Section V. Sputtering

SPUTTERING OF INSULATORS DUE TO ELECTRONIC EXCITATION, BY FAST IONS AND ELECTRONS

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The data on electronic sputtering of insulators by ions and electrons is reviewed. A repulsive-dissociative electronic mechanism associated with trapped excitation states is discussed as the process through which energy is transferred from electronic excitation into nuclear motion. Such a model is suggested indirectly by luminescence, submonolayer desorption experiments and electronic relaxation of molecules in the gas phase. The sputtering yields observed are discussed in terms of this mechanism. It is seen that an understanding of excitation diffusion and the transport of the deposited energy on relaxation are required to describe the yields. Competition between luminescence and sputter ejection is also considered.

1. Introduction

Fast ions and electrons have been found to erode (sputter) surfaces of insulating materials quite efficiently. For incident charged particles with velocities of the order of or greater than the average speeds of outer shell electrons, the sputtering yields depend on the electronic excitation deposited in the surface region [1-6], rather than on the energy input directly into atomic motion through collisions with nuclei, as is the case for conventional sputtering. This process is, therefore, a special case of electronically induced desorption. However, whereas desorption measurements have tended to focus on the easily detected ejection of ions, the results discussed here pertain to the total material loss which has been shown for most of the materials studied to be dominated by neutral species. These recent measurements have brought to light the fact that the loss of material per charged particle (yield) is surprisingly large. More importantly, they have also shown that the process does not depend on the decay of isolated, excited surface species but rather on the transport of excited state energy to the surface region, and/or on the net effect of closely-spaced excited (ionized) molecules in the solids. That is, properties other than binding energy appear to play a role in determining the observed ejection of material.

The evidence for the above statements is based on what is now a large body of measured yields for a large number of target systems: low temperature condensed-gas solids [1-4,6,7,9-12] as well as molecular, room-temperature insulators [4,5,13,15]. In this paper we first review these observations and then discuss electronic relaxation processes which occur in such materials and which may be responsible for sputtering. This discussion relies heavily on information obtained from other related phenomena, e.g. luminescence and submonolayer, electron-induced desorption measurements. The discussion focuses on the repulsive decay of highly excited states as the likely route by which atoms are set in motion and ejected from the solid. Finally we describe the observed yields qualitatively in terms of this relaxation mechanism.

2. Measured yields

The erosion yields for condensed gas solids bombarded by incident ions have been shown to be independent of temperature at very low temperatures [3,7,10]. When the constituents are molecules, the yields exhibit a temperature dependence, unrelated to normal sublimation, at higher temperatures [3,10]. This temperature dependence, in the case of condensed D₂O and CO₂, has been shown [3,11] to be associated, at least in part, with the production of new molecular species (e.g., D₂ and...
O\textsubscript{2} from D\textsubscript{2}O). Ion beam induced changes in molecular composition are discussed in a separate article in these Proceedings by Foti. Here we will concentrate on the temperature-independent erosion yields in which the dominant ejected species are the neutral molecules of the condensed gas. Brown and co-workers have shown that for fast, light ions with energies above the maximum in the electronic stopping power, these yields depend nonlinearly and very nearly quadratically on the electronic energy deposited [2,3,16], (\textit{d}E/\textit{d}x)\textsubscript{e}. In addition, the overall variation in the yield for a variety of incident ions and over a broad range of energies is close to quadratic [10,16], as seen in fig. 1 for H\textsubscript{2}O. For fast incident He\textsuperscript{+} on condensed rare-gas solids (Ar and Xe) a nonlinear dependence on (\textit{d}E/\textit{d}x)\textsubscript{e} has also been observed [6,7]. Tombrello and co-workers have studied the sputtering of certain room temperature insulators [3,13,14] using fluorine ions in the 2 to 30 MeV range. Above the maximum in the stopping power they also find yields nonlinearly dependent on the stopping power **. The yields depend faster than quadratically on the tabulated stopping power for this higher Z ion, as is also the case for erosion of water ice by fluorine in fig. 1.

The observed nonlinear dependence on (\textit{d}E/\textit{d}x)\textsubscript{e}, as well as the high values of the yields, implies that the yields depend on the density of electronic excitation produced in the solid by a single incident ion rather than simply on the probability of producing an excitation in the surface region as in typical desorption experiments [8,17].

