Ejection of Molecules from Solid Deuterium Excited by keV Electrons

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The energy distribution of sputtered D_2 from electron-bombarded solid deuterium has been studied for the first time. The spectra from this quantum solid show features that may originate from an energy release sequence of association of atoms. For ejection energies above 1 meV the gross features of the spectrum are similar to those from electronic sputtering of other much less volatile condensed gases. Sputtered D_4 molecules have been observed for the first time as well. [S0031-9007(97)04315-9]

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The solid hydrogens are not only the most volatile targets at vacuum conditions, but show also a unique behavior during bombardment by charged particles [1–3]. Energetic ions or electrons generate secondary electrons, ions, and neutral atoms along the path. Many of these secondary particles do not recombine or associate immediately and do not leave the solid by diffusion, but remain in the solid seconds or minutes after the formation [4–7].

A remarkable radiation feature in particle-irradiated solid hydrogens below 4.2 K is the observation of an optical flash accompanied by heat spikes which occur spontaneously with a period of typically a few minutes. At these temperatures the heat spike is generated by a sudden association of unpaired atoms in a sequence that is associated with emission of a broad continuum centered about 830 nm [3–6,8]. The accumulation of D atoms in the solid produced by the irradiation is primarily limited by phonon-assisted quantum diffusion, which in turn depends strongly on the local temperature [3]. At temperatures below 4.2 K the concentration of the atoms may reach a critical value at which the energy gain from the association sequence or other exothermic reactions suddenly may induce the sequence with other atoms in the neighborhood. This occurs in a macroscopic part of the sample and triggers the heat spike [3,4,6]. At temperatures above 4.2 K the enhanced diffusion of the D atoms leads to a continuous association of unpaired atoms or ions in the neighborhood and emission of light with a slight temperature increase, but without any heat spikes or optical flashes [3,4,6].

A common feature for sputtering of all condensed gases by light ions or electrons is the production of ionizations and secondary particles in the solid. The general picture is that the electronic deexcitations, which decay to repulsive states, initiate particle motion in the solid. When target particles close to the surface obtain sufficient kinetic energy, they may be ejected as sputtered particles. Although the overall pattern described here is similar for electronic sputtering of other volatile condensed gases, the electronic deexcitations vary strongly from one condensed gas to another.

In general, the sputtering yield from the hydrogenic solids per single particle impact is high, even without external or macroscopic beam heating [9–12]. Essentially, the reason for the high sputtering yield is the extremely low binding energy of the molecule to the lattice site, for example, for D_2 a binding characterized by a sublimation energy $U_0 = 12.0$ meV [9–12].

One of the striking results of sputtering of these quantum solids has been the fact that the yield is enhanced by more than 2 orders of magnitude for very thick deuterium films under keV electron bombardment compared with films of medium thickness. This yield enhancement is accompanied by an increasing accumulation of charge from electrons trapped in polaronic states or bubbles [9].

Here we present the first measurements of the energy distribution of neutral molecules sputtered from the solid hydrogens. We have measured the spectra of D_2 as well as D_4 molecules from solid D_2 at 0.5 keV electron bombardment with ejection energies over almost 4 orders of magnitude. In particular, we have observed for the first time a low-energy peak which may originate from the heat spike sequence.

The experimental setup (Fig. 1) at the Institute of Physics, Jagellonian University, consists of a cryogenic target chamber equipped with an electron gun and a time-of-flight (TOF) system. The cryostat is similar to that

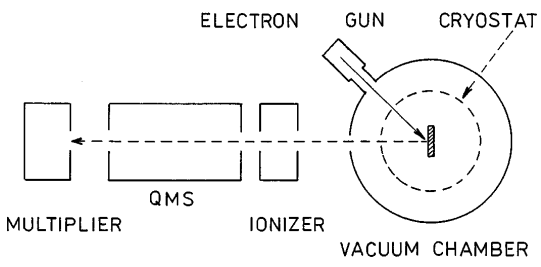

FIG. 1. Schematic drawing of the setup.

