Role of electron capture in ion-induced electronic sputtering of insulators

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(Received 20 February 2007; published 12 March 2007)

Measurements of the sputtering yield of solid O2 by 25–240-keV H+ show that it is double valued in its dependence on electronic stopping power. We propose that this is because the electronic sputtering yield is dominated by repulsion of ions in the ionization track of the projectile which, at low velocities, is augmented near the surface due to the additional ionization resulting from electron captures. This process may also be responsible for enhanced radiation damage in insulators, in particular in the production of fission tracks.

Ionization effects in insulators by fast ions are evident in a wide range of areas, including sputtering, dating by nuclear fission tracks, destruction of interstellar matter by cosmic rays, and medical therapy using ion beams. Some of the most basic information on these effects has come from the study of the sputtering of condensed gases and fission tracks, both occurring through the conversion of the electronic energy stored in electronic excitations and electron-hole pairs into repulsion between lattice atoms or molecules. Atoms set in motion when repulsive states evolve can be ejected directly or initiate a collision cascade of recoil atoms in the solid leading to sputtering or the amorphization of the ion track. The transfer of electronic to recoils depends strongly on specific details of the material, and its description can only be done in very few cases, due to the lack of knowledge of the excited electronic states in the solid state. For this reason, the understanding of ionization effects is usually limited to their correlation to the linear energy loss or electronic stopping cross section $S_e = dE/Ndx$ as the ion enters the solid. Here, $dE/dx$ is the energy loss per unit path length and $N$ is the atomic density. In the case of sputtering, it is often assumed that the yield $Y$ (molecules ejected per incident ion) is proportional to the energy deposited near the surface (several monolayers, depending on the material), which can be considered to be proportional to the energy lost by the ion in that region. However, there is evidence that parameters other than the stopping power affect the sputtering yields for a given material. Since $S_e$ increases at low $E$, passes through a maximum, and then falls at high $E$, there are two ion energies for a given value of $S_e$ and one would expect the same sputtering yield in both cases if the deposited energy was the only ion property of importance. Instead, what is found is that there is a “loop” in the $Y(S_e)$ dependence where, for the same $S_e$, $Y$ is double valued, being larger at low than at high ion energies, as well documented for Ar (Ref. 1) and H2O.3

In addition, $Y$ is often not proportional to $S_e$ but depends on a higher power $n$ ($Y \sim S_e^n$), with $n$ up to 4, depending on the type of condensed gas and the type and energy of the projectile.1 For instance, $n=1$ for Ar, and $n=2$ for water ice, a case of great astrophysical importance because of the role of sputtering in the erosion of surfaces and formation of atmospheres around icy bodies, such as the Galilean satellites.4,5 The quadratic dependence has been thought to signal that sputtering is dominated by the interaction of pairs of excitations, such as the screened Coulomb repulsion from ionized molecules.3 It has also been suggested that the quadratic behavior is caused by “thermal spikes,” temporary hot regions caused by the energy deposition of the projectile, from which evaporation can transiently occur.

The sputtering of solid oxygen has been a test bed for theories of thermal spikes, in particular because $Y$ at high energies shows an interesting nonlinear dependence on $S_e$, which has been described as a transition between linear and quadratic with increasing $S_e$.6–8 A difficulty of using solid oxygen to test models is the apparent discrepancy between the $Y(S_e)$ dependence obtained with MeV ions,6,7 keV ions,9 and keV electrons.10 As in the case of the loop behavior, this raises the question of the existence of factors other than $S_e$ that determine the $Y(E)$ behavior.

Here we examine the sputtering of oxygen by measuring $Y$ over the intermediate proton energy range 25–240 keV, encompassing the maximum of $S_e$ and bridging the keV and MeV data, and by improving the modeling of the distribution of ionization in the material. Besides the fundamental character, and the potential applications to ionization damage in wide-band gap oxides, our interest in solid O2 resides in understanding the effect of energetic ions from the Jovian magnetosphere impacting solid oxygen in cold patches on the surface of Jupiter’s moon Ganymede,11 eroding the surface and possibly contributing to the formation of ozone detected by the Hubble Space Telescope.12 In addition, solid oxygen accreted onto icy mantles in interstellar dust grains13 will be sputtered by stellar winds and it is of interest to know the efficiency of this process.

The experiments reported below indicate that previous discrepancies between keV and MeV data are due to $Y(S_e)$ being double valued. We find that the data are consistent with a screened Coulomb repulsion model if we include the additional ionization produced by electron capture by the projectile when it enters the solid, a process that is important at low projectile velocities. We propose that the effect of electron capture is of general importance and can account for the loop behavior in sputtering and other near-surface radiation effects in insulators.

