Desorption of solid hydrogen by energetic protons, deuterons, and electrons

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The yield of condensed gas released from liquid-helium-cooled surfaces under particle bombardment has been measured as a function of surface coverage. The yield has been found to increase at low coverage, then become roughly independent of coverage, and finally to decrease at very high coverage. The observed value of the yield has been found to exceed $10^9$ atoms/ion and this value has been explained in terms of a thermal spike model. Where the condensed layer thickness is greater than the range of the incident ions the yield is typically $10^7$ atoms/ion. This cannot be explained either by thermal spike or conventional sputtering, and it is suggested that ionization of the condensed gas leads to gas release.

I. INTRODUCTION

The use of cryogenic surfaces as vacuum pumps and the use of superconducting magnets in vacuum systems can lead to conditions where large amounts of gas condense on surfaces in vacuum. A case of particular technological interest is the situation where superconducting magnets are used to confine plasmas in controlled thermonuclear research. In some experiments of this type it is possible for energetic particles, ions and electrons, to impinge on the condensed gas layer leading to desorption or sputtering. The desorption process could be of considerable fundamental interest since it can be carried out on systems with very low binding energies and also on systems where a great deal is known about the interaction of the projectile and target atom from gas phase studies. We have therefore undertaken some experiments to investigate the desorption of hydrogen condensed on a surface at liquid-helium temperatures, by bombardment with keV ions and electrons.

II. EXPERIMENT

Experiments were performed using an UHV 5-t0 30-keV ion beam accelerator described previously. The target assembly used for the present series of experiments is shown schematically in Fig. 1. It consists of the following parts: (i) A copper target, which is an integral part of the helium cryostat and which can be pumped or pressurized to obtain target temperatures between 2.5 and 5 K. The temperature is measured using a calibrated germanium resistance thermometer. (ii) A liquid-nitrogen-cooled desorption chamber into which the copper target protrudes. The assembly ensures low radiation loading of the condensed hydrogen surface during an experiment. (iii) A quadrupole mass spectrometer which is used to monitor the partial pressure of the desorbing gas. (iv) A removable palladium target which is used to calibrate the mass spectrometer by leaving it in the beam until it is saturated and all incident ions are re-emitted as gas. The palladium target has a small hole in the center with another ion collector behind it, so that the current density distribution across the target can be measured by scanning the palladium target in front of the copper target. (v) A gas inlet for hydrogen or deuterium consisting of a palladium leak. The partial pressure of the gas introduced for condensation on the copper target is normally in the range $10^{-8}$ to $10^{-6}$ Torr. The background gas pressure is about $2 \times 10^{-10}$ Torr and consists mainly of carbon monoxide.

The desorption chamber is continuously pumped during the experiment via ports in the chamber and also by the cold copper surface itself. Thus all measurements are dynamic ones, and the vacuum time constant is about 0.05 sec. Since the pumping speed of the cold surface can vary with coverage for layers up to a monolayer, 3 the target is covered with a thick ($10^{17}$ molecules cm$^{-2}$) gas layer before all measurements. In order to keep the pumping speed as constant as possible during measurements the beam area is reduced to 0.3 cm$^2$, i.e., less than one-tenth the total target area.

In general, the experimental procedure for measuring the desorption rate was as follows:

(i) The copper target was cooled to 2.5 K, and hydrogen or deuterium was introduced into the desorption chamber to a pressure of 10$^{-7}$ Torr. An exposure of 10$^{-4}$ Torr·sec was given before cutting off the gas flow.

(ii) Using a 10-μA beam, the beam current density profile over a 0.3-cm$^2$ area was examined. The current density varied by about a factor of 2 within this area and was focused to produce a reasonably sharp cutoff beyond it. The palladium target at 77 K was allowed to saturate, and a calibration for the quadrupole (tuned to mass 2 or mass 4) was obtained.

(iii) The palladium target was removed and the 10-μA beam was allowed to impinge upon the gas-covered target until no further remission of condensed gas was observed. It was then assumed that the target was clean. With the palladium target repositioned in the beam, the ion current was reduced to $5 \times 10^{-10}$ A and the beam current-density profile was checked to ensure no change in the position or total area of the beam.

