Particle emission induced by ionization tracks in water ice

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Abstract

We study electron emission and sputtering during irradiation of amorphous water ice at 60 K by H⁺, D⁺, He⁺, Li⁺, Be⁺, B⁺, C⁺, N⁺, O⁺, F⁺, and Ne⁺ ions in the energy range from 10 to 100 keV. We find that for constant velocity (5 keV/amu) ions the dependence of the sputtering yields with projectile atomic number Z is proportional to the square of the Z-dependence of the electronic stopping power dE/dx, using dE/dx values predicted by Yarlagadda, Robinson, and Brandt. The electron yields increase sublinearly with dE/dx, indicating the strong influence of un-neutralized holes in the ionization track produced by the projectiles.

1. Introduction

Fast ions moving through condensed matter produce a track of excitations and ionizations that can have lasting effects depending on the properties of the medium [1-4]. A core of unbalanced holes results [5] from the fact that electrons receive almost all of the energy transfer which ejects them from the path of the ion. The central problem in describing the track is to understand the evolution of the electrons, holes, and excitations with time after the primary excitation events. In a metal the ionizations are screened very quickly by the free electrons (within 10⁻¹⁶-10⁻¹⁵ s), whereas the ion core in an insulator may survive for much longer times (> 10⁻¹¹ s). If the density of holes and liberated electrons is high, the behavior of the charged particles in the track becomes extremely complex, until neutralization eventually occurs.

The persistence of an unbalance of excess holes in the core of a track in insulators can damage the material through the action of the very large Coulomb repulsion between holes. This type of radiation damage is important in radiation biology, where it may cause the destruction of living cells [2,3]. In certain materials the damage tracks can be made visible and counted, and the information used in radiation dosimetry and in the dating of rocks [1].

The emission of particles (electrons, ions, neutral species) from the track of a projectile entering the insulator [6-9] depends on ionization events that take place not only immediately below the surface, but further into the material as well. Because ejected electrons cannot return to the track to recombine with the holes, the effects of unbalanced Coulomb forces persist until the holes diffuse away (usually slowly) eventually reaching a conducting electrode where they neutralize.

The important process of ejection of electrons from insulators is not well understood due to uncertainties in the intervening physical mechanisms. Electrons may be excited into the conduction band by transitions from the valence band or core levels either produced directly by the projectile or through cascade multiplication of the excited electrons [10,11]. As is common to other ionization processes, the energy distribution of the excited electrons falls off very rapidly with electron energy [12]. Most of the excited electrons will have insufficient energy to excite other electrons across the band gap so they will lose energy slowly through excitation of atomic vibrations as they move away from the point of ionization. For dilute tracks, this motion will be mainly affected by the residual parent hole and by strong elastic scattering with atomic cores which tends to randomize the electron motion. Those electrons with a sufficiently large kinetic energy component perpendicular to the planar surface barrier (of magnitude equal to the electron affinity of the surface) will be ejected from the solid. The time between excitation and emission is expected to be small, of the order of a few fs, the value estimated for metals [13]. In this limit of dilute tracks, the number of emitted electrons is proportional to the number of electrons excited per unit path length, which is in turn proportional to the electronic stopping power of the projectile (dE/dx) at high velocities [10,11].

The termination of the track on the surface implies that the events which lead to radiation damage in the bulk of the solid can now eject atomic and ionic species, though most are neutral [14]. This form of sputtering can be much more important than elastic sputtering by direct momen-
tum transfer by the projectile to lattice atoms, particularly for condensed gas solids [7]. Unlike elastic sputtering, where ejection occurs typically within a ps after the projectile hits the surface [15], electronic sputtering can occur over a much longer time scale (> μs). The energy required for atomic motion does not necessarily come from Coulomb repulsion between holes (this process, in fact, has not yet been conclusively demonstrated) but from the decay of excitons into repulsive neutral states or, in molecular solids such as ices of water or carbon monoxide, from more complex processes involving radicals [16–19].

