

## Deuterium bonding at internal surfaces in silicon

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The strength of deuterium bonding to the walls of closed cavities within Si was determined in ion-beam experiments. These studies circumvented an inherent indeterminacy in the analysis of external-surface desorption and thereby achieved a quantitative characterization of Si-H surface bonding. The Si-D bond energy for submonolayer coverages is  $2.5 \pm 0.2$  eV. This value has implications for the re-action path of molecular desorption.

The strength of Si-H bonding on the Si surface is a fundamental property with numerous consequences for the important reactions of H with Si, and yet this bond energy has not previously been definitively measured. Extensive and careful observations of molecular  $H_2$  desorption from Si have been made,<sup>1-6</sup> but there is an inherent indeterminacy in the relationship between the observed activation energy for such desorption and the Si-H bond energy, as we shall discuss. This difficulty was circumvented in the present study; here we used ion-implanted specimens to examine the thermally activated release of chemisorbed deuterium (D) from the walls of *internal* cavities within Si. In contrast to the direct desorption from external surfaces, the internally chemisorbed atoms first move from the bound surface state into solution within the Si lattice, then diffuse to the outer surface of the sample, and finally desorb. This different path of release permitted us to extract the strength of Si-H bonding on the Si surface.

We begin by summarizing the results of earlier, external-surface desorption studies and indicate how they impose bounds on the Si-H bond energy. Then, the present ion-beam experiments are described and interpreted. Finally, implications of our results are considered.

Previous investigators have measured the thermal desorption of  $H_2$  from external surfaces of Si and have extracted the activation energy,  $E_D$ . For the more strongly bound, monohydride state which is relevant to the present work, the following values were reported: 2.0 and 2.5 eV for the (100) surface;<sup>1,2</sup> 2.8 eV for porous Si where ir spectroscopy indicated Si-H bonding similar to that on the (100) surface;<sup>3</sup> and 2.7, 2.5, 2.6, and 2.4 eV for the (111) surface.<sup>2,4-6</sup> The bonding configurations of H on the (100) and (111) surfaces have been examined using a variety of probes,<sup>3,7-11</sup> and the lower coverages of interest here are accommodated through the attachment of H to preexisting dangling bonds on surface Si atoms.

The measured desorption activation energy,  $E_D$ , does not directly determine the Si-H binding energy,  $E_B$ . This is because the desorption of  $H_2$  involves not only the breaking of two Si-H bonds, but also H-H recombination and its associated energy release of  $E_R = 4.52$  eV, and the influence of the latter process on  $E_D$  depends on the reaction path. The energy  $E_D$  could conceivably be as small as  $2E_B - E_R$ , the difference between the initial and final energies, if the breaking of the two Si-H bonds is concurrent with H-H recombination. Alternatively, the breaking of a

single Si-H bond might be followed by the exothermic reaction  $H + Si-H \rightarrow H_2 + Si-$ , with  $E_D$  approaching  $E_B$ . Values of  $E_D$  larger than  $E_B$  appear unlikely for molecular desorption, since the release of atomic H would be expected. One then has

$$E_D = 2E_B - E_R + E_A, \quad 0 \leq E_A \lesssim E_R - E_B. \quad (1)$$

The bounded quantity  $E_A$  is also the activation energy for adsorption from  $H_2$  gas.

Recent investigators of external-surface desorption have recognized the indeterminacy in the relationship between  $E_D$  and  $E_B$  (see, for example, Refs. 1 and 3). They have generally assumed that  $E_A$  is small, or, equivalently, that  $E_B$  is above 3 eV. Using the representative value of 2.5 eV for  $E_D$  and taking  $E_A \sim 0$  in Eq. (1), one obtains  $E_B \sim 3.5$  eV. The present investigation of release from internal surfaces is complementary to the desorption experiments in that our observed release is controlled by D-atom promotion from chemisorbed states to solution and subsequent atomic diffusion to the external surface, so that the indeterminacy associated with recombination is circumvented. As will be discussed, we find  $E_B$  to be smaller and  $E_A$  larger than previously assumed.

In the present study, cavities were formed within (111) Si by He-ion implantation. The beam energy of 30 keV and fluence of  $1000 \text{ nm}^{-2}$  yielded a calculated<sup>12</sup> range of 280 nm and peak concentration of 8 at.%. The room-temperature implantation was followed by vacuum annealing at 973 K for 30 min to enlarge the cavities and reduce implantation damage. The resulting microstructure is shown in the TEM micrograph of Fig. 1 from a back-thinned specimen. Cavities are seen with sizes ranging up to about 10 nm. Regions of the specimen thinner than the He-ion range showed no cavities, demonstrating that the cavities were away from the surface and not externally vented.