(iv) The copper target was bombarded again with the lower current beam, and gas was introduced to the desorption chamber (10$^{-6}$ Torr). To start adsorption, the beam was switched off. Care was taken to ensure that the hydrogen partial pressure under "beam on" conditions was sufficiently low to maintain a clean surface. The layer thickness was controlled by variation of the gas supply and hydrogen partial pressures of up to 10$^{-6}$ Torr were used.

(v) After a known exposure, the ion beam was switched onto the condensed layer and a record of the gas release rate as a function of time was made.
The procedure was repeated using an electron beam rather than a proton beam. The electron gun was moved into the beam line before the focusing system to obtain similar beam profiles. The proton beam was still used for calibration purposes.

III. RESULTS

The general form of result obtained from the experiment is shown in Fig. 2. These curves illustrate how the deuteron yield (atoms/ion) varies as a function of time during bombardment for different initial thicknesses of condensed gas. For thin layers (curve a) the yield decreases with time as the layer is eroded away. The initial yield increases with coverage up to $10^{18}$ molecules cm$^{-2}$, after which a decrease in initial yield with increasing coverage is observed (curves a–d). This process is demonstrated dynamically during the erosion of a thick layer (e.g., curve c). The yield is observed to increase with time before decreasing as the layer is finally eroded away. It is thus clear that there is an optimum layer thickness for maximum yield. However, the shape of the yield-vs-time curves is smeared by the fact that the current density was not uniform across the beam; thus, the maximum yield was reduced and it was difficult to determine the optimum layer thickness. It was also observed that at the relatively high current densities used (~2 μA cm$^{-2}$) during these measurements, for thin layers the layer thickness and hence the yield changed within the time required to make a measurement (determined by instrumental time constants), and thus the initial yields indicated are less than the true values.

The initial yield due to proton bombardment has therefore been measured as a function of layer thickness by using much lower current densities (~$10^{-5}$ A/cm$^2$). The results for bombardment of hydrogen by 5- and 20-keV protons are shown in Fig. 3. The surface temperature was 3.2 °K so that there is negligible thermal desorption of hydrogen. The thickness of the hydrogen layer has been estimated from the time of condensation at a given pressure by integrating the function

$$\int_0^t \frac{dn}{dt} dt,$$

where $dn/dt$ is the rate of arrival at the surface and $\alpha$ is the sticking coefficient. The variation of $\alpha$ with coverage obtained by Chubb has been taken into account. The value of $\alpha$ increases from about 0.5 at zero coverage to about 0.95 at a coverage of $10^{16}$ molecules cm$^{-2}$ for H$_2$ at 77 °K. The directly measured parameter of the quantity of gas which has impinged on the surface (in Torr sec) is also shown in Fig. 3.

The yield initially increases with surface coverage, as expected. It then reaches a plateau and finally falls with increasing coverage for thick layers ($10^{18}$ molecules cm$^{-2}$). The shape of the curves for proton energies of 5 and 20 keV is similar, but the maximum yield is higher by a factor of about 2 for the 20-keV beam. Results for bombardment of deuterium by 5-keV deuterons and for hydrogen by 2-keV electrons are shown in Fig. 4. The results are again similar in form; the deuterium yields are slightly lower than the comparable hydrogen yields, and the yield due to electron bombardment is over an order of magnitude less than that due to protons.

The possibility of the surface charging up electrically has been considered. By estimating the capacitance of the condensed gas layer, the rate of increase of potential $dV/dt$ for thin layers (~10 Å) was $-10^3$ V/sec for the currents used; hence the total potential will be negligible for the times and beam energies considered. For thicker layers (~10$^3$ Å) the layer capacitance is lower and the currents used are larger so that the $dV/dt$ may have been as high as 10$^2$ V/sec. Hence, even in this case the initial yield measurements are reliable. The yield was found experimentally not to change significantly with time.

