Sputtering of Solid Hydrogenic Targets by keV Hydrogen Ions

Bjarne Stenum, [a] Jørgen Schou, Ole Ellegaard, [b] and Hans Sørensen [a]

Physics Department, Association Euratom, Risø National Laboratory, DK-4000 Roskilde, Denmark

Roman Pedrys

Institute of Physics, Jagellonian University, PL-30059 Krakow, Poland
(Received 8 April 1991)

The first sputtering measurements of the most volatile solid hydrogenic targets are reported. Bombardment of these targets by hydrogen and deuterium ions leads to erosion predominantly via electronic transitions. The magnitude of the yield depends strongly on the particular isotope. No existing theory for this electronic sputtering can explain the large yields that range from about 100 D_2/H for solid deuterium up to 800 H_2/H for solid hydrogen.

Hydrogen isotopes are the most volatile materials [1,2] from which targets in vacuum may be produced. Their pronounced zero-point motion means that the vapor pressure, in particular for solid H_2, is large even at liquid-helium temperature. Therefore, any attempt to conduct sputtering experiments with charged particles incident on these materials encounters severe difficulties. The primary beam power and the target temperature must be kept at such a low level that the mass loss from beam-induced evaporation is small compared with that from sputtering processes [3]. In contrast to evaporation, sputtering is characterized as the erosion of surfaces by individual particle impacts [4].

The recent sputtering experiments on condensed gases including solid D_2 demonstrate that the erosion predominantly takes place via electronic transitions, i.e., electronic sputtering [3,5,6]. Generally, the erosion of the surface follows a sequence of events initiated by the primary ion. The incident ion generates excited and ionized molecules along the path. Many of these excited states decay to repulsive states so that the molecules immediately dissociate. The repulsing atoms may initiate collision cascades in the material if the binding energy of the target particle to the lattice site is low compared with the energy release. When target particles close to the surface obtain sufficient kinetic energy, they can pass the surface barrier and be emitted from the material. Although the overall pattern described here is similar for electronic sputtering of the volatile condensed gases, the surface binding energy and the electronic deexcitations vary strongly from one condensed gas to another [3,5-7].

Electronic sputtering is relatively inefficient compared with ordinary (knockon) sputtering [3,7]. However, for most of the condensed gases the surface binding energy, which is usually considered to be the sublimation energy [8], is comparatively low. This means that the number of ejected particles per primary particle becomes relatively large, even when the sputtering is purely electronic. The solid hydrogenic targets constitute an extreme type of target material because of the low sublimation energy,

which ranges from 8.65 meV for solid H_2 up to 14.8 meV for solid T_2 [2]. Therefore, even for the least volatile stable isotope, solid deuterium, keV proton bombardment leads to yields higher than 100 D_2 molecules per incident proton [9].

The sublimation energy of the solid hydrogen isotopes is so low that one can expect nonlinear effects to occur even at very low stopping powers. The nonlinear regime may be characterized by collision cascades in which the moving particles collide with one another [8,10]. These dense cascades arise whenever the collision density is high or the binding of the target particles to the bulk sites is correspondingly weak. Sputtering under such spike conditions has been treated by several authors [11,12], and their models lead to a yield dependence on the primary energy similar to that of the nuclear stopping power squared. A parallel case for electronic sputtering was considered by Gibbs, Brown, and Johnson [6]. They demonstrated that the sputtering yield from an electronic spike was proportional to the square of the electronic stopping power. In view of these predictions and observations the correlation between the sputtering yield and the stopping power appears to be one of the important features.

Sputtering of thick solid hydrogenic targets has been studied relatively little. In the present setup, sputtering was measured for 2-keV electrons [13] and light keV ions [9,14] incident on solid D_2, but no measurements for the most volatile isotopes, HD and H_2, were carried out previously. In this paper we present results for the first sputtering yield measurements we believe have been made for these two materials. Preliminary measurements for solid H_2 in this setup were performed without a beam-sweep arrangement [15], so that the yield exceeded the present one by more than a factor of 3.

