Electronic sputtering of solid O$_2$

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Abstract

The bombardment of low temperature condensed gas solids by MeV light ions produces electronic excitations that can decay non-radiatively, transferring kinetic energy to the lattice and causing ejection (sputtering) of atoms. The experimental data for the sputtering yield $Y$ of solid O$_2$ and N$_2$ over a range of $dE/dx$ are proportional to $(dE/dx)^2$, where $dE/dx$ is the energy deposited per unit path length. Parametrizing an analytical thermal spike model with constant track radius gave satisfactory agreement with the data [Johnson et al., Phys. Rev. B 44, (1991) 14]. However, molecular dynamics calculations for solid O$_2$ indicate that $Y$ is proportional to $dE/dx$ at high $dE/dx$ for constant track radius and that the energy transport processes differ from those assumed in spike models. Here we propose that the quadratic dependence in the experimental data is due to a track radius that increases with $dE/dx$, opposite to the dependence predicted by the Bohr adiabatic radius. This radius is determined by fast energy transport processes prior to the principal energy release due to lattice motion: e.g. by hole repulsion and diffusion, by cooling electrons, or by excitation transport. Energy transport for a vibrationally excited track was examined, and it was found that sputtering was inefficient for vibrational excitation of solid O$_2$. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

The electronic sputtering of low-temperature, condensed-gas solids has been a topic of interest for the last 20 years. This process produces an atmosphere on Europa, a moon of Jupiter [1], and it can give insight into the non-radiative decay processes occurring in solids [2–5]. Although a significant body of data has been available and many of the controlling processes have been outlined, a quantitative, first principles model has not been found for molecular condensed-gas solids.

Analytic models of sputtering based on the so-called ‘thermal spike’ model have been used by many authors [6–11] to understand and extrapolate the experimental data. For instance, when the electronic excitations are produced by an energetic ion, a cylindrically symmetric region is assumed to be energized. This is described by an energy deposition per unit path length in the solid, $dE/dx$, and a track width $r_{sp}$. The thermal diffusion equation is then used to calculate the temperature as a function of radius and time, $T(r,t)$. The sputtering yield $Y$ is obtained by calculating the particle flux using the surface temperature...
This study used an excitation geometry where dissociation occurs following electron recombination. 

MD simulations discuss the O$_2$ molecule and the sputtering of solid O$_2$ at high density. The yield exhibits a non-linear dependence on energy, and a melt front controls the heat flow near the track. The molecule interacting with each other via a combined electronic and lattice relaxation energy, is some fraction of the electronic stopping power, $\langle \Delta E/dx \rangle_{\text{el}}$. In some earlier studies, $\langle \Delta E/dx \rangle_{\text{el}}$ has been used to represent this fraction. Here we use $\Delta E/dx$.

In Ref. [2] the spike model with constant diffusion was normalized to the experimental data and used to describe the dependence of the yield on $\Delta E/dx$. However, when the non-radiative energy release in the track of excitations has an energy density $nU$, where $U$ is the binding energy for a material of density $n$, we have shown using molecular dynamics (MD) simulations that energy transport by thermal diffusion fails. Rather, a pressure pulse carries energy away from the track, while a melt front controls the heat flow near the track [13,14]. We also showed that when a free surface is present, $T_{\text{sp}}(r,t)$ is much greater than the bulk temperature, $T_{\text{sp}}(r,t)$ [14,15], unlike the approximation used in most models [16]. Here we study sputtering of low temperature solid O$_2$ in which the internal degrees of freedom can, in principle, affect the energy transport and the sputtering yield.

Experimental data for sputtering of solid O$_2$ give $Y \propto (\Delta E/dx)^{\gamma}$ over a limited range of excitation densities as in the thermal spike models [2,3]. In Refs. [14,17] we found in MD simulations that the yield exhibits a non-linear dependence on $\Delta E/dx$ at low $\Delta E/dx$, having a spike-like character, but a linear yield for both atomic and molecular solids at high $\Delta E/dx$ when a constant track radius $r_{\text{sp}}$ was used. Since this is the region applicable to the sputtering of solid O$_2$, we compare the energy transport in atomic and molecular solids and then discuss the O$_2$ data.

2. MD simulations

Recently, vibrational to translational energy conversion following uniform excitation of solid O$_2$ was studied using classical MD calculations [18,19]. This study used an excitation geometry like that in laser ablation, where the laser spot can have a diameter of several hundred nanometers. On the other hand, a swift light ion will create a track of excitations that will extend only several tens of Å. Earlier, sputtering of small samples of an O$_2$-like material were studied in which the well depth was reduced to enhance the vibrational to translational coupling [20-23]. Recently, we showed that over a range of excitation densities the sputtering yields for atomic and molecular solids had similar dependences on excitation density [14].