If the erosion mechanism responsible for the above observations is indeed simply related to the electronic excitation density produced in the material, then one would expect to observe similar results for erosion by incident electrons. Although electron-induced desorption of ions from submonolayer and few-monolayer thick films is an extensively studied phenomenon [8,18,19], very little data exists on totally electron-induced desorption from thick films (sputtering). Recently, Schou, Sorenson and co-workers at Riso have obtained measurements on CO [20], H\textsubscript{2} [20], and Ne [21]. In fig. 2 the few data points available at present for CO sputtering by ions are exhibited along with a single value for electron sputtering [16]. The line drawn through the points is quadratic in (\textit{d}E/\textit{d}x)\textsubscript{e}, consistent with observations on other condensed gas systems. Allowing for 10–20\% uncertainties in both the measured yields and the knowledge of the correct near-surface stopping power, the electron point is consistent with the ion data. Many more measurements are obviously needed to verify the consistency of the ion and

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The (\textit{d}E/\textit{d}x)\textsubscript{e} generally used are the tabulated equilibrium charge-state values. When the charge of the incident ion differs from the equilibrium value corrections can be made [17] which tend to improve the quadratic correlation with (\textit{d}E/\textit{d}x)\textsubscript{e}.

** The temperature dependence of the yields and composition of the ejecta have not been studied extensively for these substances. This may be of importance as it is for the sputtering of the alkali-halides [15].

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Fig. 1. Sputtering yields of water ice at low temperatures (77 K) versus electronic stopping power for a number of incident ions (from ref. 10); line drawn varies as (\textit{d}E/\textit{d}x)\textsuperscript{2}.
that observed for collision cascade sputtering initiated by elastic nuclear energy deposition, \((dE/dx)_n\), in metals. Yields at low energy deposition density are linear but become nonlinear at very much higher energy deposition density [23]. We emphasize, however, that such a transition has not been observed for any target system in the electronic stopping power regime.

3. Electronic relaxation

Because most of the materials studied, particularly the condensed gases, have binding energies well below those of typical metals and semiconductors, one would expect to observe enhanced cascade sputtering from the nuclear stopping component of energy loss [23,24], particularly at energies below the electronic stopping maximum and for the higher \(Z\) incident ions [17]. For this reason we will concentrate on incident light ions at energies above the stopping maximum and on electrons, which have no significant nuclear stopping component.

The materials studied can all be characterized as having electronic band-gaps much larger than their binding energies. In fact, except for the atomic rare-gas solids and the alkali-halides, the materials are molecular insulators, in which covalent binding energies between the atoms in the molecules are larger than the intramolecular cohesive energy of the solids as determined, for instance, from sublimation measurements. In such a situation it should not be surprising that the production of electronic excited states in the materials can result in major changes in local atomic or molecular binding that can result in atomic displacements [25].

These materials are generally characterized as having very low hole mobilities and high free-electron mobilities. Therefore, upon the production of electron–hole pairs by a penetrating incident ion the holes may remain localized in a relatively small radial region along the ion track. The primary and secondary electrons produced may have several eV of kinetic energy but are confined by space charge in the vicinity of the localized holes. They lose most of their kinetic energy quickly in molecular solids by coupling to phonons associated with intermolecular vibrations. This energy transfer can ‘heat’ the solid somewhat and possibly contribute

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to surface desorption. Ritchie and Claussen [26] have suggested this could be an important mechanism at excitation densities for which the free electron gas is sustained by Auger processes. For incident electrons and light, fast ions such a contribution is certainly small. We therefore consider the relaxation of the electronic excited state of the system after the electrons have lost their kinetic energy and are localized around positive ions.

The remaining mechanism for transferring electronic excitation to atomic or molecular motion is the occurrence of repulsive forces between neighboring nuclei in the solid. The cohesive binding forces between the constituents of these solids are small because their electronic configurations are essentially closed-shell structures. When such a closed-shell structure is broken by excitation of the electronic charge cloud, major rearrangements occur [25]. A repulsive displacement can occur if the excited states produced are well-defined in times long compared to the time required to accelerate the nuclei, and do not decay radiatively or by producing low energy phonons. In these large band-gap insulators long-lived excited states are observed directly in luminescence experiments [27].