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previously utilized for sputtering measurements on solid deuterium at Risø National Laboratory [9,11,12]. The polished copper target, which is thermally connected to the cryostat, reaches routinely a temperature around 3 K. The temperature of the target was determined to within ± 0.3 K with a carbon resistor thermometer calibrated against the liquid-helium bath, but the relative variation of the target temperature was measured within ± 0.1 K. Thick films of solid deuterium were deposited on the substrate by letting D_2 gas into the chamber. The films were irradiated by a pulsed 0.5-keV electron beam at an angle of incidence of 45° with a typical current density of 0.1 $\mu A/cm^2$. The electron current could not be measured directly, but was monitored from an aperture ring at the entrance to the cryogenic system or from the instantaneous target temperature. The film thickness was estimated to be about 1000 Å from the D_2 partial pressure and the exposure time. The data presented here did not show any dependence on the thickness for thick films.

The TOF system used for the measurements was constructed at the FOM Institute, Amsterdam, and is described in great detail in Refs. [13–15]. Neutral particles ejected from the solid in a direction normal to the surface were analyzed after a flight distance of 37 cm by a quadrupole mass spectrometer equipped with an electron ionizer and an off-axis electron multiplier. The TOF distributions were determined from the correlation technique by chopping the beam pseudorandomly with a frequency of 10, 20, or 50 kHz. From these distributions the energy spectra were computed. Above 1 eV the small number of detected particles results in a relatively large uncertainty of the spectral shape for these high ejection energies.

The energy spectra of ionized species of masses 4 amu (D_2^+) and 6 amu (D_3^+) were determined. Mass 2 (D^+) was not observed within the limits of sensitivity. Since secondary positive ions cannot enter the detection system because of a repeller ring, the detected neutrals are almost certainly D_2 and D_4 molecules. The latter assumption follows from the fact that the lifetime of neutral D_3 molecules is so short [16] that the emitted species are not able to reach the entrance of the detection system and that no other high mass molecular ions of deuterium were present in the mass spectra. The existence of neutral hydrogen dimers has been confirmed in many cases, e.g., Refs. [17,18]. The abundance of D_3^+ was about 3% of that for D_2^+.

A typical spectrum for ejected D_2 ranging over almost 4 orders of magnitude in energy is shown in Fig. 2. Roughly speaking, thermal processes are responsible for the particles of kinetic energy below 1 meV, collision cascade processes are dominant for those between 1 and 100 meV, and particle ejection from deexcitation processes close to the surface are responsible for those above 100 meV. While the features above 1 meV have been observed for other condensed gases [10,19], until now similar thermal peaks have only been seen for molecules different from the target molecules [20].

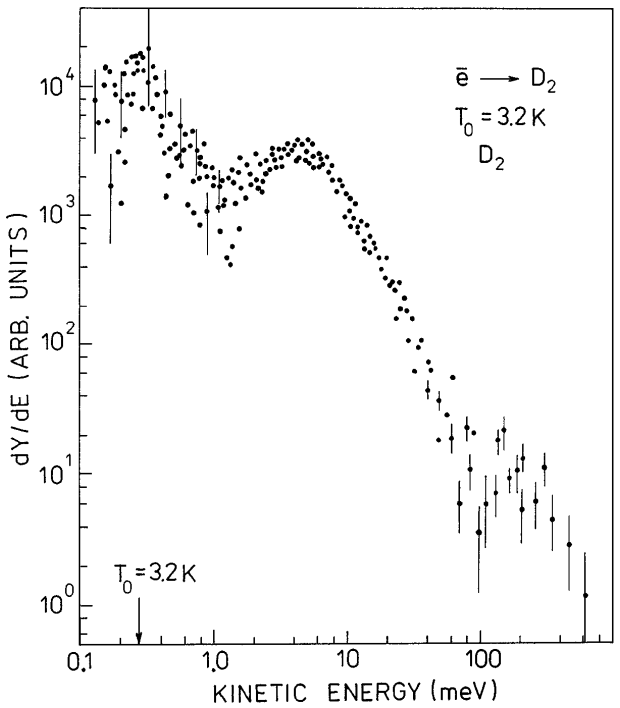

FIG. 2. Energy distribution dY/dE of sputtered D_2 from solid D_2 at a target temperature $T_0 = 3.2$ K. This temperature is indicated at the energy scale as well.