Simulation details can be found in a number of papers [13,14,17-19]. For solid Ar, which has an fcc crystalline structure, we consider atoms interacting through a Lennard–Jones (L-J) (6-12) potential. Solid O$_2$ was simulated as the atoms in each molecule interacting with atoms in neighbor molecules via an L-J potential and atoms within the molecule interacting with each other via a Morse potential. Parameters were chosen for a γ crystal. The parameters for the Ar and O$_2$ simulations are given in Refs. [13,14,17,18]. Ar and O$_2$ have the same binding energy $U=0.08$ eV, similar densities, $n=0.026$ Å$^{-3}$ for Ar and $n=0.028$ Å$^{-3}$ for O$_2$, and similar L-J lengths, $\sigma=3.405$ Å for Ar and $\sigma=2.986$ Å for O$_2$. The mean lattice spacing $l$ is $l=\sigma^{-13}$.

A cylindrical region of radius $r_{\text{sp}}$ was excited by giving each atom within this volume a kinetic energy $E_{\text{kin}}$ in a random direction. The effective $\Delta E/dx$ is $\Delta E/dx = mE_{\text{kin}}/d \ln r_{\text{sp}}^2 E_{\text{kin}}$, where $m$ is the number of particles per layer within $r_{\text{sp}}$, and $d$ is the separation between layers. Therefore, the criterion for a narrow spike is $E_{\text{kin}} \gg U$. Any time delays in the conversion of electronic excitation into kinetic energy of the atoms in the lattice are ignored here.

The energy required to dissociate an O$_2$ molecule is $E_d = 5.1$ eV. When $E_{\text{kin}} > E_d$, the current MD simulations treat atoms from a dissociated molecule on the same footing as atoms that belong to a particular molecule, and recombination is only possible with the atom that belonged to the same molecule. This is not correct, and modifications are in progress. For O$_2$, fast ion bombardment can directly dissociate molecules and dissociation occurs following electron recombination. These processes all release kinetic energy.
Simulations that were carried out earlier [24] on smaller samples suggested that the yields were insensitive to the manner in which the energy was put into the system. Here we re-examine that. Sputtering yields were calculated for the (001) surface, as in Refs. [14,18]. The local kinetic temperature of the atoms and molecules, $T(r,t)$, was calculated for cylindrical shells of mean radius $r$.  

3. Atomic versus molecular solids

Atomic fcc structures, like crystalline Ar, favor energy transport along the nearest neighbor directions (a number of figures and movies representing the cases treated in this paper can be found at our web site http://dirac.ms.virginia.edu/~emb3t/o2/o2.html). For fcc Ar, $dE/dx=10-30$ eV/Å and $r_{cyl}=2-5\sigma$, 5-10% of the energy is taken away from the track region by ‘focosons’ during the first picosecond. After that, a supersonic pressure pulse takes away another 20% of the energy. In the track, the molten solid controls heat flow and lasts for several picoseconds. For the molecular solid studied the scenario changes. $r_{O_2}$ has a pair distribution function similar to that for liquid $O_2$ [20–23], which quenches focusons. The pressure pulse exists, but it is not as pronounced. For solid $O_2$, $T_{tr}$ and $T_{rot}$ are 50% larger at the region by ‘focosons’ during the first picosecond. After that, a supersonic pressure pulse takes away another 20% of the energy. In the track, the molten solid controls heat flow and lasts for several picoseconds. For the molecular solid studied the scenario changes. $r_{O_2}$ has a pair distribution function similar to that for liquid $O_2$ [20–23], which quenches focusons. The pressure pulse exists, but it is not as pronounced. For solid $O_2$, $T_{tr}$ and $T_{rot}$ are 50% larger at the

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Temperature profiles in the first tens of picoseconds control the sputtering. Energy can go into vibrational and rotational modes as well as translation. Rotational modes equilibrate with translational modes, but vibrational modes do not, as seen in the radial temperature profiles in Fig. 1 for $r_{cyl}=2\sigma$ and $E_{exc}=0.5$ eV/atom ($dE/dx=3.9$ eV/Å). After 6 ps (dotted lines), $T_{tr} \approx T_{rot} \approx T_{vib}/4$ inside the track. These profiles are not Gaussian and their evolution does not follow a simple diffusion equation. If the ‘bumps’ in the translational temperature profiles (not clearly seen in Fig. 1 owing to the logarithmic scale) due to the pressure pulse are neglected, then the data can be roughly fit to a Gaussian with an effective but changing thermal diffusivity $\kappa$ [25,26]. The effective diffusivity is in the range 8–25 Å$^2$/ps, close to the thermal diffusivity for $O_2$ at 50 K (calculated using data from Ref. [27]) and that of liquid $O_2$ at 60 K, $\kappa \approx 9$ Å$^2$/ps (calculated using data from NIST Chemistry WebBook [28]).