The case of water ice is particularly interesting because of multiple applications. Among them are radiation biology, since amorphous ice is a good analog to liquid water, and astrophysics, where ices on cosmic grains and outer solar system objects are bombarded by ionizing radiation [19]. Brown et al. [17,20] have shown that ice can be sputtered readily by fast protons and found that the sputtering yield is proportional to the square of the electronic stopping power at MeV energies but deviates from this behavior for protons of tens of keV with similar values of electronic stopping power [20].

The energy release processes that lead to particle ejection during electronic sputtering of ice are not known in detail. Presumably, the ionizations and some of the higher-energy excitations initiate a sequence of processes from which one or several radicals are generated. When radicals from different ionization events react, some of the processes are sufficiently exothermic that intact molecules or fragments can be ejected [7,19,21,22].

In this work we present studies of the dependence of electron yields and sputtering on electronic stopping power for H+, D+, He+, Li+, Be+, B+, C+, N+, O+, F+, and Ne+ ions in the energy range from 10 to 100 keV. We analyze the data in terms of the density of the ionization track.

2. Experimental

Experiments were performed in an ultrahigh vacuum chamber (Fig. 1) connected to a 120 keV ion accelerator. The base pressure in the chamber was \( \sim 10^{-10} \) Torr, rising to \( 2-5 \times 10^{-9} \) Torr during the measurements. The rotatable target assembly is cooled by a closed-cycle refrigerator which can reach 20 K. A gold-coated quartz-crystal microbalance positioned at the target is used to measure the sputtering yields and film thickness. A second crystal mounted behind the target (not shown in Fig. 1) is used in a heterodyne method as a reference to compensate the temperature dependence of the crystal frequency [23]. In this system, the areal mass sensitivity corresponds to about 0.1 monolayer of ice. Surrounding the target is an aluminum cylinder which acts as an anode for electron collection (when biased at \(+300 \) V) as well as a thermal shield against the heat from the chamber walls. Between the target and the anode is a 92% transparent nickel screen which is biased at \(-90 \) V from the anode to suppress secondary electron emission from the anode.

Amorphous ice films of 1200–1500 Å were grown by flowing vapor of outgassed high purity water through a capillary array doser onto the target crystal held at 60 K, then bombarded by 10–100 keV ions at normal incidence. The ranges of these ions in ice are all greater than the film thickness. Sputtering yields are determined by measuring the ion beam dose (typically \( \sim 10^{14} \) ions/cm\(^2\)) and the frequency change of the crystal. The electron yields (possibly including a very small fraction of negative ions) are determined by measuring the ion beam current to the target assembly and the electron current to the anode.

3. Results and discussion

3.1. Sputtering

The sputtering yield \( Y_s \) from water ice induced by 10–90 keV protons is shown in Fig. 2. Sputtering induced by ion bombardment depends primarily on the binding energy of surface atoms and the stopping power of the incident ion [7]. The dependence of the sputtering yield on the electronic stopping power is often analyzed in terms of a power law

\[
Y_s = c(dE_x/dx)_x^n,
\]

where \( c \) is a constant for a given material and \( n \) is determined empirically. The value of \( n \) is related to different physical processes: \( n = 1 \) implies that sputtering results primarily from individual excitation or ionization events, while \( n = 2 \) implies that excitations or ionizations interact to give rise to sputtering. Values in between and beyond
indicate that varying degrees of interaction processes are responsible for sputtering. For our data in Fig. 2 we obtain \( n = 1.3 \pm 0.2 \), using the experimental \( dE/dx \) values of Bauer et al. [24] which we extrapolate below 30 keV.

In Fig. 3 data for sputtering as a function of atomic number of the projectiles are presented together with the corresponding stopping powers, at a constant velocity corresponding to 5 keV/amu \( (9.8 \times 10^7 \text{ cm/s}) \). The square root of the sputtering yield as well as the stopping power have been normalized to the proton value. Since there are no measurements of stopping powers of ice for heavy projectiles, we use the \( Z \)-dependence of stopping power given by Yarlagadda et al. [25], which have been shown previously to describe accurately the \( Z \)-dependence of the electron yields from aluminum [26], valid in the limit of low velocities. The \( Z \)-dependence of stopping power \( (dE/dx)_Z \) for slow ions at constant velocity is given by:

\[
(dE/dx)_Z = CZ^2[1 - \exp(-0.95Z^{-2/3})]^2,
\]

which describes the overall trend but not the structure apparent in the experimental data of Fig. 3 as \( Z \) goes from 5 to 6. We believe this structure is due to shell effects \((Z\text{-oscillations [26]})\) in the stopping power. Unlike the case of sputtering by protons of different energy, we see that changing \( dE/dx \) at constant velocity produces a quadratic dependence of the sputtering yield with stopping power, as found for MeV protons. These two apparently inconsistent results can be reconciled by a velocity dependent \( c \) factor in Eq. (1).

