Hydrogen Desorption from The Monohydride Phase on Si(100)

by

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Hydrogen Desorption from The Monohydride Phase on Si(100)

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Abstract

The kinetics of the thermal recombinative desorption of hydrogen from the monohydride phase on the Si(100) surface has been studied by laser-induced thermal desorption (LITD). A rate law that is first order in the atomic hydrogen coverage with an activation energy of 45 kcal/mol gives an accurate fit to the data over a temperature range of 685 - 790 K and a coverage range of 0.006 to 1.0 monolayer. A new mechanism is proposed to explain these surprising results, namely, that the rate limiting step of the reaction is the promotion of a hydrogen atom from a localized bonding site to a delocalized band state. The delocalized atom then reacts with a localized atom to produce molecular hydrogen which desorbs. Evidence to support these conclusions comes from isotopic mixing experiments. Studies of recombinative desorption from other surfaces of silicon, which had been assumed to obey second-order kinetics, are discussed in the light of these results.
I. INTRODUCTION

For many years reactions on single crystalline metallic surfaces have been studied as model systems for understanding the mechanisms of heterogeneous chemical reactions. Only recently have reactions been studied in detail on single crystalline surfaces of covalent solids. Silicon is a particularly interesting example of a covalently bonded material from both a practical and a fundamental point of view [1-4]. A recent review of the properties of silicon surfaces gives an account of the numerous theoretical and experimental techniques that have been applied to this problem [5]. The Si(100) surface is particularly appropriate for such studies because the stable reconstructed (2x1) structure is well characterized and relatively simple. In the absence of any reconstruction, each surface atom would have two "dangling bond" orbitals. Upon reconstruction of the surface, the silicon atoms in adjacent rows "pair up" to form a (2x1) array of dimers. This leaves one dangling bond orbital on each surface silicon atom [6].

Atomic hydrogen adsorbs readily on silicon surfaces, and the chemisorbed H-Si bond is considerably stronger than the Si-Si bond [1]. On the Si(100) surface two ordered hydrogenated phases were detected by Sakurai and
Hagstrum [7]. Initial exposure to atomic hydrogen populates the monohydride phase in which one hydrogen atom is bonded to each surface silicon atom, resulting in the saturation of each dangling bond at the surface and the preservation of the (2x1) reconstruction [8]. Additional exposure to hydrogen atoms results in cleavage of some of the Si-Si dimer bonds, and a dihydride phase is formed. The dihydride phase has been shown to consist of alternating H-Si-Si-H and SiH$_2$ species [9]. High exposures can also result in Si$_x$H$_y$ species [10,11] with a higher H/Si ratio than the dihydride phase, but there is no apparent long-range order to the structure of such species. In this paper we focus our attention on the recombinative desorption of hydrogen and deuterium from the monohydride phase on the Si(100) surface. A study of the desorption kinetics of the dihydride phase will be reported elsewhere [12].

Several investigators have previously analyzed H$_2$ desorption from the monohydride phase on various silicon surfaces in terms of second-order desorption kinetics [13-17]. Such a mechanism might be expected by analogy to metal surfaces where recombinative desorption proceeds via migration of adatoms from site to site until two adjacent adatoms ultimately recombine and desorb. Even on metals, however, hydrogen may in some cases undergo recombination via an Eley-Rideal type of mechanism [18,19]. We show that the desorption of hydrogen from the monohydride phase on
Si(100) follows a first-order mechanism over a broad range of coverage and temperature.

In a previous report, we examined the isothermal recombinative desorption of monohydride hydrogen from Si(100) and proposed a new mechanism for the desorption reaction [20]. The new mechanism is necessary for the following two reasons: (1) The desorption kinetics are found to be first-order in hydrogen coverage; and (2) The activation energy is considerably lower than the overall enthalpy of desorption of H₂. In the new mechanism, the rate-limiting step in the desorption kinetics of H₂ is the irreversible thermal excitation of chemisorbed hydrogen atoms into a two-dimensional delocalized state. A hydrogen atom in the delocalized state then combines with an immobile hydrogen atom to effect the recombinative reaction.