The solid hydrogen isotopes are unique with respect to electronic sputtering. Since the electronically excited states are practically similar for H_2, HD, and D_2 [2], the energy release, which leads to the production of moving target particles and, eventually, to particle ejection, is ex-

pected to be fairly similar as well. The only quantity that differs substantially is the sublimation energy, and consequently, the surface binding energy of the particles. The sublimation energy at 3.5 K increases about 50% from solid H_2 up to D_2. No other elements exhibit a similar isotopic behavior for the surface binding energy U_0.

The experimental setup is a modified version of that described previously [9,14,16] (Fig. 1). Hydrogenic films of a thickness from 2×10^{18} to 10×10^{18} molecules/cm² are produced by letting a jet of cooled gas impinge on an oscillating-quartz-crystal microbalance suspended below a liquid-helium cryostat. With this system it is possible to make hydrogenic films of known thickness and to measure the mass loss during irradiation. Beams of 4.5–10 keV H^+, H_2^+, H_3^+, and D_3^+ ions are extracted from a duoplasmatron ion source and selected by a 45° magnet. Since the magnet does not allow us to distinguish between H_2^+ and D^+ beams, all comparisons between deuterium and hydrogen ions have been performed with D_3^+ and H_3^+ ions. In order to ensure a homogeneously irradiated area on the target, the beam was swept both horizontally and vertically over an aperture in front of the target. The beam current was measured before and after irradiation by deflecting the beam into a Faraday cup. An open repeller ring (biased at -90 V) in front of the target suppresses the secondary-electron emission, and charge-up problems are largely reduced. The accuracy of the data as well as other experimental details are discussed in Refs. [9] and [16].

During the measurements the pumped helium bath reached a temperature of 2.0 K. The thermal connection from the cryostat bottom to the silver electrode of the quartz crystal was improved substantially, so that it was possible for the first time to perform controlled sputtering measurements of solid H_2 and HD. The conductive glue
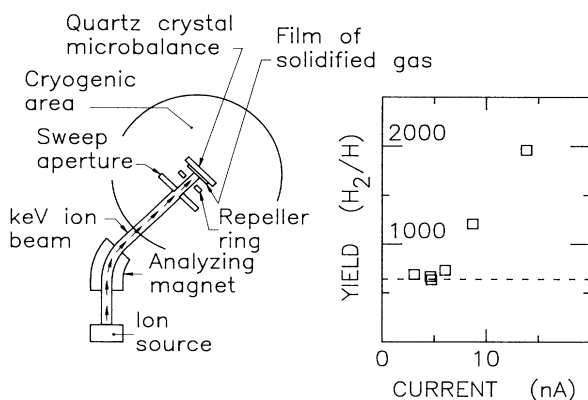
between the quartz-crystal holder and the electrode was replaced by a low-temperature-solder point directly on the 4000-Å-thick silver electrode. The precise temperature of the substrate electrode cannot be measured during operation because of the high-frequency oscillation. Moreover, we applied hydrogen-ion beams instead of the keV-electron beams previously used. Since the sputtering yield for hydrogen ions is at least 1 order of magnitude larger than that for electrons, the beam power deposited in the hydrogenic targets can be reduced significantly for the same mass loss.

The important test showing that sputtering rather than beam-induced evaporation takes place, is shown in the inset of Fig. 1. Note that the yield is independent of the current below 5 nA; above this current it increases strongly. This behavior is a clear indication of beam-induced evaporation at high currents [16]. Consequently, only beam currents less than 5 nA were utilized for the present sputtering measurements on solid H_2 and HD. The procedure of varying the beam current is the most direct way of changing the temperature at the beam spot. For the least volatile material, solid D_2, no dependence on the beam current up to more than 15 nA was observed.

The sputtering yield for all hydrogenic targets decreases slowly with increasing film thickness [9,13,17], but reaches a constant plateau for thicknesses exceeding the range of the primary ion [9]. These constant (bulk) yields are shown in Fig. 2. A single point from Erents and McCracken [17] was not included in Fig. 2 or in the discussion because their yield did not reach a constant value even for thicknesses larger than the ion range.