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**FIG. 2.** Yield of desorbed deuterium as a function of time during bombardment by 5-keV protons at 2 μA/cm$^2$ for condensed D$_2$ gas at 4.2 °K. (a) 3.2×$10^{17}$ molecules cm$^{-2}$; (b) 6.6×$10^{17}$ molecules cm$^{-2}$; (c) 6.8×$10^{17}$ molecules cm$^{-2}$; (d) 1.2×$10^{18}$ molecules cm$^{-2}$; (e) 2.3×$10^{18}$ molecules cm$^{-2}$.
IV. DISCUSSION

A. Yield

The high desorption rates which have been observed are not unreasonable when considered superficially in energetic terms. The sublimation of $2.5 \times 10^4$ molecules at 0.0108 eV/molecule requires a total energy of 270 eV, compared with the incident ion energy of 5 keV. However, it is clear that at low concentrations of hydrogen on the surface ($10^{18}$ molecules cm$^{-2}$) the energy transfer cannot be by direct interaction of the incident proton with the target hydrogen. The incident proton will go through the thin layer of hydrogen, and most of its energy will be deposited in the copper substrate. It is thus interesting to consider whether the effect observed is due to a thermal spike in the substrate.

The thermal spike has previously been considered in applications such as sputtering at high temperatures. However, in the present case where the sublimation energy is low and the specific heat of the surface is low, which allows a high temperature rise, it may also be applicable. A thermal spike could cause a large enough area of surface to be heated to supply the large yield observed. Taking the maximum yield of $5 \times 10^4$ atoms/ion at a coverage of $10^{18}$ molecules cm$^{-2}$, that part of the surface heated by the thermal spike must have a radius of at least 90 Å. The mean projected range $R_p$ of protons in copper calculated from the theory of Schiött$^5$ is 250 Å, with a range distribution of 210 Å, so that the thermal spike radius will have to be in the range 250–300 Å on average to produce sufficient evaporation. The total energy dumped in this volume is about 1 J/g, which from enthalpy data corresponds to a temperature rise of 45 K. This is of course more than high enough to evaporate hydrogen from the substrate, provided the lifetime of the spike is sufficiently long.

The yield $Y$ due to a thermal spike will be given in principle by an expression of the form

$$Y = \int_0^T A(t)R(t)dt,$$

where $A$ is the projected area of the spike at the surface and $R$ is the rate of evaporation which is a function of temperature $T$ and time $t$. The variation of the thermal spike temperature with time and radius can be determined by solving the diffusion equation. This is straightforward where the thermal diffusion coefficient $D = K/C_p$ is constant ($K$ is the thermal conductivity, $C$ is the specific heat, and $p$ is the density of the material). Under these conditions Seltz$^7$ has pointed out that the temperature is roughly constant over a region of radius $r = (4Dt)^{1/2}$ and the temperature varies as

$$T = T_0(\tau/\tau_0)^{3/2},$$

where $T_0$ is the initial spike temperature and $\tau$ is the spike characteristic lifetime, given by

$$\tau = (Cp/4K)^{1/2}.$$  

However, at the low temperature being considered here, both $C$ and $K$ are strongly temperature dependent. The variation of specific heat with temperature obtained experimentally$^8$ can be approximated in the temperature range 5–50 K by a power law of the form

$$C = 2 \times 10^{-6}T^{2.7} \text{ J g}^{-1} \text{ K}^{-1},$$

which is close to the Debye $T^3$ dependence expected in this region. Careful consideration has to be given to the values for thermal conductivity. The energy of the incident proton will be given partly to the lattice and partly to electrons. Similarly, the heat will be conducted away partly by the lattice and partly by electrons. The mean free path for electrons at these temperatures is very long. For electron-electron collisions it is typically 3 cm at 6 K in monovalent materials.$^9$ For electron lattice collisions a mean free path can be calculated from electrical conductivity to be $~10^4$ cm at 4 K; even at 300 K it would be $5 \times 10^4$ cm. In the case of electron lattice collisions the energy transfer will be small, and so many collisions would be necessary to transfer a significant fraction of the electron energy that the energy

![FIG. 4. Initial yield of desorbed gas as a function of thickness when bombarded by 5-keV deuterons and 2-keV electrons.](image-url)

TABLE I. Range $R_p$ and nuclear energy loss term $E_n$ for protons and deuterons in copper.

