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Surface silicon-deuterium bond energy from gas-phase equilibration

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The bond strength of deuterium (D) to the surface of silicon was determined to be 2.67±0.1 eV from measurements of the amount of D on the surface in equilibrium with D_2 gas at various pressures. This was done by measuring the amount of D on surfaces of closed internal microcavities using nuclear reaction analysis. The binding of D to a silicon surface is significantly weaker than the Si-H bond in silane which has been assumed in the past to indicate the strength of the surface Si-H bond. The fact that the Si-D bond strength is comparable to the activation energy for thermal desorption of H from Si suggests a possible reaction path for desorption in which the first and rate-determining step is the dissociation of a Si-H bond followed by the exothermic reaction between the released H atom and a second Si-H to form a H_2 molecule and two Si- dangling bonds. Our result also gives a value of 1.8 eV for the activation energy for dissociative adsorption of D_2 on silicon. The number of bond sites is comparable to the number of Si atoms on the cavity surfaces calculated from the total cavity surface area determined by TEM.

I. INTRODUCTION

Many of the processes used in silicon semiconductor device production, such as etching with wet chemistry[1] or plasmas,[2] and growth of epitaxial layers by chemical vapor deposition,[3] cause the silicon dangling bonds on the surface to be terminated with hydrogen. The hydrogen termination may have beneficial effects, such as protecting the surface from oxidation,[4] or detrimental effects such as inhibiting epitaxial growth.[3,5] A key parameter in understanding such effects is the strength of the Si-H surface bond which until very recently had not been measured. The Si-H bond strength has been discussed previously in the context of thermal desorption of hydrogen from silicon surfaces.[6,7] However, the strength of the Si-H bond cannot be determined unambiguously from thermal desorption measurements since thermal desorption involves not only the breaking of Si-H bonds but also the formation of H_2 molecules. The activation barriers for adsorption and desorption of hydrogen depend on the reaction path between $2(\text{Si-H}) \Longleftrightarrow 2\text{Si-} + H_2$, and the reaction paths have been uncertain. Here Si- denotes a surface silicon atom with one dangling bond. In the absence of direct measurements, the Si-H surface bond strength has often been assumed to be comparable to that of the H_3Si-H bond in silane of about 3.9 eV.[7]

Recently we reported a measurement of the Si-H surface bond energy using a technique which circumvents the indeterminacy inherent in thermal desorption studies.[8] Those experiments examined the release of H from the surfaces of internal microcavities in silicon rather than from external surfaces. For this configuration the rate-controlling processes in the release are promotion of H from Si-H on the cavity surface into solid solution, and diffusion through the lattice to the external surface. The release rate thus depends on the Si-H bond strength, the energy of solution, and the diffusion activation energy. Since the latter two quantities are known, we were able to determine a value for the Si-H surface bond strength of $E_B = 2.5 \pm 0.2$ eV, which is considerably smaller than previous widely accepted values.

A more direct method of measuring the bond strength is to measure the population of Si-H surface bond states in equilibrium with a state of known free energy such as H_2 gas. This method of gas-phase equilibrium is a standard technique widely used to study chemisorption of hydrogen on metal surfaces.[9] However, a large activation barrier for the dissociative chemisorption of hydrogen on silicon surfaces has prevented the use of gas-phase equilibrium to determine the Si-H surface bond strength. Due to the large activation barrier, high temperatures are required to reach equilibrium between the gas and surface states. Furthermore, at the temperatures where equilibrium can be achieved, high gas pressures are required to populate a significant fraction of the surface states due to the meager energy difference between the gas phase and surface states. Difficulties with maintaining clean surfaces and measuring H surface coverage in the presence of high H_2 pressures have precluded the use of this method for study of Si-H bonds on external surfaces.

