ION-INDUCED CHEMISTRY IN CONDENSED GAS SOLIDS

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Solids of H₂O, D₂O, CO₂, and SO₂ have been bombarded by MeV and keV ions, and the sputtering of these materials investigated by measuring the total yield and the mass and energy spectra of ejected particles. One observes the results of considerable chemical activity in these low temperature solids. With MeV ions incident on D₂O and CO₂, the production of D₂, O₂ and CO, O₂ respectively are found, while keV ions on SO₂ produce SO, SO₂, and O₂.

1. Introduction

It has been shown [1-4] that when condensed gas solids are bombarded by ions they sputter efficiently, whether the energy deposition is predominantly electronic excitation [1,3,4] or in the form of nuclear motion [2]. While a high yield might be expected in the case of nuclear collisions because of the small surface binding energies of these solids, the high yield due to electronic excitation has been a surprise and indicates very efficient transfer of electronic to kinetic energy of motion of the nuclei of the solids. It has also been observed that when the solid is molecular, containing more than one atomic species, a variety of atoms and molecules are ejected from the surface [5]. This indicates that the incident ion has induced chemical changes within the solid, even at the rather low temperatures at which many of the experiments were performed. Understanding the interaction of ions with these solids is not only important from a fundamental point of view, but also because of the implications of this understanding, for example, to astrophysics and planetary science.

2. Experimental

We have studied experimentally the interaction of MeV and keV ions with the condensed gas solids H₂O, D₂O, SO₂, and CO₂. The apparatus is described elsewhere [6]. The following aspects of the interactions have been studied: (1) the sputtering yield (molecules ejected per ion), (2) the masses of the ejected particles, and (3) the energy distribution of ejected particles. In some cases these studies have been made as a function of target temperature, providing information about the role of diffusion on the processes initiated by the incident ion.

The targets were formed by condensing a gas onto a cold (10-30 K) substrate until a thickness of 100-1000 nm was achieved. The measurements of absolute yield were performed by observing changes in the target thickness by Rutherford backscattering (RBS) (usually with a probe of 1.5 MeV He⁺). The mass distribution of ejected particles was studied by ionizing them in an electron impact ionizer and measuring the masses in a quadrupole mass spectrometer. We measured the transients in this mass distribution and thus the buildup of chemical activity in the solid to a steady state under excitation by the beam by preparing a fresh target, suddenly allowing the beam to strike it, and then observing the dependence on time (over several seconds) of the mass spectrometer signals. The investigation of energy distributions of ejected particles involved the pulsing of the ion beam in a pseudorandom sequence and the study of the time spectrum of ejected particles by time-of-flight techniques. These methods generally involve target bombardment for several minutes.

3. Results

An important aspect of the interaction of ions with solids is the division of their deposited energy into electronic excitation and the production of nuclear motion. For metals and small band gap semiconductors the energy deposited in nuclear motion seems to control the amount of sputtering produced, even in the situation...
where the electronic energy is much larger than the nuclear [7]. However, for a variety of insulating solids [1,3,4] it has been shown that if the energy deposition is predominantly electronic, the sputtering is determined by the magnitude of this energy, although the precise mechanisms for ejection are still not understood. For the case where the energy deposited in an insulator is largely nuclear it is not clear at present to what extent a collision cascade model describes the sputtering of the target, especially if the solid contains more than one kind of atom.

We present first the results of measuring the yield as a function of temperature from Brown et al. [8]. Fig. 1 is a plot of absolute yield $Y$ versus temperature for 1.5 MeV He$^+$ on H$_2$O, SO$_2$, and CO$_2$ targets. These yields were determined from RBS measurements, which provide information about the total film erosion, but not about the species ejected. In fig. 1 all species exhibit a temperature range in which the yield is independent of temperature, and above which the yield increases rapidly with temperature. It should be noted that the yield plotted here is in excess of any decrease in film thickness due to the directly measured sublimation of the target.

