data retrieval systems for cross sections


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