In the experiment described here we use gas-phase equilibration to measure the bond strength of deuterium (D) to the surface of internal microcavities in silicon. Previous studies have shown how internal microcavities can be produced in silicon by implanting helium and annealing.[8] In the study described here, silicon samples containing internal microcavities were equilibrated with D_2 gas. In these experiments, the D goes into solution at the external Si surface, then diffuses through the Si lattice to the microcavities where it forms Si-D bonds on the cavity surfaces. The amount of D bonded to the cavity surfaces was measured using $D(^3He,p)^4He$ nuclear reaction analysis. In equilibrium with the gas, the fraction of Si- bonds on the cavity surfaces which are terminated with D depends on the Si-D bond strength relative to the gas and on the gas pressure. By measuring the amount of D bonded to the cavity surfaces in equilibrium with gas

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at various pressures, both the strength of the Si-D surface bond and the number of bond sites can be determined. This method avoids the problem of surface contamination, since the internal microcavity surfaces under investigation are not exposed directly to the gas, and only the D is mobile enough to reach the cavities by diffusion through the silicon lattice. The number of bonding sites calculated from the total cavity surface area observed with transmission electron microscopy (TEM) is comparable to the number of D atoms detected at the cavities.

II. EXPERIMENTAL METHOD

The samples used in this study were *n*-type silicon with a room-temperature resistivity of 2 kΩ cm, a polished (001) surface, and dimensions of $12\times12\times0.25$ mm^3. A new sample was used for each measurement to avoid the possibility of D trapping at lattice damage from the analysis beam. The silicon was first implanted at room temperature with 30-keV helium to a fluence of 10^{17} He/cm^2 and then annealed in vacuum at 800 °C for 10 h to stabilize the microstructure and remove lattice damage. Calculations based on the known solubility and diffusivity of He in Si show that after annealing at 800 °C for 10 h the amount of helium remaining in the cavities is negligible.[8] Thus the cavities can be considered as empty voids.

Cross-section TEM shows that the above procedure produces microcavities from about 150–350 nm beneath the surface as seen in Fig. 1.[10] This distribution is consistent with the He implantation profile calculated using the TRIM-90 Monte Carlo particle transport code.[11] Figure 1 shows a TEM image of the cavities in a cross-sectioned sample. A detailed analysis of TEM images was carried out to determine the size and number per unit area of the cavities.[10] Thickness contrast fringes obtained with two-beam conditions and stereo imaging were used to determine the thickness of the imaged region. The results are an average cavity diameter of 15 nm, a cavity surface area per sample surface area of 4.8 ± 0.7, and a cavity volume per sample surface area of 17 nm^3/nm^2. Many cavities were faceted, with predominantly $\{111\}$ surfaces and a smaller amount of $\{100\}$ surfaces.

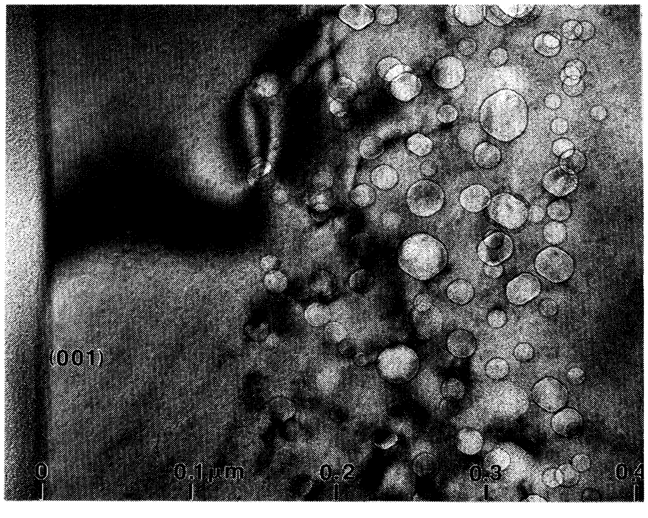

FIG. 1. A [110] cross-section TEM image of cavities beneath the (001) surface of silicon after implanting with helium and annealing. The depth beneath the implanted surface is indicated at the bottom of the picture.