The yields for all three isotopes increase strongly with primary energy. This behavior is an argument against knockon sputtering, since the nuclear stopping power decreases in this energy interval. The knockon-sputtering yield predicted from linear collision cascades [8], from elastic cylindrical spikes [11], or from nonoverlapping subspikes [18] decreases for these energies as well.
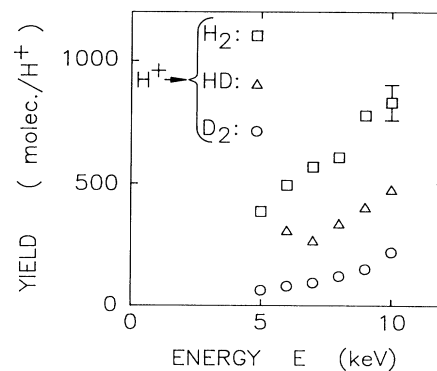
FIG. 1. Schematic drawing of the setup. The inset shows the yield *per atom* of 2×10^{18}-H_2/cm²-thick films as a function of the beam current for 8-keV H_2^+ ions incident on solid H_2. The dashed line indicates the average value of the sputtering yield for a large number of measurements on film thicknesses exceeding 1.5×10^{18} H_2/cm² with the beam current below 5 nA.

FIG. 2. The sputtering yield as a function of the proton energy for a film thickness of 3×10^{18} molecules/cm². Usually, each point was an average of at least three individual data points. A typical standard deviation is indicated.

Figure 3 shows the bulk yield *per atom* for H_3^+ and D_3^+ ions incident on solid H_2. One notes that ions of the same velocity produce practically identical yields, and that all the yield points seem to lie on a single curve. The results demonstrate that the yields are determined solely by the electronic stopping power of the projectiles and indicate in a convincing manner that the erosion is dominantly electronic sputtering. Even though the molecular ions break up at the impact on the surface, each atom deposits the electronic energy so close to the others that one may consider the impact of the molecule as one event. The analysis of sputtering yields from solid D_2 [14] and from H_2 [19] showed that the *total* yield is determined solely by the *sum* of the electronic stopping power of the individual atoms in the molecule.

The key point is how the energy stored in electronic excitations is converted into translational energy of the target molecules. Luminescence studies of electron-irradiated solid deuterium have demonstrated that very little light is emitted from these materials during charged-particle bombardment [20]. Therefore, the energy deposited in the solid is efficiently converted either to kinetic energy of free target particles, to phonon production in hydrogenic lattices, or to excitations of the vibrational and rotational states of the molecules.

At these primary energies the cross section for ionization is low [21]. For 5-keV protons it means that the projectile loses about 250 eV in terms of electronic stopping over an average distance of 150 Å for the production of one ion-electron pair [22]. Thus excitations below the ionization threshold are dominant, and this trend has been confirmed by collision spectrometric measurements at a proton energy of 50 keV by Park [23].

An efficient way of releasing kinetic energy for sputtering in hydrogenic targets is direct dissociation of molecules from particle impact. Celiberto, Cacciatore, and Capitelli [24] have shown that the majority of the released atoms have a kinetic energy practically peaking at
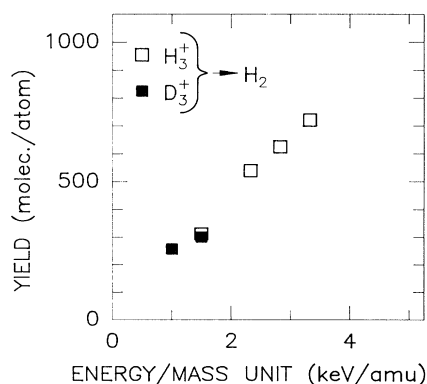
0 eV. This low-energy peak that originates from the repulsive part of the bound states of the electronically excited molecules may play a role in the erosion.

In addition to this low-energy peak, which may appear in the gas phase as well as the solid phase, one may consider the relaxation dynamics of the excited states in the solid. Very little is known about the electronic transitions of the solid, but basically one expects that the system terminates on the strongly repulsive triplet state $b\,^3\Sigma_u^+$ because intermolecular and intramolecular vibrations make all electronic transitions allowed [25]. Since the results from Park [23] show that excitations of the $B\,^1\Sigma_u^+$ level or the many close-lying molecular states just about this level from the ground state prevail, the deexcitation to the triplet state and the subsequent ground-state repulsion liberate from 5 to 11 eV imparted on the two atoms. However, it is unknown how much of the energy is actually available for sputtering, and in which fractions it is released.