In this paper we provide a detailed description of the laser-induced thermal desorption (LITD) studies presented earlier [20]. We confirm the LITD results with a second isothermal desorption technique, which also allows us to extend the results over a larger temperature range. An isotopic mixing study is presented which shows that the first-order kinetics do not result from "pre-pairing" of the atoms on the surface. We also present a study of the reactivity of chemisorbed deuterium atoms with hydrogen atoms that are incident from the gas phase. This study
demonstrates that when hydrogen atoms adsorb on the surface their kinetic energy is equilibrated quite slowly. It also requires that the adsorption mechanism, which was previously thought to follow a Langmuir-type reaction, be reinterpreted in a fashion that is consistent with our mechanism of desorption. Taken together, this body of data shows that even one of the simplest examples of covalent bonding in surface chemistry behaves in a manner that had not been previously considered.

II EXPERIMENTAL METHODS

A. Apparatus and Crystal Preparation

The techniques used in the present experiments are temperature programmed desorption (TPD), laser-induced thermal desorption (LITD), and isothermal desorption. The TPD technique has been used to calibrate the coverage of hydrogen and deuterium on the surface, to measure activation energies of desorption, and to measure the decrease in deuterium coverage resulting from reaction with hydrogen atoms supplied from the gas phase. Both the LITD and the isothermal desorption techniques were employed primarily to measure the isothermal desorption kinetics (rate coefficients) for hydrogen recombination on the Si(100) surface.

All experiments were performed in an ultrahigh vacuum (UHV) chamber with a base pressure below $2 \times 10^{-10}$ Torr. A
schematic diagram of the system is shown in Fig. 1. The Si(100) crystal was grown by the method of Czochralski and is B-doped, p-type material with 10 ohm-cm resistivity. The crystal was oriented by Laue diffraction to within 1°, and was cut and polished into specimens of 16 x 16 x 2 mm dimension.

The silicon crystal was mounted following the method of Bozack et al. [21] with 1 mm diameter tungsten wires which supported two tabs of 0.1 mm thick tantalum sheets to form a spring contact wedge. The tantalum tabs were wedged into two 0.4 mm slots cut into the edges of the silicon crystal. Temperatures were measured by means of a chromel-constantan (type E) thermocouple which was spot welded to a third tantalum-sheet spring that was wedged into a slot on the bottom edge of the crystal, halfway between the two mounting wires. Thermocouple temperature readings were confirmed with an optical pyrometer for temperatures between 985 and 1225 K. For these measurements the pyrometer reading was corrected using the emissivity versus temperature measurements of Allen [22]. The crystal could be cooled to 110 K with liquid nitrogen.

Heating techniques commonly used with metallic substrates [23] are difficult to apply to silicon because the resistivity of the crystal changes dramatically with temperature. For metallic crystals, linear heating rates are usually achieved by employing temperature controllers
that monitor either the voltage or current delivered to the crystal, each of which changes slowly with temperature. For semiconductors the applied current and voltage changes rapidly as the crystal temperature increases. This problem has been solved by controlling the power delivered to the crystal rather than the current or voltage separately [24]. The temperature controller is configured to control the power by a feedback circuit permitting the silicon crystal to be ramped linearly in temperature from 110 to 1000K. The controller is also able to hold the silicon surface at temperatures above 500 K to within ± 0.3 K.

In situ preparation of the Si(100) surface was carried out by Ar⁺ sputtering (1.5 kV, 6μA) for one hour, followed by annealing at 875 K for 30 min., 1175 K for 10 min., and 1275 K for 1 min., and cooling slowly. This procedure produced a sharp (2x1) low-energy electron diffraction pattern. After cleaning, no carbon signal was observed in the Auger spectrum. Given the signal-to-noise ratio of our spectrometer this implies that the C/Si ratio ≤ 4 atom%.