Deuterium was introduced into the Si by ion implantation at room temperature and an energy of 19 keV, or by annealing in  $D_2$  gas at 873 K and a pressure of 87 kPa (650 torr) for 48 h. The state of the D was examined through ir vibrational spectroscopy,<sup>13</sup> and analogous measurements were performed using the  $^1H$  isotope for direct comparison with earlier spectroscopic studies. Representative ir spectra following gas charging are presented in Fig. 2. Nuclear-reaction analysis showed the areal densi-

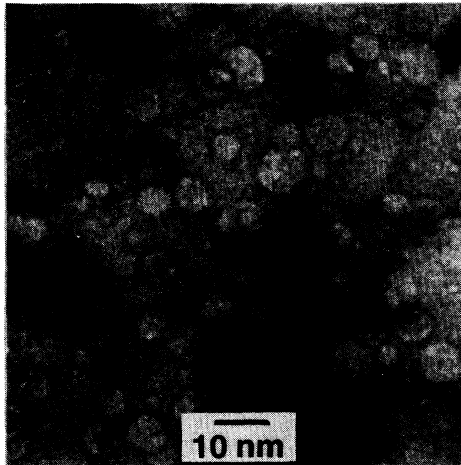


FIG. 1. Bright-field, 200-keV TEM of cavities within He-implanted Si after annealing at 973 K. The cavities are imaged at slight underfocus to provide contrast.

ty of bound D to be approximately  $90 \text{ nm}^{-2}$ .

The clustered peaks in Fig. 2 are due to stretching modes of the Si- $^1\text{H}$  and Si-D bonds, and the spectrum for D is shifted by factors of 0.73 in frequency and 0.5 in intensity due to the larger deuterium mass. These data are similar to spectra reported for  $^1\text{H}$  chemisorbed on external (100) and (111) surfaces, in that the dominant absorption occurs in a band near  $2100 \text{ cm}^{-1}$ .<sup>7,8</sup> The similarity is especially close for the (100) surface,<sup>8</sup> where two dominant peaks at 2087 and  $2099 \text{ cm}^{-1}$  may be compared with the dominant peaks at 2087 and  $2103 \text{ cm}^{-1}$  in the present system. This suggests that the cavity walls may have (100) character, but the point is not critical, since the previously discussed desorption studies indicate similar binding energies for (100) and (111) surfaces. More importantly, the  $^1\text{H}$  spectrum in Fig. 2 is clearly

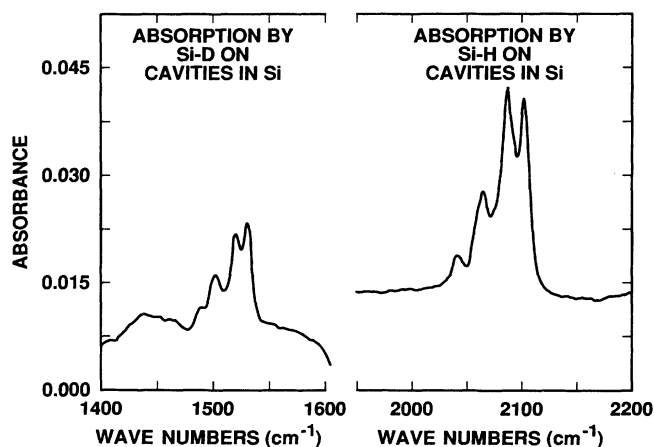


FIG. 2. Room-temperature IR absorption by Si with internal cavities after heating in  $^1\text{H}_2$  or  $\text{D}_2$  gas, obtained using internal-reflection plates. The four principal peaks for  $^1\text{H}$  occur at 2042, 2065, 2087, and  $2103 \text{ cm}^{-1}$  while those for D are at 1490, 1505, 1524, and  $1532 \text{ cm}^{-1}$ .

distinct from that of H bound to implantation damage in Si, where the IR absorptions occur mainly outside the band near  $2100 \text{ cm}^{-1}$ .<sup>13</sup> When D was introduced by ion implantation at room temperature, the IR spectrum initially corresponded to defect trapping, but during subsequent heating it changed to the form characteristic of cavity-wall bonding before the onset of release from the specimen.