Recent measurements of the energy distribution of the particles sputtered from electron-irradiated solid D_2 have demonstrated that the overwhelming part of the energy release events liberate less than a few tenths of an eV [19]. This means that direct dissociation processes are possible, but also that the energy relaxation of the solid takes place via many minor rather than one great energy release event.

The mean free path for an average 10-eV excitation event along the ion track of a 5-keV proton is 5 to 10 Å. This distance is so small that the small spike volumes from subsequent events may interact and eventually merge to a cylinder that encompasses the track. (The atoms in a molecular ion generate cylinders that overlap at the point of impact at the surface.) The cylindrical geometry means that the yield behavior might be explained by the cylindrical-spike model [6,12]. Since the sputtering yields for solid H_2 as well as HD shown in Figs. 2 and 3 increase linearly with energy, the yields actually show the predicted quadratic dependence on the electronic stopping power [22]. The yield for solid D_2 shows a somewhat stronger dependence than indicated by these models [14]. However, the dependence on the sublimation energy [12] is fulfilled only for an initial string temperature that leads to a yield about 1 order of magnitude too low [19]. Obviously, the existing spike treatments are not feasible for these volatile solids. The analysis of the data will be described elsewhere in great detail.

The large yield (Fig. 2) from the most volatile isotopes indicates a significant isotopic effect. In principle, one may distinguish between two possibilities; the energy release in the solid is more efficient in solid H_2 and HD, or the escape probability of the particles set in motion is considerably larger in solid H_2 and HD than in D_2. The pronounced predissociation of electronically excited molecules with H atoms [20] might lead to an enhancement of

FIG. 3. The sputtering yield per atom as a function of the energy per mass unit from solid H_2 for D_3^+ and H_3^+ ions incident on 3×10^{18}-H_2/cm²-thick films.

the energy release. On the other hand, the emission process may be more efficient for solid H_2 and HD because of the low sublimation energy. For these solids the sublimation energy is a questionable measure of the surface binding energy U_0. One may argue that for sufficiently large yields the standard concept, the planar surface barrier, loses its meaning. Many ejected molecules or atoms may be ejected in clusters [26] and are not influenced by other remaining surface atoms. In this case, the efficient energy loss per molecule during the ejection process will be less than U_0. As a result the yields for the most volatile solids are larger than expected. In addition to this possibility, a minor contribution from thermal evaporation from the surface may not be excluded. Studies of the energy distributions of the emitted target particles from solid HD and H_2 are expected to extend our knowledge.

Although the isotropic effect is considerable, the yield dependence does not indicate that sputtering of these volatile solids by light ions differs substantially from that known from other frozen gases [3,5,6,14]. In this context one may mention that yield dependences on the third or much higher powers of the stopping power have been observed at high collision densities in volatile solids [27] or at very large electronic stopping powers [28]. These results have been interpreted largely on the basis of ejection models recently developed [26–28].

In summary, we have presented the first sputtering measurements for the most volatile solid hydrogens. The erosion mechanism is electronic sputtering, but the deexcitation processes leading to energy release are not identified in detail. No existing model can account satisfactorily for both the yield dependence on the primary energy or the sublimation energy as well as the absolute magnitude of the yield. The extreme volatility of the hydrogenic solids does not lead to any yield dependence on the stopping power which contrasts other frozen gases.

(a)Present address: Department of Optics and Fluid Dynamics, Risø National Laboratory, DK-4000 Roskilde, Denmark.
(b)Present address: Odense University, DK-5230 Odense, Denmark.

[1] I. F. Silvera, Rev. Mod. Phys. 52, 393 (1980).

[2] P. C. Souers, Hydrogen Properties for Fusion Energy (Univ. California Press, Berkeley, 1986).

[3] J. Schou, Nucl. Instrum. Methods Phys. Res., Sect. B 27, 188 (1987).

[4] Sputtering by Particle Bombardment I, edited by R. Behrisch, Topics in Applied Physics Vol. 47 (Springer-Verlag, Berlin, 1981); Sputtering by Particle Bombardment II, edited by R. Behrisch, Topics in Applied Physics Vol. 52 (Springer-Verlag, Berlin, 1983).