Such states, associated with electronic configurations rather different from that of the ground state, survive four times longer than $10^{-10}$ s. Further, absorption features in such solids also are suggestive of the existence of reasonably well-defined excited states [28]. In fact, the large difference in wavelength observed, particularly in the condensed rare-gas solids, between absorption and emission features, directly indicates that lattice rearrangements (displacements) are associated with excitation in large band-gap insulators [22,28,29].

The argument that repulsive decay between nuclei is the energizer for the sputtering process can also be made by analogy with other closely related phenomena. Models for the production by heavy fast ions of etchable tracks in insulators [30] as well as models for electron-induced desorption of gases adsorbed on surfaces [18,19,31] all invoke the production of repulsive forces between neighboring nuclei. Further, electron–ion recombination and excited-state relaxation of molecules in the gas phase is known to occur most efficiently by a repulsive–dissociative mechanism [32]. For the molecular insulators and condensed gas solids this provides a particularly useful analogy. For example, in water vapor the following reactions occur:

\[
\begin{align*}
\text{H}_2\text{O}^+ + e & \rightarrow \text{H} + \text{HO} + \Delta E, \\
\text{H}_2\text{O} + \text{H}_2\text{O}^+ + e & \rightarrow \text{HO} + \text{H}_2\text{O}^+ + e \\
& \rightarrow \text{HO} + \text{H} + \text{H}_2\text{O} + \Delta E.
\end{align*}
\]

After recombination one of the product species remains in an excited state and the energy transfer to the kinetic energy of the products ($\Delta E$) is of the order of two volts.

Even in atomic gases the repulsive–dissociative mechanism determines the recombination rate, unless the density is extremely low; e.g.

\[
\begin{align*}
\text{Ar}^+ + 2\text{Ar} & \rightarrow \text{Ar}_2^+ + \text{Ar}, \\
\text{Ar}_2^+ + e & \rightarrow \text{Ar} + \text{Ar} + \Delta E.
\end{align*}
\]

The analogous processes in the solid and their relationship to electronic sputtering have been discussed by Johnson and Inokuti [25]. The sequence of events can be ascertained from the potential curves in Fig. 3 for solid argon. On production of an electron–hole pair the hole (Ar$^+$) can bind (in the upper state shown) with a neighboring atom.

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Fig. 3. Interactions potentials between an excited or ionized argon atom and a neighboring argon atom in an argon solid. Axis on the right corresponds to the average internuclear separation in the solid when atoms are in the ground state, the states indicated are seen on absorption: these are the free exciton energies. Upper curve indicates continuum for electron–hole pair formation. Wavey lines indicate luminescence band observed. Attractive potentials lead to self-trapped molecular-like excitons. Repulsive potential leads to energy transfer from electronic to nuclear motion.
forming a self-trapped molecular-like hole. Electron–hole recombination occurs favorably at such sites. That is, in the presence of free electrons a non-adiabatic transition (recombination) occurs to a repulsive state which crosses (is degenerate with) the attractive bound state. The molecular-like exciton dissociates producing energetic argon atoms, one of which is in an excited state. This input of energy (∼ 2 eV) in a solid with a cohesive binding energy of the order 0.08 eV is sufficient to energize a large number of atoms, hence, to drive the sputtering process. The excited argon atom produced in the above recombination event can, on losing its kinetic energy, bind at another site, forming a molecular self-trapped exciton. This is the dominant species observed in luminescence spectra [27] and the shift in wavelength between absorption and emission described earlier can be understood from fig. 3.

The low-lying molecular exciton in an argon solid does not appear to decay repulsively, even as the temperature is varied, because the ground and excited state curves are well-separated at all inter-nuclear spacings of interest. Whereas non-radiative relaxation dominates the decay of the higher excited states the non-radiative and radiative decay mechanisms to the ground state can be competitive in some solids, depending on the relationship between the excited and ground-state potential curves. As the temperature of the solid is increased additional repulsive energy may be deposited in the solid. An increased sputtering yield corresponding to the decreased luminescence yield has been observed for the alkali-halides [15,22]. Such an effect may also contribute to the temperature dependence of the sputtering yield found for the molecular condensed gas solids and may account for the weak temperature dependence observed in the sputtering of Xe [6] but not Ar [7].