Samples were soaked at 800 °C in D_2 gas at pressures from 0.65 to 650 Torr until equilibrium was reached between the gas phase and D at the cavities. This was done as follows. Samples were placed in a quartz tube which was evacuated to about 10^{-7} Torr. The tube and sample were then heated by a cylindrical furnace to 800 °C. The tube was then filled with high-purity (impurity concentration <20 ppm) deuterium gas to the desired pressure. After equilibrating, the sample was cooled by sliding the furnace back from the quartz tube. The cooling rate of $\sim100°$/min was fast enough to prevent any significant change in the amount of D at the cavities during the cooldown. Soak times were 1–3 h which is long compared to the time required to reach equilibrium[8] calculated using the known solubility and diffusivity of hydrogen in silicon.[12] Measurement of the amount of D at the cavities after tripling the soak time confirmed that equilibrium had been reached. Since soak times were much less than the 10 h used for the initial vacuum anneal, evolution of the cavity microstructure during the soak should be negligible.

The temperature of 800 °C was chosen as the optimum for the equilibration because at lower temperatures the time to reach equilibrium becomes very long, especially for the low gas pressures needed only to partially populate the surface sites, and at higher temperatures inconveniently high gas pressures are required to approach full occupation of the sites. Furthermore, at temperatures above 800 °C evolution of the microstructure of the cavities becomes a concern.

After equilibration the samples were rinsed in buffered hydrofluoric acid to remove residual D from the external surface, and then mounted in a target chamber for measurement of the amount of D at the cavities. An analysis beam of 700 keV ^{3}He was directed onto the sample. Energetic protons from the D(^{3}He,p)^{4}He nuclear reaction were counted using a solid-state detector which subtended a solid angle of 0.77 sr centered at a scattering angle of 135°. A stainless-steel range foil 0.25 mm thick between the sample and detector prevented all charged particles except the 13-MeV protons from the ^{3}He-D reaction from reaching the detector. Since the nuclear reaction cross section is known,[13] the number of D atoms at the cavities per unit area of the sample surface, i.e., the areal density of D, can be calculated from the measured proton yield. With an analysis beam energy of 700 keV, protons will be produced from D at depths from the surface down to about 1 μm beneath the surface, which includes the entire region containing the cavities. Due to the very low solubility of D in Si, the proton yield from the small amount of D in solution in the Si lattice is negligible. Furthermore, the amount of D_2 gas inside the cavities after equilibration with the external gas is equal to the cavity volume times the atomic density of the gas which is 1.2×10^{19} D/cm^3 at 650 Torr and 800 °C assuming the ideal gas law. The amount of D_2 gas inside the cavities is therefore less than 2×10^{13} D/cm^2, and is much less than the amount of D bound to the cavity surfaces. Thus the analysis accurately measures the D bound to the cavity surfaces.

III. RESULTS AND ANALYSIS OF DATA

The results from the measurements of the areal density of D at the cavities in equilibrium with D_2 gas are plotted in Fig. 2 versus the square root of the gas pressure during soaking. The Si-D bond strength and the number of Si-dangling bonds on the cavity surfaces per unit area of the sample surface (N_T) can be extracted from this data using the following model. The model assumes there is a single value for the Si-D surface bond strength, and that in equilibrium the fraction θ of surface sites bonded to D is related to the atomic fraction C of D in solid solution by a Boltzmann population distribution

$$\theta/(1-\theta)=C/(1-C)\exp[(E_S-E_T)/kT] \approx C\exp[(E_S-E_T)/kT] , \quad (1)$$

where T is the temperature, and E_S-E_T is the energy gained by taking a D atom from a solution site and bonding it to a surface silicon atom. E_S is the energy gain per atom in moving D from solution to the molecular state, i.e., the energy of solution, and E_T is the energy gain per D atom in taking D from the surface state to the molecular state. Implicit in this model is the assumption that the entropy term in the free energy is the same for D at a solution site and D bound to a surface Si atom.