The measurements were done in an ultrahigh vacuum ($\sim 1 \times 10^{-10}$ Torr) chamber equipped with a gold-coated quartz-crystal microbalance with a sensitivity of $\sim 0.1$ monolayers, mounted at the tip of a LHe-cooled manipulator. Oxygen films were condensed onto the microbalance at 5 K by dosing pure O2 gas through a microcapillary array.3 The film growth was done at $\sim 0.7$ nm/s to a thickness of typically $\sim 400$ nm, smaller than the ion range to avoid electrostatic charging of the films. The irradiations were at normal inci-
moving molecules arriving at the surface are ejected if they can overcome the surface binding energy. We note that, for light projectiles, the density of the deposited energy is insufficient to generate nonlinear collision cascades (collisions between moving recoils). Therefore the nonlinearity with stopping power observed for O$_2$ should occur in step (i), i.e., the conversion of energy deposition into molecular motion.

We must first mention sputtering processes that have been observed with low-energy incident electrons (low $S_e$). A strong increase in the yields above $\sim 12.5$-eV electron energy suggests that the main prerequisite to sputtering may be the formation of ion pairs followed by dissociative recombination, which releases $\sim 5$ eV. In addition, many other channels exist, some involving neutral and ionized ozone. All these processes by themselves can initiate collision cascades but since the number of single dissociation events is proportional to the energy deposition, they should lead to sputtering yields that are linear with $S_e$, in contradiction with much of the evidence in Fig. 1.

Thus another type of process besides single dissociations is needed to explain the nonlinear dependence on $S_e$. We disregard hot spikes because, although the $S_e$ dependence appeared quadratic in simplified analytical models, more accurate molecular-dynamics simulations of hot spikes resulted in a linear behavior. A nonlinear dependence of $S_e$ is obtained in the most recent molecular-dynamic simulations of Coulomb explosions that show that the sputtering yield is quadratic in the ionization per unit path length near the surface, $dY/dx$:

$$Y \propto (dY/dx)^2.$$  

(1)

In the bulk of the sample, $dY/dx$ is related to the stopping cross section by $dY/dx = S_e N/W$, where $W$ is the mean energy to produce an electron-hole pair ($\sim 30$ eV).

We note in Fig. 1, however, that neither a linear nor a quadratic dependence of the sputtering yield on $S_e$ can fit all the experimental data. In addition, the mechanisms discussed above cannot explain the loop shown by Fig. 1. A common assumption has been that the loop, or velocity effect, as it is also called, is due to the dilution of the track of deposited energy as its radius increases with ion velocity. The track radius is determined by the range of ionizing secondary electrons (the ultratrack). We approximate its size in solid O$_2$ to that of condensed water, for which a Monte Carlo simulation shows that the radius containing 80% of the energy deposited by protons from 10 keV to 1 MeV is $<3.5$ Å and increases by only $\sim 10\%$ between 100 and 300 keV, whereas $Y/S_e$ falls by 70%. Therefore, in our energy range, the variation of the radial distribution of the deposited energy is not responsible for the different sputtering yields observed for low- and high-speed ions with the same stopping cross section.

Instead, we propose that the electronic sputtering yield at low velocities is dominated by (screened) Coulomb repulsion between ions, which is enhanced near the surface of the solid by the additional ionization produced by electron capture by the projectile. We show below that the inclusion of this process can explain the nature of the loop behavior in Fig. 1.

Near or below the energy of the stopping maximum, pro-

![Image](image_url)
ions may capture efficiently an electron near the surface, forming neutral H which can be subsequently ionized in an electron loss event. Electron capture results in an ionized target molecule (from which the electron was captured), while electron loss also produces a free electron. At high velocities, the cross section for electron capture, $\sigma_C$, is so small that the projectile remains a proton within the depth responsible for sputtering (a few nm in the solid) and ionization results from proton-O$_2$ collisions and collisions involving secondary electrons.