In a crystalline material, excited (excitonic) states may be quite mobile. Such states eventually become self-trapped, or trap at an impurity and then decay radiatively or non-radiatively. The surface therefore can form an important sink for this excitation energy if, indeed, the states have large diffusion lengths. At the surface the trapped excited state can decay repulsively as in the Menzel–Gomer–Redhead model for electronic desorption [18,19]. This has been shown to occur in the sputtering of alkali-halide crystals [15,22]. Further, bulk defects and impurities have been shown to modify the effective diffusion length [21,22]. Therefore the state of the solid before irradiation or induced by irradiation may modify the yields.

4. Linear yields

Yields which are linear in (dE/dx)\(c\) can be simply modeled. These yields can be usefully written as [17]

\[ Y = \frac{\Delta Z}{\lambda} \]

where \( \lambda \) is the mean distance between the excited (ionized) states produced by the incident charged particle, hence \( \lambda = (dE/dx)_c/W \), where \( W \) is an average energy deposited per excitation or ionization produced. The quantity \( \Delta Z \) is a transport quantity indicating an averaged depth over which the energy deposited electronically can be transferred to the surface producing sputtering. For the decay of excited states which are self-trapped, an atom (molecule) repelled collides and rapidly loses its energy to the surrounding atoms. \( \Delta Z \) is the size of the region over which the resulting molecular motion can produce ejection at the surface. It is determined by the repulsive energy input, the surface binding energies and the cross section for collisions. Using an estimate of \( \Delta Z \) [eq. (3a) in ref. 17], appropriate parameters for condensed \( \text{H}_2 \), and an energy input of the order of 1.5 eV (e.g., \( \text{H}_2 + e \rightarrow \text{H} + \text{H}^* \)) per decay gives a yield in reasonable agreement with preliminary observations [20]. Similar estimates for condensed Ne give a yield which is much too small [21]. Whereas in condensed \( \text{H}_2 \), excitonic diffusion is most likely small, in solid Ne free excitons are not readily trapped and the diffusion lengths have been determined to be large (∼ 2500 Å, [27]). Luminescence data indicate that, unlike the heavier rare-gas solids, in Ne the self-trapped molecular-like excitation, discussed earlier, is not the most favored species [27]. Hence, in solid Ne, transport to and decay at the surface of excited state energy may be the dominant source of sputtering. Therefore \( \Delta Z \) is related to the free exciton diffusion length. Molecular-like exciton transport is thought to be important for sputtering of alkali-halides. In both, the alkali-halides and Ne impurities act as trapping sites reducing the yields [15,21].

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5. Nonlinear yields

Yields which are nonlinear in \((dE/dx)_e\) are more difficult to discuss in a definitive way. Nonlinear yields will result when the excitation density is sufficiently high that neighboring excited (ionized) states have an affect on one another. This occurs at very high excitation density if an ionization spike is formed, as has been suggested for track formation in insulators [30] and which was an early model for electronic sputtering [33,1]. The rapid response of the electrons in these materials indicates such a spike may be severely screened. Models for high excitation density and continuous, screened excited regions have been discussed extensively [17,4,34]. For the light incident ions and electrons such models are probably not relevant.

Based on our description of non-radiative electronic relaxation one would expect the yield to become nonlinear when the “hot spots” produced on repulsive relaxation overlap spatially and temporally. That is, the relaxation must occur in times short compared to the thermal diffusion time \((\leq 10^{-11} - 10^{-12} \text{ s})\). This is indeed the case for the repulsive decay processes discussed. Using estimates of \(\Delta Z\) [based on eq. (3a) in ref. 17] for the decay of the hot spots, the observations of nonlinear yields for most of the insulators studied are not inconsistent with the possibility of spatially overlapping heated regions [16]. These criteria are more easily satisfied if one also imagines a thermal trap forming. Bottiger et al. [6], and Seiberling et al. [4] suggest that a phase change at the boundary of the cylindrical region could retard the radial dissipation of the deposited energy, enhancing the likelihood of a thermal spike forming.