In order to provide more information concerning the ion-induced processes occurring within the solid we present in fig. 2 a plot of the signals from the mass spectrometer versus temperature when D$_2$O ice is bombarded by 1.5 MeV He$^+$. The partial yield of mass 20 (D$_2$O) has a broad temperature independent region extending up to temperatures just below the sublimation of ice. In contrast, the yields for mass 4 (D$_2$) and 32 (O$_2$) exhibit no clear region where they do not increase with temperature (except possibly at the lowest temperatures where there is large scatter in the data). This seems to indicate that a thermally activated process such as diffusion is important in the production of these species from the fragments produced by the incident ions. The curves of fig. 2 do not have absolute normalizations. The D$_2$ curve has been placed at twice the O$_2$ curve corresponding to the average ejection of D$_2$O, but their location with respect to the mass 20 curve is only approximately what would be required to give the temperature dependence of total yield as in fig. 1.

The transient dependence of the ejection of different mass species when a dc beam is suddenly allowed to strike a freshly prepared D$_2$O target is shown in fig. 3. The three curves are for the production of D$_2$, D$_3$O, and O$_2$ by 1.5 MeV Ne$^+$ ions. The D$_2$O curve rises suddenly, indicating immediate production of this species. On the other hand, the O$_2$ signal rises slowly until a steady state is established. If the beam current is increased this rise is more rapid, indicating that the transient is one that depends on fluence rather than time. We interpret these curves as indicating that incident ions produce O$_2$ molecules which are subsequently ejected by the arrival

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**Fig. 1.** Sputtering yield versus temperature for 1.5 MeV He$^+$ on H$_2$O, SO$_2$, and CO$_2$. Points indicate data. Reproducibility is about 20%.

**Fig. 2.** Mass spectrometer signals versus temperature for 1.5 MeV He$^+$ on D$_2$O. Data normalized to total yield for 1.5 MeV He$^+$ on H$_2$O at lower temperatures. $Q$ is the beam charge.
Fig. 3. Transient curves of masses 20 (D₂O), 32 (O₂), and 4 (D₂) for 1.5 MeV Ne⁺ on D₂O. Vertical axis is proportional to the yield.

of later ions. This idea is supported by observing that if, during the rise of the O₂ signal, the beam is turned off and then turned back on some seconds later, the signal immediately returns to the value it had when the beam was turned off. The transient signal for mass 4 (D₂) exhibits a sharp peak when the beam is turned on, and then increases slowly, indicating immediate production of some D₂ near the surface, followed by a two-step process as in the case of O₂.

Fig. 4 gives total yields versus fluence for 1.5 MeV He⁺ ions on CO₂. It can be seen that for this ice the
45 keV Ar$^+$ + SO$_2$

Beam current 2 $\mu$A/cm$^2$

YIELD (ARB. UNITS)

TIME (seconds), FLUENCE ($1.25 \times 10^{13}$ ions/cm$^2$)

Fig. 5. Transient curves of masses 64 (SO$_2$) and 80 (SO$_3$) for 45 keV Ar$^+$ on SO$_2$. Vertical axis is proportional to the yield.

Fig. 6. Energy spectra for D$_2$O ejected from a D$_2$O Target. The yields are arbitrarily normalized at 1 eV to emphasize their similarity at the higher energies and their differences at the lower energies. The dotted curve is a fit using the Thompson distribution.

chemical activity indicated by the fluence dependence affects the sputtering yields significantly even at low temperatures. Furthermore, this dependence on fluence is sensitive to temperature. Transient studies with the mass spectrometer show a prompt CO$_2$ signal but slow buildup of both the CO and O$_2$ signals.

Fig. 5 shows transients for masses 64 (SO$_2$) and 80 (probably SO$_3$) when a freshly prepared SO$_2$ target is bombarded by 45 keV Ar$^+$ ions. This case is different from that discussed for D$_2$O, in that the energy deposition is largely nuclear. Nevertheless, the same transient pattern is observed. Molecules that were originally present (SO$_2$) are produced immediately, while the production of the species that requires atomic rearrangement (SO$_3$) proceeds more slowly. Production of O$_2$ has also been observed.