<table>
<thead>
<tr>
<th>Energy (keV)</th>
<th>$R_p$ (Å)</th>
<th>$\Delta R_p$ (Å)</th>
<th>$E_n$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>250</td>
<td>210</td>
<td>420</td>
</tr>
<tr>
<td>20</td>
<td>1060</td>
<td>480</td>
<td>680</td>
</tr>
<tr>
<td>5</td>
<td>265</td>
<td>290</td>
<td>980</td>
</tr>
</tbody>
</table>

would be dissipated over a large volume leading to a low
temperature rise. We will therefore consider only the
energy given directly to the lattice by the incident proton
and the thermal conductivity associated with the lattice.
The energy given to the lattice by a 5-keV proton slow-
ing down to zero energy was calculated to be 420 eV by
integrating the nuclear loss term given by Schiott
(Table 1). To obtain an order-of-magnitude estimate of
the thermal conductivity of the copper lattice, we as-
sumed it to be similar to insulators (e.g., glass and
quarze), the thermal conductivity of which\textsuperscript{13} can be ap-
proximated within a factor 2 in the temperature range
5–50 K by the equation
\begin{equation}
K = 10^{-4} T \text{ W cm}^{-1} \text{ K}^{-1}.
\end{equation}
Since \( \tau \) is temperature dependent, it is difficult to pre-
dict the time dependence of the spike radius and tem-
perature. In view of the many other approximations in this

FIG. 5. Calculated yield of desorbed gas using the thermal
spike model as a function of the thermal spike radius. The
spike temperature and spike lifetime we also show as a func-
tion of initial radius. (a) 5-keV \( \text{H}^0 \) on \( \text{H}_2 \), (b) 20-keV \( \text{H}^0 \) on \( \text{H}_2 \),
(c) 5-keV \( \text{D}^0 \) on \( \text{D}_2 \).
Table II. Evaporation constants for $H_2$ and $D_2$, obtained from the data of Mittelhauser and Thodos (Ref. 6) at 30 K.

<table>
<thead>
<tr>
<th></th>
<th>A (molecules cm$^{-2}$ sec$^{-1}$)</th>
<th>Q (cal/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H_2$</td>
<td>$1.75 \times 10^{17}$</td>
<td>248 (6.0109 eV)</td>
</tr>
<tr>
<td>$D_2$</td>
<td>$2.22 \times 10^{17}$</td>
<td>315.5 (6.0137 eV)</td>
</tr>
</tbody>
</table>

Simple model, we obtain an order-of-magnitude estimate of the yield for various spike radii $r$ by assuming a spike with a temperature which is constant for a time given by the initial time constant. Thus, the yield $Y$ is given by

$$Y = \left[ \pi (r^2 - R_s^2) \right] \left[ \frac{Q}{RT} \right] \left( \frac{C(T)P}{4K(T)^2} \right)^{rac{1}{2}},$$

(6)

where the temperature $T$ is obtained from enthalpy data and is given in the temperature range 5–50 K by $T = 45.51 + 26t$; the enthalpy $\epsilon = 3E/4\pi r^2$, $E$ is the energy transferred to the lattice (Table I), and $C(T)$ and $K(T)$ are given by Eq. (4) and (5). The first term gives simply the area of the surface which intersects the spherical thermal spike. The second term gives the specific evaporation rate, and the constants $A$ and $Q$ given in Table II are obtained from the data of Mittelhauser and Thodos for the vapor pressure of $H_2$ and $D_2$ at temperatures up to 30 K. The third term as discussed above is the lifetime of the thermal spike. The values of yield obtained from Eq. (6) are shown in Figs. 5(a)–5(c). Two curves for yield have been plotted in each case. The first is that given directly by Eq. (6), which predicts that if the spike radius is less than the mean projected range $R_s$ then the yield will be zero. However, the range distribution is large, so that there will be a considerable number of incident ions with ranges much less than the mean projected range. The effect of this has been illustrated by plotting the yield curves and assuming $R_s$ is zero. It is seen that for the 5-keV ions the yields are the correct order of magnitude to explain the experimental results when the spike radius is in the range 100–500 Å, whether the ion range is taken to be the calculated projected range or zero. In the case of 20-keV ions, only if $R_s$ is assumed to be much smaller than the calculated value of 1000 Å can the experimental yield be explained. It is clear that the correct range distribution of the incident ions must be taken into account in order to get a better estimate of the theoretical yield. By taking the calculated yields and assuming $R_s = 0$ for the three cases considered, it is seen that the maximum yield is predicted to be larger for 20-keV $H^+$, in agreement with experiment, but the yield for 5-keV $D^+$ on deuterium is also predicted to be larger than 5-keV $H^+$, in contradiction to the experimental results.