The concentration of D in solution in equilibrium with D_2 gas at pressure P is given by[12]

$$C=P^{1/2}C_0\exp(-E_S/kT) , \quad (2)$$

where $E_S=1.86$ eV and $C_0=0.0035$ D/(Si Torr$^{-1/2}$).

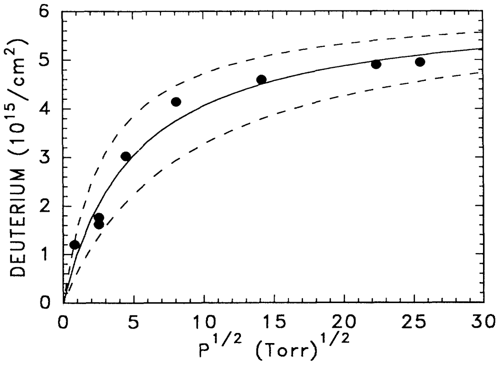

FIG. 2. The measured areal density of deuterium at the cavities after gas-phase equilibration vs square root of the gas pressure (dots). The solid curve shows the least-squares fit of the model described in the text to the data. The dashed curves were calculated using values for the Si-D bond strength differing by ±0.05 eV from the fitted value.

Here we assume that the solubility of D in Si is the same as that of H. The number of D atoms at the cavities per unit area of the sample surface, which is what is measured here, can therefore be expressed as

$$N=N_T\theta=N_T/\{1+1/[P^{1/2}C_0\exp(-E_T/kT)]\} . \quad (3)$$

The solid curve in Fig. 2 shows a least-squares fit to the data using Eq. (3), with E_T and N_T as adjustable parameters which are determined from the fit. The parameter values obtained from the fit and their estimated uncertainties are $E_T=-0.37\pm0.1$ eV and $N_T=61\pm10$ nm^{-2}. The negative sign of E_T signifies that the surface state is lower in energy than the gas phase. The features of the data which mainly determine the parameter values are the saturation level at high pressures for N_T and the slope at low pressures for E_T.

The method of gas-phase equilibration provides a very sensitive measurement of the surface Si-D bond energy as shown by the dashed curves in Fig. 2 which were calculated using $N_T=61/\text{nm}^{-2}$ and $E_T=-0.37\pm0.05$ eV. This sensitivity is largely due to the fact that the reference state, i.e., the gas phase, is close in energy to the surface state.

IV. DISCUSSION

A. Si-D bond energy

The surface Si-D bond energy E_B is the energy required to separate a D atom from a surface silicon atom, leaving a surface silicon atom with a dangling bond and a D atom in vacuum, i.e., the energy for the reaction Si-D$\rightarrow$Si-+D. The value of E_B can be determined directly from our measurement of E_T. The relationship between them is

$$E_B=\tfrac{1}{2}E_R-E_T , \quad (4)$$

as shown in Fig. 3. E_R is the energy required to dissociate a D_2 molecule, which has the well-established value[14] of 4.60 eV. Equation (4) with our value of E_T gives $E_B=2.67\pm0.1$ eV for the surface Si-D bond energy. This value agrees with the value of $E_B=2.5\pm0.2$ eV for the Si-D bond energy determined in our earlier measurements of the thermal release of D from internal microcavities in silicon.[8]

B. Adsorption, desorption, and the activation energy for adsorption

Adsorption and desorption of deuterium on silicon involves not only the formation and dissociation of Si-D bonds but also the dissociation and formation of D_2 molecules. Figure 3 illustrates the energetics of the adsorption and desorption processes. Thermal desorption of H_2 from monohydride states on external (100) and (111) Si surfaces has been studied by several groups, and their activation energies are in fairly good agreement. In the case of the (100) surface, values of 2.0 and 2.5 eV were reported.[6,7] In porous Si, where IR spectroscopy indicated Si-H bonding similar to that on the (100) surface, the re-