[5] W. L. Brown and R. E. Johnson, Nucl. Instrum. Methods Phys. Res., Sect. B 13, 295 (1986); C. T. Reimann, W. L. Brown, and R. E. Johnson, Phys. Rev. Lett. 53, 600 (1984); Phys. Rev. B 37, 1455 (1988).

[6] K. M. Gibbs, W. L. Brown, and R. E. Johnson, Phys. Rev. B 38, 11101 (1988).

[7] J. Schou, O. Ellegaard, H. Sørensen, and R. Pedrys, Nucl. Instrum. Methods Phys. Res., Sect. B 33, 808 (1988).

[8] P. Sigmund, in Sputtering by Particle Bombardment I (Ref. [4]), p. 9.

[9] B. Stenum, O. Ellegaard, J. Schou, and H. Sørensen, Nucl. Instrum. Methods Phys. Res., Sect. B 48, 530 (1990).

[10] D. A. Thompson, Radiat. Eff. 56, 105 (1981); D. J. Oostra, R. P. van Ingen, A. Haring, A. E. de Vries, and F. W. Saris, Phys. Rev. Lett. 61, 1392 (1988).

[11] P. Sigmund and C. Claussen, J. Appl. Phys. 52, 990 (1981); C. Claussen, thesis, University of Odense, 1982 (unpublished); P. Sigmund and M. Szymonski, Appl. Phys. A 33, 141 (1984).

[12] R. E. Johnson, J. Phys. (Paris) 2, 251 (1989).

[13] P. Børgesen and H. Sørensen, Phys. Lett. 90A, 319 (1982).

[14] B. Stenum, O. Ellegaard, J. Schou, H. Sørensen, and R. Pedrys, Nucl. Instrum. Methods Phys. Res., Sect. B 58, 399 (1991).

[15] P. Børgesen, Risø National Laboratory Report No. 457, 1982 (unpublished); P. Børgesen, J. Schou, and H. Sørensen, in Proceedings on Sputtering, edited by P. Varga, G. Betz, and F. P. Viehbock (Technische Universität, Vienna, Austria, 1980), p. 822.

[16] J. Schou, P. Børgesen, O. Ellegaard, H. Sørensen, and C. Claussen, Phys. Rev. B 34, 93 (1986); J. Schou, H. Sørensen, and P. Børgesen, Nucl. Instrum. Methods Phys. Res., Sect. B 5, 44 (1984).

[17] S. K. Erents and G. McCracken, J. Appl. Phys. 44, 3139 (1973).

[18] O. Ellegaard, J. Schou, and H. Sørensen, Europhys. Lett. 12, 459 (1990).

[19] B. Stenum, J. Schou, O. Ellegaard, H. Sørensen, R. Pedrys, and B. Warczak (to be published).

[20] J. Schou, B. Stenum, H. Sørensen, and P. Gürtler, Phys. Rev. Lett. 63, 969 (1989); B. Stenum, J. Schou, H. Sørensen, and P. Gürtler, Radiat. Eff. Def. Solids 109, 235 (1989).

[21] M. E. Rudd, Y.-K. Kim, D. H. Madison, and J. W. Gallagher, Rev. Mod. Phys. 57, 965 (1985).

[22] H. H. Andersen and J. F. Ziegler, Hydrogen Stopping Powers and Ranges in All Elements (Pergamon, New York, 1977).

[23] J. T. Park, in Collision Spectroscopy, edited by R. G. Cooks (Plenum, New York, 1978), p. 19.

[24] R. Celiberto, M. Cacciatore, and M. Capitelli, Chem. Phys. 133, 369 (1989).

[25] O. Oehler, D. A. Smith, and K. Dressler, J. Chem. Phys. 66, 2097 (1977).

[26] H. M. Urbassek and K. T. Waldeer, Phys. Rev. Lett. 67, 105 (1991).

[27] V. Balaji, D. E. David, T. F. Magnera, J. Michl, and H. M. Urbassek, Nucl. Instrum. Methods Phys. Res., Sect. B 46, 435 (1990).

[28] K. Wien, Radiat. Eff. Def. Solids 109, 137 (1989); (to be published).