3.2. Electron emission

It is well known from the electron emission literature on metals that the electron yield is proportional to the stopping power [10,26–29]. This is a direct result of the fact that the electrons are dominantly produced by cascades rather than primary ionization alone [10,30] which is proportional to the ionization cross section. Primary ionization alone is important for slow projectiles on insulators with a large band gap, like water ice. However, since the dependence of the stopping power [24] and the ionization cross section [31] with proton energies above 10 keV are fairly similar, and since the ionization cross section for other ions is not available, we will use the existing stopping power data.

The electron yields for protons increase with energy from about 1.7 electron/proton at 5 keV up to about 3 electrons/proton around 70 keV in the region of the maximum of \( dE/dx \) (Fig. 2). The yields increase slower with energy than expected from the variation in the stopping power; we will return to that point below. The electron yield was found to be independent of the beam current density over an order of magnitude around the current densities used in these measurements \((\sim 0.2 \mu\text{A/cm}^2)\), indicating that electron emission from these thin films is a single incident ion effect and does not involve macroscopic charging.

The electron yield for a number of ions incident on water ice with energy 5 keV/amu is shown in Figs. 3 and 4 as a function of the atomic number of the projectile, \( Z \). The yield increases towards a value around 3.6 electrons/ion for larger atomic numbers. The electron yield for a number of ions incident on aluminum [26] is also shown in Fig. 4 to compare to the case of metals. One notes that \( \gamma \) for aluminum is much lower than that from water ice for light projectiles, but that the ratio \( \gamma_{\text{ice}}/\gamma_{\text{Al}} \) decreases to a value around 1.4 for high \( Z \). The lower electron emission for aluminum than for ice is consistent with the fact that metals generally have a low \( \gamma \) compared with

![Fig. 2. Sputtering and electron yields of H$_2$O ice films vs proton energy. The hollow circle and filled triangle are 10 keV D$^+$ points. The squares are sputter yields from Brown et al. [20]. Only some representative relative error bars are shown, while the lines are to guide the eye.](image1)

![Fig. 3. Electron yields and sputter yields from water ice as a function of the atomic number \( Z \) normalized to the proton yield; stopping power from Yarlagadda et al. [25] normalized to the proton stopping power.](image2)
insulators, but the strong decrease in the yield ratio suggests that an additional effect due to high ionization densities is acting in the insulator.

The Z-dependence of the electron yield from aluminum has been shown to be described very well by the stopping power expression from Yarlagadda et al. [25] mentioned above. Unlike the case of Al discussed by Alonso et al. [26], where there is a good agreement between the Z-dependence of the electron yields and the Z-dependence of the stopping power, for water ice, the \( y(Z) \) dependence lies far below the stopping power curve (Fig. 3). Therefore, one is led to the conclusion that electron emission from water is not just determined by the stopping power, but is strongly influenced by track processes. The decisive difference between Al and ice is that, unlike the case of Al, the ions in the track of ice are not screened during the electron ejection process. As indicated schematically in Fig. 5, the unbalanced holes in ice attract the electrons, preventing them from escaping, and, consequently, reduce the yield for a high hole density, i.e., a high stopping power. The magnitude of this effect caused by the unbalanced holes will be studied quantitatively in the following section on the basis of a simple model.