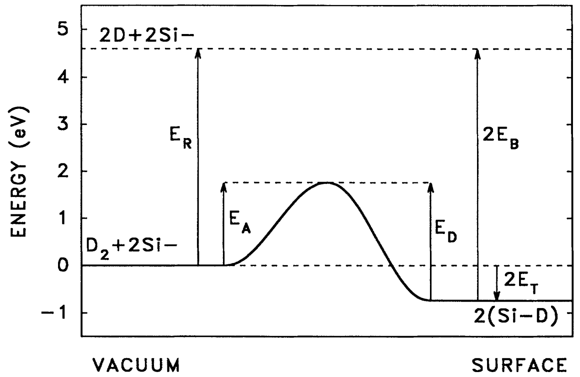

FIG. 3. Energetics of adsorption and desorption of deuterium on silicon. The total energy is indicated for the transition between the surface state 2(Si-D) and the molecular state D_2+2Si-. E_D and E_A are activation energies for desorption and adsorption, respectively. Also shown is the bond energy E_R of the D_2 molecule.

sult was 2.8 eV.[15] For the (111) surface, activation energies of 2.7, 2.6, 2.5, and 2.4 eV were obtained.[6,16–18] Here we will not distinguish between the (100) and (111) surfaces, since the respective ranges of values of E_D overlap; instead, we use the average value $E_D = 2.5 \pm 0.3$ eV, and we assume that E_D is the same for H and D.

The activation energy for desorption is much larger than the energy difference between the initial and final (i.e., adsorbed and molecular) states, indicating that the reaction passes through a higher-energy intermediate configuration. A consequence of this is that adsorption is inhibited by a large activation barrier. This contrasts with adsorption and desorption of hydrogen on metals where the barrier to adsorption is usually very small.[19]

The activation energy E_A for dissociative adsorption of D_2 onto silicon is related to E_D and E_T by

$$E_A = E_D + 2E_T \ , \tag{5}$$

as shown in Fig. 3. With our value for E_T, Eq. (5) gives $E_A = 1.8$ eV for the activation barrier to dissociative adsorption of D_2 onto a Si surface. This large value for E_A is consistent with the experimental observation that H_2 does not easily adsorb onto silicon surfaces, whereas thermally dissociated atomic H does adsorb.[20]

At sufficiently high temperatures, the activation barrier to dissociative adsorption can be overcome and equilibrium can be reached between D_2 gas and surface states. However, the fact that the surface states are only 0.4 eV lower in energy than the gas phase means that relatively high gas pressures are required to populate a significant fraction of the surface states at the high temperatures where equilibrium can be achieved. Difficulties with maintaining clean surfaces and measuring H surface coverage in the presence of high gas pressures have prevented the use of gas-phase equilibration to study Si-H bonds on external surfaces. The use of internal microcavities in the present experiment avoids the problem of surface contamination, since the surfaces under investigation are not exposed directly to the gas, and only D is mobile enough to reach the cavities by diffusion through the silicon lattice.

C. Reaction paths for desorption and adsorption

The result that the surface Si-H bond strength and the activation energy for thermal desorption have similar values ($E_B \approx E_D$) points to a possible reaction path for thermal desorption of H, in which the first and rate-determining step is the thermal dissociation of an Si-H bond followed by the exothermic reaction between the released H atom and a second Si-H to form a H_2 molecule and two Si- dangling bonds according to

$$2(\text{Si-H}) \rightarrow \text{Si-H} + \text{Si-} + \text{H}^* \rightarrow 2\text{Si-} + \text{H}_2 \ . \tag{6}$$