Measured velocity spectra for erosion of UF\(_2\) [4] and velocity and mass spectra for erosion of condensed gases show that the ejection in the surface region is not very energetic and for the condensed gases at low temperatures predominantly whole molecules are ejected. Such observations are consistent with a continuous “heated” region being formed. The observation of a thickness dependence in the erosion of condensed rare gases has also been used to support the notion of a thermal spike. Based on our earlier discussion of exciton transport alternate explanations of the thickness dependence can be made. We consider this below.

In the molecular condensed gases no thickness dependence is observed down to a thickness of the order of 100 Å. This is consistent with the notion that the holes and excited states are not mobile, i.e. are rapidly self-trapped, in amorphous molecular solids. For Ar and Xe on metal surfaces, however, a large reduction in yield with decreasing thickness has been observed [6,7]. By contrast, for Xe on a molecular insulator a large enhancement with decreasing thickness is observed [6]. These thickness dependences can be understood, at least in part, in terms of free (mobile) exciton transport and the decay of self-trapped (immobile) excitons. Whereas excited state energy transferred to a metal substrate is dissipated, it may become self-trapped when transported to the surface of a molecular insulator. Indeed excitons produced in the molecular substrate may also contribute to the erosion of the overlying material. Therefore the observed thickness dependence cannot be used as supportive evidence for thermal energy dissipation.

Two additional points, however, must be considered. First, the thermal transport properties are very different for a rare-gas atomic solid, in which collision diameters are much smaller than the spacings, and a molecular solid where they are comparable [17]. Secondly, we have assumed that in the atomic insulators, as well as the molecular insulators, the holes are not mobile. Indeed the trapping of holes must vary greatly between materials and depend on impurity and ionization density. This implies that when the solid is sufficiently thick two components may contribute to the observed erosion:

- the formation of a heated region due to rapid trapping, recombination and relaxation,
- exciton (hole) transport to and decay (recombination) at the surface.

Based on the model described for forming a thermal spike, the nonlinear yields should give way to linear yields at low excitation density [16,17]. Although this result is expected it has not yet been observed in any single target system as mentioned earlier. If indeed the erosion yield for sputtering of ice, for instance, remains quadratic in \((dE/dx)\), down to very low excitation densities this would imply that the non-radiative electronic relaxation process responsible for energetic displacement of atoms requires the occurrence of two closely spaced excited states [17]. Such a result would also imply that the process we have considered, non-radiative decay of an isolated excited state, occurs by the production of a large number of low energy pho-
ions which dissipate rapidly producing no erosional effect. This would cast serious doubt on the existence in these solids of repulsive potentials of the type indicated in fig. 3, except at the surface, and therefore is an important question to answer.

6. Conclusion

Two products of the deposition of electronic energy in large band-gap insulators, luminescence and sputtering, provide complementary information on the electronic relaxation processes which occur in these solids following ionization due to passage of an ion or electron and the thermalization of the free electrons produced. Luminescence gives information predominantly on the low-lying excited states of the solid whereas sputtering (desorption) gives indirect information predominantly on higher lying states. These radiative and nonradiative decay processes can compete, depending on the level structure.

The above discussion of the sputtering yields and the electronic relaxation processes occurring in insulators strongly indicates that the repulsive decay of self-trapped holes and excitonic states near the surface, and the transport of mobile holes and excited states which become trapped and decay at the surface are responsible for the sputtering of insulating materials by light ions and electrons. Electron ejection of halides from alkali-halides is dominated by the decay of excitons near the surface if the impurity and defect density is small. In the rare-gas solids both processes appear to contribute. As the diffusion lengths of free excitons in these solids varies strongly in going from Ne to Xe, differences in the dependence of the yields on (dE/dx)_e should be observable. In the amorphous molecular solids, on the other hand, the excitons are not expected to be very mobile and the yields are determined by decay of trapped holes or excited states produced near the surface. Whether the yields are linear or non-linear in (dE/dx)_e depends therefore on the spatial and temporal relationships between excited and ionized states.

Because sputtering and desorption of insulating materials by electrons and fast, light ions is determined by the picosecond processes occurring in these materials it can provide a useful diagnostic tool if it becomes better understood. Therefore, a considerable experimental and analytic effort is warranted to answer the many outstanding questions about this process.

References


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