Fig. 6 shows energy spectra of ejected D$_2$O obtained when D$_2$O is bombarded by 1.5 MeV He$^+$, 1.5 MeV Ar$^+$, and 50 keV Ar$^+$. The curves have been normalized to each other at the higher energies, where all three have a dependence that goes roughly as $E^{-2}$ (which is characteristic of a collision cascade). We see here that there is the greatest contribution at the low energies for 1.5 MeV He$^+$, the case for which the electronic deposition
is largest. For 50 keV Ar$^+$ predominantly nuclear energy deposition occurs and the spectrum is close to that described by the Thompson distribution \[7\].

\[ Y(E) = \frac{K E}{(E + E_b)^{1.5}} \]

where \(K\) is a constant, \(E\) is the ejected energy, and \(E_b\) is an effective binding energy, which for this fit is much less than the normal sublimation energy (0.52 eV for D$_2$O). The error bars on the data are large enough, however, so that other models (e.g. thermal spikes) might also be considered as candidates.

4. Discussion

We see from the foregoing data that it is quite possible for an ion incident on a condensed gas solid to produce permanent changes in the chemical character of material, even at temperatures in the 10-30 K range. This requires the breaking of chemical bonds and, in some cases, rearrangement to produce other molecular species. This appears to occur whether the energy deposition of the ion is largely electronic or nuclear, indicating that bonds can be broken either by a sufficient disturbance of the electronic structure or by displacing atoms from their original positions by hard collisions (nuclear). The free radicals thus produced may then combine with other atoms or molecules to produce new chemical species, aided by diffusion if the temperature is sufficiently high. Such new species near the surface may leave the solid material if they are volatile enough, although in our experiment they were dominantly ejected by subsequent incident ions.

In the yield versus temperature plot for H$_2$O as shown in fig. 1, it is clear that in the temperature independent region the production of new species is unimportant in the total yield. The beginning of the rise in the yield curve is due to the rise of produced species such as H$_2$ and O$_2$, as shown in fig. 2 (for D$_2$ and O$_2$) [9]. At still higher temperatures the ejection of the original molecule D$_2$O (and presumably H$_2$O) increases rapidly with temperature (fig. 2). In this highest temperature regime the temperature is almost large enough for the solid to sublime, so that the addition of energy from the incident ion easily causes the ejection of a large number of water molecules. A similar effect is seen in the ejection of argon atoms from solid argon [3]. As shown in fig. 1, the rise in the yield for CO$_2$ occurs well below the temperature required for significant sublimation, indicating that the increase in this case is due to the production of new species which must significantly alter the character of the ice.

We have observed the production of D$_2$ and O$_2$ when D$_2$O is electronically excited by bombardment with MeV light ions. We also find SO$_2$ as a product when SO$_2$ is bombarded by keV heavy ions where the energy deposition is mostly nuclear. This type of chemical activity in condensed gases bombarded by keV heavy ions has also been seen for H$_2$O, CO$_2$, and NH$_3$ bombarded by 3 keV Ar$^+$ ions [5]. We have also observed the production of formaldehyde when a mixture of H$_2$O and CO$_2$ is condensed as a target, bombarded by 1.5 MeV He$^+$, and then heated to release the molecular products [8].

In considering the energy deposited in the form of electronic excitation one can imagine two kinds of effects: (a) the electronic energy can become a source of nuclear motion through a dissociative recombination process [10] and, (b) the effective binding energy at the surface may be momentarily reduced by virtue of the excitation of binding electrons along the particle path [10,11]. The low energy behavior of the spectra of fig. 6 tend to show that in the vicinity of the track the effective binding changes as the relative amount of electronic excitation is increased. The values of the absolute yields at the larger ejection energies are, however, several times larger than would be obtained from a cascade calculation with the nuclear deposition as energy input, even with a chosen binding energy of zero. This implies that the electronic energy input may not only alter the surface binding energy, but also serve as a source of nuclear motion which leads to sputtering beyond that produced by collision cascades.

The results given here indicate that incident ions significantly alter the character of molecular condensed gas solids. This is indicated by the mass spectra, where new species requiring chemical rearrangement are produced by the influence dependence in the production of new species, and by the energy dependence of the ejected molecules.

References