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For solid $O_2$, $T_{tr}$ and $T_{rot}$ are 50% larger at the
surface, but in the atomic case the mismatch between the bulk and surface temperature is larger. Outside $r_{cyl}$, $T_{coh}$ is roughly the same at the surface and in the bulk. We can define a 'shell occupation' $n(r,t) = N(r,t)/N(0)$, where $N(r,t)$ is the number of particles at time $t$ in the shell of mean radius $r$. When $E_{exc} \geq U$ a crater is formed. For a sample of 15 layers, $\nu(r)$ can decrease by 20–30% at the crater rim. Outside the rim, $\nu(r)$ does not differ much from one. Taking only the surface layer, an increase of 50% in occupation is seen up to $r \approx 25\sigma$. This lattice expansion was also observed for uniform excitation [18,19] and a large $T_{coh}$ is maintained due to the reduced coupling to translational nodes. For uniform excitation, the onset of equilibration of the vibrational modes occurred when the lattice became highly disordered and fluid-like [19]. Here the lattice is disordered, but only within the track. For the simulations performed, no onset of rapid conversion $T_{coh} \rightarrow T_{vib}$ was seen.

For $r_{cyl} < 5\sigma$ and $E_{exc} > U$ MD simulations show that the energy deposited in translational modes is rapidly carried away from the track and, therefore, the hot region does not last long enough to produce a 'thermal spike'. When the energy is deposited as a vibrational excitation it has been shown [18,19] that the gradual coupling to translational modes can take several tens of picoseconds. This may lead to a longer-lasting hot region that behaves closer to a model spike. In Section 4 we also explore this scenario.

4. Vibrational excitations

Vibrational excitation of the solid was initiated by giving each atom of the O$_2$ molecules inside $r_{cyl}$ a kinetic energy $E_{exc}$ in outward-opposite directions. For uniform vibrational excitation, as in laser ablation, and no expansion (constant molecular density) the translational modes coupled with the vibrational modes and the translational temperature eventually increased [18,19]. However, if the solid was allowed to expand rapidly, which was the case when there was a free surface, the vibrational coupling to the lattice was much less efficient. When only a cylindrical track is vibrationally excited, the sample expands along the track and coupling is very small during the first 100 ps. By contrast, the principal contributions to sputtering typically occur in much shorter times when the cylinder is 'excited' by giving the molecules translational energy. For $E_{exc} = 2$ eV, $r_{cyl} = 5\sigma = 15\,\text{Å}$, $dE/dx = 74.6\,\text{eV/Å}$, $T_{coh}$ is roughly the same as before excitation, at least during the first few hundred picoseconds. For larger energy deposition, as for $E_{exc} = 4$ eV, $r_{cyl} = 5\sigma = 15\,\text{Å}$, $dE/dx = 149.3\,\text{eV/Å}$, there is a little coupling and the translational temperature increases slightly, but $T_{vib}$ remains below 100 K all the time, even inside the track, as does the rotational temperature. Unlike the random excitation case above, surface temperatures are only slightly larger than bulk temperatures. Of course, vibrational energy must eventually diffuse out of the track and slowly couple to the translational modes, possibly inducing very late sputtering.

Fig. 2 shows temperature profiles for $E_{exc} = 4$ eV and $r_{cyl} = 5\,\text{Å}$ using vibrational excitation, $dE/dx = 149.3\,\text{eV/Å}$, 0.01 ps after excitation (solid line), 1.01 ps after excitation (dashed line), 5.51 ps after excitation (dotted line).
4.2 eV, i.e. the excitation energy is a rectangular distribution in energy, instead of a delta function. For this case, 25% of the particles have energies above the dissociation threshold and energy is transported away from the center by the dissociated particles transferring energy to the cold lattice outside of \( r_{\text{rel}} \). After 10 ps the number of ejected molecules is 500, whereas it was one for the excitation of a single vibrational energy of 4 eV, which is below the dissociation limit. In a more realistic simulation, the dissociated \( O \) would react with the nearest \( O_2 \) molecule to form ozone in a highly vibrational state. In solid \( N_2 \), however, the free atoms do not recombine rapidly and transfer energy to translational modes more effectively.