Since  $\text{D}_2$  molecules are not detected by IR spectroscopy, it is appropriate to consider whether a significant quantity of molecular gas formed within the cavities. In the case of gas charging, the areal density of D encapsulated as  $\text{D}_2$  gas could be obtained simply by multiplying the estimated cavity volume per unit area of sample surface by the atomic density of the external  $\text{D}_2$  gas with which the sample was equilibrated. In this way we determined an upper limit of  $0.6 \text{ D/nm}^2$ , which is only 0.7% of the total bound quantity measured by nuclear-reaction analysis. Hence, the internally chemisorbed state in our samples was strongly favored by free energy for areal densities  $\lesssim 90 \text{ D/nm}^2$ . In the case of implanted specimens, we restricted our fitting of experimental release data to areal densities below this bound. Hence, while continuous D exchange between encapsulated  $\text{D}_2$  gas and internal chemisorption was expected during the experiments, the population of the chemisorbed states was much larger and therefore controlled the evolution of the system.

To quantify the binding energy of D at the cavity walls in Si, release from D-implanted specimens was observed during temperature ramping at 2 K/min. The release was detected by using the nuclear reaction  $\text{D}(^3\text{He}, p)^4\text{He}$  to monitor the areal density of D remaining within the trapping region. As discussed elsewhere,<sup>14</sup> 700-keV  $^3\text{He}$  periodically impinged on the sample without interruption of the temperature ramp, and protons from the nuclear reaction were counted. Resulting data are given by solid circles in Fig. 3. Additional release profiles are shown for two D-implanted specimens not injected with He; one re-

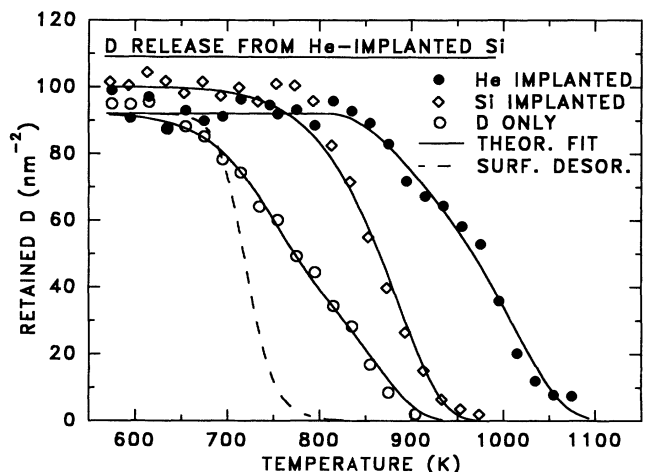


FIG. 3. Deuterium release from Si during temperature ramping for specimens implanted with He ( $\bullet$ ), or irradiated with Si ions ( $\diamond$ ), or implanted only with D ( $\circ$ ). The dashed curve shows predicted desorption from an external surface. The solid curves represent fits of diffusion-trapping theory.

ceived no prior implantation treatment, while the other was initially bombarded with Si ions to simulate He-ion damage without introducing cavities. The Si-ion bombardment was performed at room temperature, 200 keV, and a fluence of  $90 \text{ Si/nm}^2$ , and, as in the case of He injection, vacuum annealing at 973 K followed before the implantation of D. The dashed curve shows predicted desorption from an external surface based on representative experimental desorption-rate equations.<sup>3</sup>

It is apparent from Fig. 3 that the internal cavities in Si produced a distinct, high-temperature release stage near 1000 K. This indicates D trapping stronger than that at the implantation damage. Based on the ir spectroscopy discussed above, the strong binding is attributed to the formation of Si-D bonds at the walls of the cavities. The release of D from internal cavities is seen to occur at a much higher temperature than desorption from the external surface. This reflects the more difficult path for the former process, which requires promotion from the chemisorbed state to solution followed by solid-state diffusion.

The solid curves in Fig. 3 represent fitted solutions of diffusion-trapping theory discussed elsewhere.<sup>14</sup> Briefly, a diffusion equation including terms for the local exchange of D between solution sites and trap sites with relative binding energy  $E_T$  was solved numerically. The diffusion coefficient of atomic H in Si was taken from the literature,<sup>15</sup> leaving undetermined *only* the binding energies and areal densities of the D-trapping sites, and these were adjusted to produce agreement with the experimental data. In the case of implanted Si not containing He cavities, the data were fitted with two types of implantation-damage trap, one with  $E_{T1} = 1.4 \text{ eV}$  and the other with  $E_{T2} = 1.7 \text{ eV}$ . The fitted areal density of the traps was greater when the specimen had been prebombarded with Si ions.