A multitude of electronic processes in the solid, e.g., formation of D_3^+ and predissociation of D_2^*, may liberate from 2 to 8 eV as kinetic energy to atoms or molecules in the lattice [21,22]. If such an event takes place close to, but not directly at, the surface, the energy will be shared among many collision partners, but some particles will be ejected with an energy above 100 meV. The suggested energy transfer to lattice molecules from electron trapping in bubbles or in polaronic states described above is probably of less importance at primary electron energies below 1 keV. This follows from the strongly decreasing yield with decreasing primary energy reported in Ref. [9].

The spectrum in the intermediate region resembles one from a linear collision cascade produced by electronic deexcitations somewhat below the surface. The slope of the spectrum from 10 to 100 meV shows the characteristic E^{-2} tail and the maximum at 5 meV is very close to the predicted value at $U_0/2 = 6$ meV [10,19]. On the other hand, we cannot exclude that there is some structure in the curve for ejection energies above 10 meV because of the scattering of the data points. Nevertheless, it is surprising that the spectrum from this quantum solid has a collision cascade component that is similar to particle ejection features from solids with a binding energy more than 2 orders of magnitude larger than that for solid D_2 [10].

The part of the spectrum at lowest energy originates from thermal processes in the solid. The peak around 0.3 meV corresponds to an absolute temperature of 3.2 K, which actually is identical to the substrate temperature T_0 within our limits of uncertainty. Therefore, this peak can be ascribed to evaporation induced by the macroscopic heating by the beam. It is not the low-energy part of the collision cascade, since such a curve would fall markedly for decreasing ejection energies [10,19].

Two spectra of sputtered D_2 molecules at enhanced current densities are shown in Fig. 3 together with that from Fig. 2. The higher current density leads to a temperature increase to 3.5 and 4.0 K of the target. Surprisingly, this temperature increase is not accompanied by a corresponding "evaporation" peak at the same target temperature, but a *new* peak occurs at about 1.0 meV. This peak is completely dominant at the highest temperature, whereas the spectrum at 3.5 K can be considered as a superposition of the new peak and the original one for $T_0 = 3.2$ K. We have analyzed the spectra in terms of the Maxwell-Boltzmann-type (MB) distribution $dY/dE = CE\exp(-E/k_BT_B)$, where C is a constant, k_B is Boltzmann's constant, and T_B is the temperature of the ejection volume [14,15,20]. At the target temperature 4.0 K the peak is approximated well by this distribution with $T_B = 12$ K. At $T_0 = 3.5$ K the superposition of two distributions with $T_B = 12$ K and $T_B = 3.2$ K leads to a much better approximation than one MB distribution with an intermediate temperature between 3.5 and 12 K.

The energy spectrum of the emitted D_4 molecules (Fig. 4) exhibits a similar structure as that seen in Fig. 3 for D_2. The spectrum was taken at 3.5 K as a compromise between sufficient signal intensity and not too fast target erosion. Even though the binding energy is 2.8 meV [1], some of the D_4 molecules appear with energies exceeding 100 meV. The similarity between the spectra of D_2 and D_4 is a strong indication of common ejection processes. The D_4 molecules are formed partly during the local heat processes that lead to low ejection energies and partly via soft encounters in a collision cascade. In fact, the falloff of the high-energy side is steep, since only a minor fraction of the weakly bound D_4 molecules survive the cascade.