5. Sputtering yield

Experimental data for the yield of \( O \) bombarded with MeV \( \text{He}^+ \) from Ref. [2] is presented in Fig. 3. The effective stopping power is only a fraction \( \eta \) of the tabulated stopping power: \( \eta = 0.24 \) Ref. [2]. The data from Ellegaard et al. [3] KeV \( \text{H}_2 \) and \( \text{H}_2^+ \) is also included, treating \( \langle \text{d}E/\text{dx} \rangle \), as additive [3]. In addition, because the particles have lower velocities we used a higher efficiency, \( \eta = 0.48 \) [29]. Both yields are quadratic in \( \text{d}E/\text{dx} \). On the other hand, bombardment with KeV electrons or mega-electron-volt protons for which \( \langle \text{d}E/\text{dx} \rangle \) is low gives \( \gamma \langle \text{d}E/\text{dx} \rangle \) [2,12,30].

The average energy necessary to produce one ion pair in \( O_2 \) is \( W = 32.5 \) eV. For 0.25 MeV/amu \( \text{He}^+ \), \( \langle \text{d}E/\text{dx} \rangle = 22.6 \) eV/A, the mean free path for producing an electron-hole excitation \( \lambda \) is \( \lambda = \frac{W}{\langle \text{d}E/\text{dx} \rangle} = 1.44 \) Å. The layer separation is 6.78 Å, giving 4.7 excitations per layer. If we take the radius of the track core to be the Bohr adiabatic radius \( r_a \) [31], then \( r_{\text{rel}} = r_a = h/v(2W) = 1.18a \), giving a fully excited cylinder. In Ref. [2] the yield was normalized to the yield in the ‘linear’ regime, so the thermal conductivity \( \kappa \) was not needed. The yield from Ref. [2] calculated at high \( \langle \text{d}E/\text{dx} \rangle \) using a constant diffusivity and fixed \( r_{\text{rel}} = 2.9l \), where \( l = n^{-1/3} \), can be written as:

\[
Y = B(\alpha / n)(\langle U / U \rangle)^2 \langle \text{d}E/\text{dx} \rangle^I, \]

where \( B \) is a constant, \( \alpha \) is a coefficient for the reflection of energy from the surface; \( \alpha = 1 \) for no reflection and \( \alpha = 2 \) for total reflection. Using \( \kappa = 12.4 \) Å²/ps, similar to the one found from MD, and \( \alpha = 1.5 \), we obtain the fit shown in Fig. 3.

Using a gas-like \( \kappa \) [2,6] gives a larger yield. Since analytic spike models do not give a good quantitative description of the energy transport for \( E_{\text{exc}} > U \) and require an empirical diffusivity, below we apply the MD results for the yield in order to explain the \( O_2 \) data.

In Ref. [17] the sputtering yield of a number of atomic solids was shown to increase roughly with increasing cylindrical radius for fixed \( \langle \text{d}E/\text{dx} \rangle \) in the high \( \langle \text{d}E/\text{dx} \rangle \) regime. Here, we have shown that in excitation of solid \( O_2 \) such a scaling also roughly applies. Therefore, the MD yields from a cylindrical spike in the high \( \langle \text{d}E/\text{dx} \rangle \) regime can be approximately parametrized using the following formula:

\[
Y \simeq C(r_{\text{rel}}/l)^2(\langle U / U \rangle )\langle \text{d}E/\text{dx} \rangle^I, \quad x \simeq 1.
\]

For \( \gamma \text{O}_2 \) and \( r_{\text{rel}} = 2\sigma \) our MD results give \( C \approx 0.092 \). Therefore, if we assume that the effective cylindrical radius for the energy deposition at the time when dissociative recombination occurs increases with \( \langle \text{d}E/\text{dx} \rangle \), the experimental data are understandable in terms of a cylindrical region energized by dissociative recombination, a spike. That is, writing \( r_{\text{rel}} = \kappa (\langle U / U \rangle )\langle \text{d}E/\text{dx} \rangle \), with \( \kappa \) a constant, \( Y \simeq CA(\langle U / U \rangle )^2\langle \text{d}E/\text{dx} \rangle^I \). Using this expression, the MD calculation of yields from a cylindrically energized region can be used to fit the experimental results, giving \( A = 0.026 \). In this fit \( r_{\text{rel}} \) only has to vary between \( 2\sigma \) and \( 6\sigma \) (6–18 Å) over the relevant range of \( \langle \text{d}E/\text{dx} \rangle \). Below we discuss the possibility that the effective track radius increases with \( \langle \text{d}E/\text{dx} \rangle \).