The intermediate state in this reaction then consists of one surface Si-H, one surface Si- dangling bond, and one H atom, which may still be weakly bound to the surface. The energy of the intermediate state relative to the molecular state (see Fig. 3) is

$$E_A = 2E_T + E_D = 2E_T + E_B + E^* \ , \tag{7}$$

where $E^* = E_D - E_B$ is the energy of the H atom in the intermediate state relative to a H atom in free space. Adsorption from the molecular state would occur via the inverse process with an activation energy of E_A. This proposed reaction path is consistent with the notion that, on a H-terminated silicon surface, the H is localized by the Si-H bonds which are strong and highly directional, and the H atoms are much farther apart [0.38 nm on Si(111)] than in a H_2 molecule (0.074 nm), so that a Si-H bond must first be broken before two H atoms can get close enough together to form a H_2 molecule. The above reaction path is also consistent with the conclusions of Wise *et al.*[6] and Boland[21] that desorption from the Si(100) monohydride surface occurs by recombination of pairs of hydrogen atoms from the same dimer unit. The initially released H atom will have the highest probability for recombination with its nearest neighboring H, which on the Si(100) surface is the other H on the dimer unit. The above reaction path for recombination is not specific to a particular surface structure and is compatible with both first-order release kinetics from correlated recombination due to islanding or pairing of surface H, and with second-order release kinetics from recombination by random encounters of mobile H.

An alternative mechanism has been proposed by Sinniah *et al.*[7] in which desorption proceeds via an irreversible excitation of H from a Si-H bond to a delocalized state which is still bound to the surface by 1.95 eV. H in their delocalized bound state then reacts with a second Si-H, resulting in desorption of a H_2 molecule. They proposed a delocalized bound state to reconcile their measured activation energy for thermal desorption ($E_D = 1.95$ eV) with their assumption (in the absence of any direct measurement) that the surface Si-H bond strength is 3.9 eV. Our new measurement of $E_B = 2.67 \pm 0.1$ eV, together with recent thermal desorption studies[6] giving higher values of $E_D = 2.67 \pm 0.17$ eV for Si(111) and $E_D = 2.51 \pm 0.09$ for Si(100), show that binding of the H atom in the intermediate state to the surface is weak, $|E^*|=|E_D-E_B|<0.16$ eV in the context of our proposed reaction path.

The above mechanism for desorption of immobile H covalently bonded to surface Si atoms contrast with desorption of H from metal surfaces where the adsorbed hydrogen atoms are very mobile, allowing a continuous transition from separated H atoms close to the metal surface, to a molecule where the H atoms are close to each other and far from the metal surface. Thus in the case for metals, typically $E_A \ll E_D \sim 2E_B - E_R$.

D. Similarity between Si-H on internal cavities and external surfaces

The areal density of Si- dangling bonds available for attachment of D can be estimated from the observed microstructure of the cavities. TEM shows that the cavity surface area per sample front surface area is 4.8±0.7, with mostly {111} surfaces.[10] The number of Si-H bonds per unit area for monohydride terminated silicon surfaces is $7.8/\text{nm}^2$ for the (111) surface and $6.8/\text{nm}^2$ for the (100) surface. The number of dangling bonds on the cavity surfaces per sample surface area should therefore be about $(4.8\times7.8)\sim40/\text{nm}^2$. This value agrees reasonably well with the value of $61\pm10/\text{nm}^2$ determined from our gas-phase equilibration measurements. This agreement shows that the number of sites available for D attachment at the cavities per unit area of cavity surface is similar to that of a monohydride on an external surface.

Next, we discuss the questions of whether the Si-H states on the internal cavities are representative of Si-H states on external surfaces, and the extent to which various crystallographic orientations of the cavity surfaces might influence the Si-H bond energy. The infrared-absorbtion spectrum has been measured for Si samples with internal cavities similar to ours.[22] After soaking in hydrogen gas, two strong peaks appeared at wave numbers of 2084 and 2100 cm^{-1} for samples with cavities. IR-absorbtion peaks at these frequencies have also been observed for H on external Si surfaces, and are associated with stretch vibration of the surface monohydride on the (111) and (100) surfaces, respectively.[1,2,3] We therefore believe that the surface monohydride states on the cavity surfaces are essentially the same as those on external surfaces. The IR spectroscopy also shows that, as the samples are annealed to successively higher temperatures, these two peaks both disappear at the temperature where hydrogen leaves the cavities. This indicates that the surface monohydride bond strength is essentially the same for the (100) and (111) surfaces. In view of the different arrangement of Si atoms on these two surfaces, we take this as evidence that the Si-H bond energy depends primarily on what the other three bonds of the Si atom are attached to. In particular, we suggest that the Si-H bond strength may be similar for surface silicon atoms bonded to three other silicon atoms, and depend only weakly on the longer-range ordering of the Si lattice. Since dangling bonds are a high-energy configuration, silicon surfaces tend to reconstruct to minimize the number of dangling bonds; for example, the dimerization of the (100) surface reduces the number of dangling bonds from two to one per Si atom. For this reason it is likely that very few of the surface atoms in the cavities have more than one dangling bond. Thus it is not surprising that we find a well-defined value for the Si-H bond energy at the cavities in spite of the various surface orientations within the cavities.