In Fig. 5 the spike temperatures and lifetimes have also been plotted as a function of radius. The spike temperature is within the range of values over which our approximations for the data used are reasonable. The spike lifetime of $\sim 10^{-15}$ sec is not varying by more than a factor of 3 within the range of spike radii of interest, and it is clearly large enough for there to be thermal equilibrium in the lattice. A factor which has been neglected is that evaporation from the surface will cool the spike, though this is partly compensated by the assumption that the spike volume is always a sphere, whereas it is less than a sphere for radii greater than the ion range. The results indicate that the sublimation energy for the yields observed is in all cases less than the energy given directly to the lattice (Table I), although in the case of the 20-keV $H^+$ the sublimation energy is 80% of that given to the lattice. It is possible that there is a contribution due to electrons as discussed in Sec. IV B, or that the hydrogen layer is not evaporated but blown off in lumps by the thermal pulse. If this were the case, then there would not be the same energy limitation.

B. Effect of electrons

As was discussed in Sec. IV A, the large mean free path of electrons is expected to result in their energy being distributed over a large volume and hence leading to a negligible temperature rise. However, since the energy is deposited so close to the surface, approximately half the conduction electrons must interact with the surface before they interact with the lattice. We must therefore ask whether they will give up energy to the surface. In investigations of the effect of surfaces on electrical conductivity of thin films, Fuchs concluded that about 90% of the energy was elastically reflected from the surface. Taking 10% to be inelastically scattered, one would expect the yield due to the energy given to the electrons to be of the same order as that due to the lattice.

In the experiments using electrons to bombard the surface, all the energy is expected to go to electrons in the copper and none to the lattice directly. Thus the yield from an electron would be expected to be lower than that for an ion. In practice the situation is complicated, as the electron range in copper is higher than the ion range for a given energy. Experimentally, the yield decreased

Table III. Yield calculated from ionization of condensed layer by incident particles.

|       | 5-keV $H^+$ → $H_2$ | 20-keV $H^+$ → $H_2$ | 5-keV $D^+$ → $D_2$ | 2-keV e→$H_2$
|-------|----------------------|----------------------|----------------------|----------------------|
| $\sigma$ (cm$^2$) | $2.5 \times 10^{-17}$ | $5.5 \times 10^{-17}$ | $1.5 \times 10^{-17}$ | $1.5 \times 10^{-17}$
| $m_p$ (Å)     | 51                   | 23                   | 123                  | 86                   |
| Energy (eV)   | 0.28                 | 0.6                   | 0.12                 | 0.17                  |
| Yield         | 52                   | 114                  | 17                   | 31                   |
with increasing energy when electrons in the range 2–5 keV were used. At 2 keV the maximum yield was only about 5% of that for protons, which indicates that only a very small fraction of the electron energy is used in the release process.

C. Effect of layer thickness

Considering again the experimental results shown in Fig. 3, we see that below a coverage of 10^14 molecules cm^-2 the yield increases approximately linearly with coverage, as expected from the thermal spike model. Above this coverage the yield stays roughly constant and then decreases slowly, which is not explained by the simple thermal spike model. The constant yield between 10^14 and 10^15 molecules cm^-2 may simply be due to the limited amount of energy available for evaporation. At a surface coverage of ~10^15 molecules cm^-2 the yield drops rapidly. The range of protons in hydrogen, again calculated from the Schiött theory, is 190 Å (0.74 × 10^18 molecules cm^-2) for 5-keV protons and 5100 Å (2 × 10^18 molecules cm^-2) for 20-keV protons. It thus seems reasonable to correlate the change of yield in thick layers with the fact that the energy is now being deposited in the hydrogen and no longer in the copper. Since the range of protons is much larger in hydrogen than in copper, for thick condensed layers the energy is deposited much further from the surface and over a much larger volume, which thus makes a lower yield probable. However, it is surprising that there is no marked difference in the layer thickness at which the yield decreases for the two proton energies used, despite the factor-of-3 difference in their calculated ranges. The results in Fig. 4 for electrons and deuterons are very similar qualitatively to the proton results. The decrease in yield comes at lower coverage for deuterons than protons despite the fact that the range is similar, being 3700 Å or 1 × 10^18 molecules cm^-2.