The D release stage near 1000 K associated with cavity-wall traps yielded a binding energy of  $E_{T3} = 2.1 \pm 0.2 \text{ eV}$  relative to D in solution. We find that the fitted position of the 1000-K stage is determined almost exclusively by  $E_{T3}$ , with the weaker traps  $T1$  and  $T2$  having influence only at lower temperatures. Hence, the evaluation of  $E_{T3}$  has a high confidence level. The trap energy  $E_{T3}$  differs from the desired Si-H surface bond energy  $E_B$  in that the first quantity is referenced to the H atom in solution while the second is specified relative to the H atom in vacuum. The conversion is straightforward using the relation

$$E_B = E_{T3} - E_S + \frac{1}{2} E_R, \quad (2)$$

where  $E_S = 1.86 \text{ eV}$  is the endothermic energy of solution per H atom from  $\text{H}_2$  gas<sup>15</sup> and  $E_R = 4.52 \text{ eV}$  is the vacuum dissociation energy of  $\text{H}_2$ . The basis for this relation

is apparent when one notes that the energy to move an atom from solution into vacuum is  $-E_S + \frac{1}{2} E_R$ . Equation (2) gives  $E_B = 2.5 \pm 0.2 \text{ eV}$ .

The internal surfaces examined in this work were not subject to the usual characterization by low-energy electron diffraction, and the atomic ordering may well have differed from the external (100) and (111) surfaces studied in the past. We propose, however, that the strength of the Si-H bond at low coverage is not strongly affected by such differences; as discussed above, this view is supported by the similarity of desorption activation energies for the (100) and (111) surfaces. With this perspective, we conclude by noting four implications of the Si-H bond energy determined here.

(i) The bond energy is close to the measured activation energy for the detachment of H from Si dangling-bond defects at the Si-SiO<sub>2</sub> interface,  $2.56 \pm 0.06 \text{ eV}$ .<sup>16</sup> This is expected, since Si dangling bonds at the Si-SiO<sub>2</sub> interface are widely separated by intervening Si-O, and as a result the energy absorbed in breaking the Si-H bond cannot be diminished by simultaneous H-H recombination.

(ii) The bond energy is also close to the observed activation energy for H desorption from *unoxidized* Si; the average of the reported values for desorption from the monohydride state is about 2.5 eV, as indicated above. The similarity of  $E_B$  and  $E_D$  leads us tentatively to suggest a two-step reaction path for molecular desorption in which the activation barrier arises predominantly from the breaking of the first Si-H bond, and molecular desorption occurs subsequently through the exothermic reaction  $\text{H} + \text{Si-H} \rightarrow \text{H}_2 + \text{Si}$ . This hypothesis represents a possible alternative to the model discussed above where the breaking of two Si-H bonds and H-H recombination are concurrent.

(iii) The present Si-H bond energy of 2.5 eV is smaller than those reported for molecular species containing Si and H, the latter ranging from 2.8 to 3.9 eV.<sup>17</sup> This may reflect a dependence of the Si-H bond strength on the other bonds formed by the same Si atom, as is suggested by the large range of values for the molecular species.

(iv) When  $E_B \approx 2.5 \text{ eV}$  and  $E_D \approx 2.5 \text{ eV}$  are substituted into Eq. (1), one finds that the activation energy for chemisorption from  $\text{H}_2$  gas,  $E_A$ , is about 2.0 eV. This large barrier is consistent with the generally recognized difficulty of chemisorbing  $\text{H}_2$  gas on Si.

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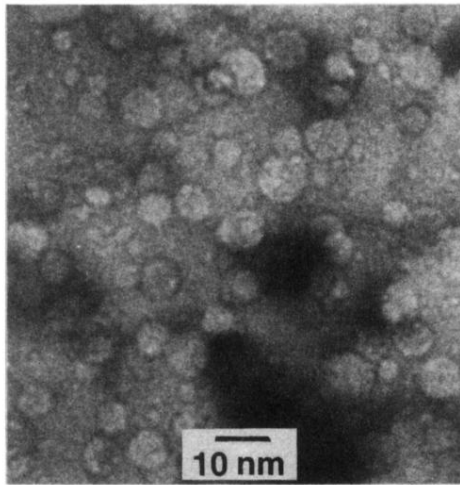


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