3.3. Model for track effects in electron emission

The electron yield from a metal can be well approximated by [10,28]:

\[
y = B \frac{dE}{dx}.
\]

\( B \) is a material dependent factor that takes into account the energy distribution of electrons in the solid and the transmission of electrons through the surface barrier:

\[
B = \int f(E)T(E) \, dE.
\]

As mentioned in the introduction, the internal energy distribution of excited electrons, \( f(E) \), is a decreasing function of \( E \), but the precise shape is not known for ice. We model it as \( f(E) = b/E^2 \) where \( b \) is a constant and assume that this functional form is independent of the track density. Since low energy electrons undergo strong elastic scattering inside the solid, they will arrive at the surface as an isotropic flux in the half space inside the solid. The probability of transmission through the planar surface barrier of magnitude \( U \) is given by [10]:

\[
T(E) = \frac{1}{2} \left( 1 - \sqrt{\frac{U}{E}} \right).
\]

The sublinear increase of the electron yields with \( dE/dx \) observed here has been reported by Jacobsson and Holmén [32,33] for ion bombarded SiO\(_2\). These authors proposed that it is due in part to an additional barrier created by the space charge of the track. They fitted their data using an additional planar surface barrier to account for the space charge. We attempt here to calculate the average track potential acting on the escaping electrons. Furthermore, we assume that this potential will act similarly to a spherical barrier which is added to the planar barrier that the electron must overcome to escape. The spherical barrier is included by changing the limits of integration in Eq. (4) and by simply shifting the electron energy in the transmission function by \( U_s \). Then:

\[
B = b \int_{U_s}^{\infty} \frac{dE}{E^2} \left( 1 - \sqrt{\frac{U}{F - U_s}} \right).
\]

The form of the transmission function accounts for both barriers: for \( U_s = 0 \) the transmission function is identical to the planar value (Eq. (5)), whereas for \( U_s \gg U \), it approaches the standard expression for a spherical barrier of height \( U_s \). Integration yields

\[
y = \frac{b}{U_s} \left[ 1 - \sqrt{\frac{U}{U_s}} \left( \frac{\pi}{2} - \arctan \sqrt{\frac{U}{U_s}} \right) \right] \frac{dE}{dx},
\]

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which tends to \( \gamma = (b/U_s)(dE/dx) \) for large track potentials.

Calculation of an effective potential \( U_s \) is based on the assumption that the incident projectile produces a line of holes from the surface to the substrate separated by \( W/(dE/dx) \) where \( W \) is the mean energy required to create an electron–hole pair (29 eV for water [34]). The potential is calculated at the surface by assuming that the number of unbalanced holes is equal to \( \gamma \) and that the potential is produced from the total charge placed at a depth \( L/2 \), where \( L = \gamma W/(dE/dx) \). This leads to a potential \( U_s \)

\[
U_s = \frac{2q^2}{4\pi\epsilon} \frac{dE}{dx} \frac{1}{W},
\]

where the dielectric constant \( \epsilon/\epsilon_0 = 1.7 \) [35], appropriate for energy transfers of eVs and tenths of eV. Using the density of 0.82 g/cm\(^3\) for vapor deposited water ice [36] we obtain \( U_s = 0.161(dE/dx) \) (eV/(10\(^{15}\) H\(_2\)O/cm\(^2\)), which gives a track potential of \( \sim 9 \) eV for the highest stopping power used.

Fig. 6 shows the results of plotting \( \gamma = B(dE/dx) \) from Eq. (7) with the data from Figs. 2 and 3. The stopping cross sections used for the proton data are from Bauer et al. [24] and those used for the other ions are obtained from the proton data using Eq. (2). For these calculations we applied the potential \( U_s \) obtained from Eq. (8) and in \( W \) [38].

4. Conclusions

Electronic sputtering and electron emission for keV ions incident on water ice are determined by the electronic stopping power and additional processes in the ionization track. The electronic sputtering yield grows linearly with the square of the electronic stopping power but the proportionality factor is velocity dependent for slow ions. The electron yield induced by light ions is larger for water ice than for metals, but the yield grows sublinearly with electronic stopping power, due to the increased barrier produced by unbalanced holes in the insulator. A relatively simple model that includes a track potential acting as a spherical barrier can account for this effect.

This model may also be used to explain reduced electron yields from insulator surfaces bombarded by energetic biomolecular ions [39].

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References


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