We now calculate the linear ionization density $dJ/dx$ resulting from individual collisions, taking into account the change of charge of the ion beam during penetration. The fraction of projectiles that are H$^+$ is given by 23

$$ f_0 = \frac{\sigma_C}{\sigma_C + \sigma_L} \left[ 1 - \exp\left[ -(\sigma_C + \sigma_L)N x \right] \right] $$

and

$$ f_1 = 1 - f_0, $$

where we have neglected the small fraction of H$^-$. The protons and hydrogen atoms ionize the solid with cross section $\sigma_{sl}$ and $\sigma_{0t}$, respectively (we neglect here multiple ionization) producing a track of ionizations with a linear density distribution $dJ/dx$,

$$ dJ/dx = \alpha N \left[ f_1 (\sigma_{sl} + \sigma_C) + f_0 \sigma_{0t} \right], $$

where the multiplication factor $\alpha$, which takes into account the additional ionizations produced by secondary electrons is given by

$$ \alpha = \frac{S_c}{W} \left[ f_1 \left( \sigma_{sl} + \frac{\sigma_C}{2} \right) + f_0 \left( \sigma_{0t} + \frac{\sigma_L}{2} \right) \right]^{-1}. $$

In this equation, the expression between brackets describes the production of target ions and free electrons in primary collisions by the projectiles without considering ionizations by secondary electrons. While the electron capture and loss processes only produce one charge (ion or electron), the measured $W$ gives the number of charge pairs from all processes.

As a result of the asymmetry introduced by the surface, the charge fractions [Eq. (2)] and therefore $dJ/dx$ depend on depth. Figure 2 shows the result of a calculation of $dJ/dx$ vs depth for 5–500-keV H$^+$ using tabulated gas-phase cross sections and charge fractions23,25 in Eqs. (3) and (4). This entails the common approximation of using gas-phase values for describing solids with weak intermolecular binding. One can see, e.g., that a 35-keV H$^+$ produces a similar number of ions in the bulk as a 200-keV H$^+$ (they have a similar $S_c$), but 40% more ions near the surface.

Figure 3 shows $dJ/dx$ for fixed values of depth and as function of proton energy, indicating that near the surface the total number of ionizations cannot be evaluated from just the stopping cross section [Eq. (1)]. As expected, the ionization density is equal to $S_c N/W$ when evaluated in the bulk. The enhancement due to electron capture disappears at around 200 keV, corresponding to the fall in the ratio of the electron capture to ionization cross sections shown in Fig. 3 (top).

We now use the results of the molecular-dynamics simulations20 that show that sputtering is quadratic in $dJ/dx$ [Eq. (1)] but taking into account the depth distribution of $dJ/dx$ and an exponential decay of the collision cascade with depth of energy deposition,26 described by a characteristic depth $\lambda$:

$$ Y \approx \int_0^\infty (dJ/dx)^2 \exp(-x/\lambda) dx. $$

The result of this calculation is shown in Fig. 4 together with data from Fig. 1 as a function of the projectile energy rather than the electronic stopping cross section, using $\lambda = 5$ Å, the value that best fits the energy dependence of the
FIG. 4. Sputtering yields vs projectile energy. ●: this work; △: Gibbs et al. (Refs. 7 and 8); ◻: Ellegaard et al. (Ref. 9). The solid line is a fit of Eq. (5) with $\lambda = 5$ Å. The dotted line is the energy dependence considering linear processes, i.e., $dI/dx$ instead of $dI/dx$^2 in Eq. (5). The thin-solid and dash-dotted lines represent curves proportional to $S_e$ and $S_e^2$, respectively.

sputtering yield. As can be seen from the energy dependence of $dI/dx$, also shown in Fig. 4, addition of a term linear in $dI/dx$ to take into account sputtering by dissociative recombination of $O_2^+$ (Refs. 6 and 9) cannot improve the agreement with experiment, suggesting that this process does not contribute significantly to the sputtering yield.

The close agreement between the model results and experiments suggest that electron capture plays a crucial role in the sputtering yield of solid oxygen below 100 keV and explains the loop behavior of $Y(S_e)$. Electron capture may also be able to explain the loop behavior in solid water and argon. In the latter case, sputtering is not caused by Coulomb repulsions, but $Y$ is proportional to the number of excimers, which is enhanced by additional ionizations produced by electron capture. The mechanism discussed in this paper for proton impact will also play a role in ionization tracks created by heavy ions such as cosmic rays. At any given velocity the effect will be larger for incident ions with charge $q$ larger than the equilibrium charge $\bar{q}$ since in this case electron capture cross sections are small. Modeling for heavy ions will be complex since it must include the multitude of processes involving multiple charge states and their depth dependence. Finally, we remark that the importance of electron capture shown here implies that radiation effects by energetic ions cannot be simulated by studies with low-energy electrons and points to the incompleteness of the common description of radiation effects in terms of energy deposited per target molecule.

This paper is based upon work supported by the National Science Foundation under Grant No. 0506565.