Finally, while it is possible to attach more than one hydrogen to a surface Si atom to form dihydride or trihydride states, for example, by exposure to atomic hydrogen, these higher hydride states are less strongly bound than the monohydride.[24] This is shown by the fact that desorption from dihydride and trihydride states occurs at substantially lower temperatures than desorption from the monohydride configuration.[24] In our gas-phase equilibration experiment, the fraction of surface Si atoms with a D atom attached depends very strongly on the bond energy, as shown in Fig. 2. Thus the more weakly bound multihydride states will not be occupied and should not play any significant role in our experiments. The bond strength determined by our experiments is that of the most strongly bound, i.e., the monohydride, state.

V. CONCLUSIONS

The experiments described here and in Ref. 8 provide direct measurements of the bond energy of monohydride Si-D bonds on a silicon surface. A value of $E_T=-0.37\pm0.1$ eV is obtained for the surface Si-D bond strength referenced to the D_2 molecule. From this result, the bond energy of surface Si-D referenced to the D atom in vacuum $E_B=2.67\pm0.1$ eV is obtained directly, since E_T and E_B differ only by the dissociation energy of D_2 which is well known. This agrees with the value $E_B=2.5\pm0.2$ eV determined recently by a different experimental method,[8] but is much smaller than the bond energy of H in silane of 3.9 eV which has been assumed in the past to indicate the strength of the surface Si-H bond.

The fact that E_B is comparable to the activation energy $E_D=2.5\pm0.3$ eV for thermal desorption of H from Si suggests a possible reaction path for desorption in which the first step is the dissociation of an Si-H bond followed by an exothermic reaction between the released H atom and a second Si-H to form a H_2 molecule. Our result has the additional implication that the inverse process of dissociative adsorption of H_2 on silicon is impeded by a large activation barrier $E_A=1.8$ eV. This conclusion is supported by the experimental observation that H_2 does not easily adsorb onto silicon surfaces unless it is first dissociated into atoms.

ACKNOWLEDGMENT

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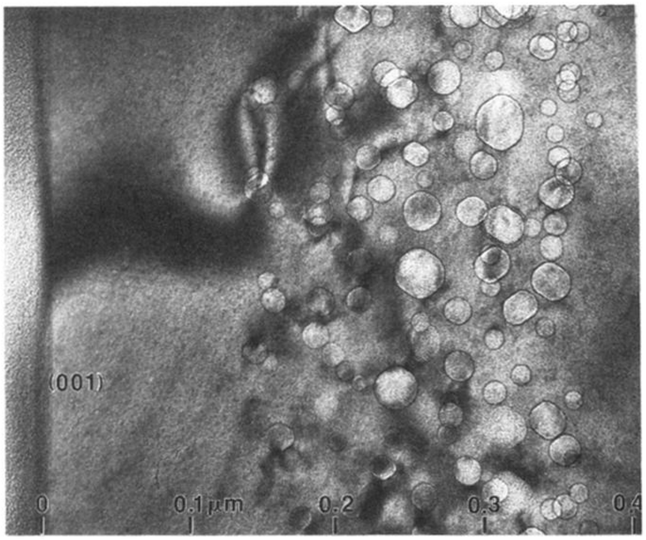

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