For the MeV \( \text{He} \) ions, the infratrack, where primary excitations are created, has a size usually taken to be the Bohr adiabatic radius, which decreases with increasing \( \langle \text{d}E/\text{dx} \rangle \) above the maximum in the stopping power, as pointed out often. However, the energy density deposited in this region becomes very large, with neighboring atoms often multiply ionized. Therefore, rapid migration of energy from this region must occur before the non-radiative relaxation events energize the lattice. Whereas in atomic condensed-gas solids the radial
transport by excitons prior to sputtering is large [4,29], it has been shown that the transport prior to sputtering must be <50 Å in solid N\textsubscript{2}. Rapid (<1 ps) transport of excitation energy over distances of the order of a few lattice spacing occurs by charge exchange of multiply charged species with neighbors, by migration of holes and mutual repulsion of neighboring holes, by the cooling electron cloud (delta rays), and finally by excitation transport. Here, we presume that when the excitation density in the track core is very high, transport occurs until a critical energy density is reached, by non-radiative decay processes (e.g. dissociative recombination [29]).

Outside of \( r_B \), the initial radial excitation density produced by a fast ion is determined by the delta electrons. These electrons can travel several tens of Å before they thermalize and their range is proportional to the energy of the primary ion. Therefore, this radius also decreases with increasing \( dE/dx \) over the ion velocities of interest. As the range of the electrons decreases and \( dE/dx \) increases, the energy density in the track increases rapidly, and the radius at which the critical energy density is attained increases. Using eq. (8) from Ref. [32] to estimate that radius at which the critical energy density is reached, we find it varies roughly linearly with \( dE/dx \). Using \( \eta = 0.24 \) and a critical density equal to \( U \) gives \( A = 0.02 \), which is close to the value obtained above from the MD fit. Therefore, we propose that a small variation of the track radius can account for the observed sputtering yield. However, we also realize that a non-linear energy deposition process, like Coulomb explosion [33–35], could also account for the observations. A critical energy density has

Fig. 3. Yields for \( O_2 \) as a function of \( dE/dx \). Experimental data for He\textsuperscript{+} bombardment [2] (solid circles), and H\textsubscript{2} and H\textsubscript{3} bombardment [3] (solid squares). Fit from MD parametrization, using \( r_{rel} = 0.02 \eta U (dE/dx) \) (solid line), which is the same as the fit from Ref. [2] using \( r_{rel} = 2.9, x = 12.4 \text{Å}^2/\text{ps}, \) and \( \eta = 1.5. \)
also been used to explain electronic sputtering of ionic solids (LiF) [36]. A track radius that changes with energy may also be able to explain [37,38] large sputtering yields in the nuclear regime for cluster self-bombardment of gold [11,39].

6. Summary and conclusions

As we showed earlier for atomic solids [13,14], the radial energy transport in $\gamma$O$_2$ cannot be easily modeled by a diffusion equation. For the O$_2$ sample studied there is a molten core and a pressure pulse, but fusons do not play a role. Fusons appear in the $\tau$ phase, which is stable below 24 K. Again we showed that the surface plays a crucial role; having a temperature higher than the bulk indicates that energy transport towards the surface is important [15].

Vibrational excitations alone cannot explain the large sputtering yields observed for solid O$_2$, since they do not couple significantly to other modes during the first several hundred picoseconds. For the laser-ablation case [18,19], disorder was necessary for the vibrations to couple to translations. For an amorphous solid, or for a crystal with defects, this coupling may increase. However, $\gamma$O$_2$ studied here is already ‘disordered’, so only small changes are expected. More realistically, dissociations, either formed initially or on recombination, will transfer large amounts of kinetic energy to the lattice, leading to sputtering.

We showed that the $dE/dx$ regime over which the O$_2$ sputtering yields are quadratic corresponds to a yield linear in $dE/dx$ if the track radius if fixed. Therefore, the electronic sputtering yield measurements for solid O$_2$ can be explained by assuming that the effective track radius increases with deposited energy over the relevant range of $dE/dx$, and the size range of $r_{cyl}$ obtained from this analysis is reasonable.

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