The low temperature features can be understood from the suggested sequence for the emission of the continuum and the heat spike. The deuterium atoms form a negative ion via electron attachment, e.g., with a free or trapped electron in the neighborhood,

$$D + e^- \longrightarrow D^-,$$

in which a photon in the continuum is emitted for electron energies exceeding 0.35 eV [6]. The negative ions may associate with an atom by

$$D^- + D \longrightarrow D_2 + e^-,$$

where the electron gets the excess energy, up to about 3 eV. Then, the fast electron heats the lattice by elastic collisions. When a large number of these processes takes place, the local ejection volume will reach an equilibrium described by the temperature T_B in the MB distribution. At the higher current densities the electron beam does not

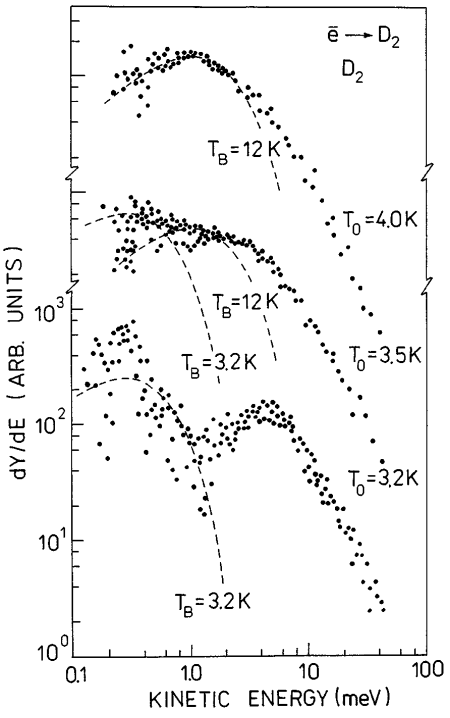

FIG. 3. Energy distributions of sputtered D_2 at different target temperatures $T_0 = 3.2$ K (from Fig. 2), 3.5 K, and 4.0 K. The distributions have been approximated by MB distributions of the type $CE\exp(-E/k_BT_B)$.

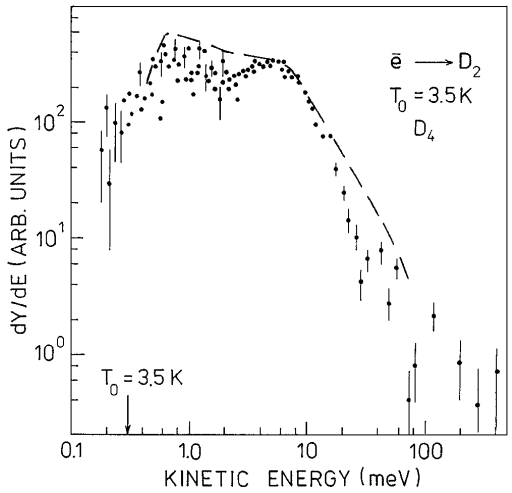

FIG. 4. Energy distribution of sputtered D_4 from solid D_4 at a target temperature $T_0 = 3.5$ K. The dashed line indicates an "average" curve of the spectrum of D_2 at 3.5 K from Fig. 3. This curve has been normalized to that for D_4 at the peak at 5 meV.

only heat the sample directly, but the density of fragments, e.g., D atoms, becomes much higher. This combination of a higher temperature leading to an enhanced diffusion and a high atom density can be considered to initiate the sequence continuously in local volumes.

The heat spike has been observed to reach 10 K in other experiments, but these groups have in all cases measured the temperature of a sample, in which the walls were a part of the thermal system. In contrast, we have derived the local temperature directly from the MB distribution. One other difference is that the sequence in our experiment at 3.5 and 4.0 K takes place continuously, whereas a spontaneous heat spike will be averaged out in our system over many recording cycles.

In summary, we have measured the energy distribution of sputtered D_2 and D_4 from the quantum solid deuterium for the first time. At very low energies a Maxwell-Boltzmann distribution occurs in the spectrum with a characteristic temperature of 12 K. A striking point is the pronounced enhancement of the peak at 12 K even with a small increase in substrate temperature. This feature may originate from the association of negative ions and atoms previously reported for the solid hydrogens.

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