Once the layer thickness is larger than the range of the incident ions, the yield must be independent of layer thickness. It is seen that the experimental yields are approaching constant values in all cases. These constant values thus correspond to the sputtering coefficients of bulk solid hydrogen. The yield expected on the basis of a conventional sputtering model is calculated to be ~5 atoms/ion and is thus quite insufficient to explain the observed yield. The possibility of a thermal spike in hydrogen has also been investigated. However, the large range and the high specific heat of hydrogen compared with copper leads to a maximum temperature for a spike reaching the surface of 5 K and a maximum yield of ~10 atoms/ion. Thus the thermal spike seems unable to explain the yield from thick layers. A further possibility is that ionization of the condensed hydrogen by the incident particle could lead to desorption of gas. This process is a likely one since the incident ions have a high probability of charge exchanging at the surface and it is known that the major energy loss mechanism of fast atoms passing through hydrogen is ionization. The ionization cross section for 5-keV atoms is 2.5 × 10^-17 cm^2. Thus, for 5-keV H^+ on H_2 the mean distance between ionization events can be simply calculated to be about 50 Å and the electrostatic energy between charges can be calculated to be 0.28 eV, which is sufficient to desorb 25 molecules. Corresponding estimates for the 20-keV protons, 5-keV deuterons, and 2-keV electrons have been made as shown in Table III. The yields are seen to be qualitatively in agreement with the experimental results. The release of many molecules in the form of a cluster has been observed previously for electron bombardment of solid hydrogen, and for ion bombardment of ice. The clusters are charged and are thought to be produced by an induced dipole attraction of neutral molecules around an H^+ ion. Their size has been observed to range from H_2 up to H_30 with a most probable size of H_15. Thus a few ionization events in the solid could account for the high yield observed.

V. CONCLUSIONS

The desorption rate of condensed hydrogen by incident keV ions has been observed to be greater than 10^13 atoms/ion. These high yields can be explained semi-quantitatively by a thermal spike model. It appears from the relatively much lower yield due to electron bombardment that the energy transfer from the electrons to the hydrogen condensed layer is poor. On the other hand, the energy which the protons transfer directly to the substrate lattice atoms is transferred to the condensed hydrogen layer extremely efficiently. A further experimental test of the present model would be to use other ions over a wider range of mass and energy to examine the effect of different energies being given to the lattice in the same ion range.

The thermal spike model outlined is recognized as being very much oversimplified. The effect of evaporation cooling of the surface, which has been neglected, is obviously important since it carries away a high proportion of the energy dumped. The model could also be further developed by taking into account the time dependence of the temperature such that the rate of evaporation throughout the spike is properly integrated to obtain the total yield. The sputtering yield of thick layers of condensed gas is an aspect that has not been investigated in any detail but is of fundamental interest. Measurements of the mass distribution of the sputtered particles could give an answer as to whether the cluster mechanism proposed is contributing to the sputtering yield.

From the practical point of view of cryopumping, the high yields observed are rather disturbing. It is clear that if the yields are to be kept small, then either a very high or very low coverage is desirable. In the case of high coverage it is unlikely that a yield below 100 atoms/ion will be obtained. Going to low coverage means going to less than 10^14 molecules cm^-2 before the yield will be less than 100 atoms/ion. On the other hand, if low yields are desirable, provided the coverage of exposed surfaces can be reduced to 10^16 molecules cm^-2 by thermal desorption, for example, then the high desorption rate of incident ions will lead to rapid cleanup of the surface and low yields will ultimately be obtained.

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