A differentially pumped quadrupole mass spectrometer (QMS) was employed to monitor molecules desorbed from the surface. The mass spectrometer was enclosed in a stainless steel tube pumped by a freshly deposited titanium getter film in an appendage to the QMS shield maintained at 77 K. A variable aperture assembly located on the QMS axis admitted gas to the QMS. One of two apertures, 0.3 cm or
1.75 cm in diameter, could be chosen. During a TPD experiment, the 0.3 cm aperture was used, and the silicon surface was positioned approximately 2 mm from the aperture. This arrangement ensures that desorbing molecules that enter the mass spectrometer originate from the center section of the silicon surface and not from the metal supports or the thermocouple. During the LITD experiments, the crystal surface was positioned 2 cm from the 1.75 cm aperture. This geometry gave a large signal since a significant fraction of the desorbing molecules entered the mass spectrometer chamber. For these experiments, desorption from surfaces other than the crystal is not an issue since the spot size of the incident laser beam is approximately 0.026 cm², and only molecules within that spot are desorbed.

B. Adsorption of H(D) on Si(100)

Since molecular hydrogen does not adsorb readily on a Si(100) surface [25], a hot tungsten spiral filament [26], 3 cm from the front face of the silicon surface, was used to dissociate H₂ (and D₂) molecules. The H (and D) atoms adsorb readily on the Si(100) surface. The filament was heated resistively to 2100 K, as measured using an optical pyrometer. Using the voltage drop across the filament as a secondary reference, the temperature could be reproducibly controlled. Either H₂ or D₂ was allowed to flow through the
chamber via a leak valve with the gate valve to the diffusion pump closed slightly, and the exposure was controlled by adjusting the time and pressure (usually $10^{-6}$ Torr) of the $H_2$ or $D_2$ exposure. The purity of the $H_2$ ($D_2$) was maintained by use of a freshly deposited titanium getter film, deposited in the UHV chamber, to scavenge any impurities produced by reactions at the walls or in the ionizer of the mass spectrometer. After dosing the surface with the required coverage, the gate valve to the diffusion pump was opened completely, and the gas was evacuated within two minutes. The flux of hydrogen or deuterium atoms on the surface was calibrated using the integrated areas of the TPD curves for several exposures to the surface [27].

In this paper we define coverage in terms of the saturated monohydride (or monodeuteride) phase (determined by completely filling of the monohydride TPD state). Thus $\theta = 1$ implies a coverage for which every surface silicon atom has bonded to it one hydrogen (or deuterium) atom. An exposure that would result in less than or greater than the monolayer coverage is calibrated by the ratio of the area of the hydrogen desorption peak (or peaks) with respect to that of the monolayer coverage and is defined as $\theta^H$. Since the gain of the mass spectrometer changed from $10 - 15\%$ from day to day, a specific coverage, $\theta^D = 0.26$, of deuterium was used each day to calibrate the results obtained during that day.
C. Isothermal LITD and Isothermal Desorption of $H_2$ and $D_2$

Two independent and complementary methods were employed to study the kinetics of $H(D)$ recombinative desorption. The first, isothermal LITD [13], employed LITD as a monitor of the decrease in $H(D)$ coverage during $H_2$ ($D_2$) desorption under isothermal conditions. This technique is useful over a wide temperature range and especially at lower surface temperatures. The second, isothermal desorption, used the continuous rate of evolution of $H_2(D_2)$, as determined by continuous mass spectrometric measurements under isothermal conditions, to determine the rate of change of the $H(D)$ coverage. This isothermal desorption technique extends the data range to higher temperatures.

For both the isothermal LITD measurements and the isothermal desorption measurements, the Si(100) surface at 110 K was exposed to atomic hydrogen or deuterium until the desired initial coverage was obtained, and was then heated rapidly (18.3 K/s) to the desired isothermal desorption temperature. Any dihydride created upon atomic hydrogen (deuterium) adsorption was thermally desorbed in the programmed heating before the desired isothermal condition was reached. In the isothermal LITD measurements, nonoverlapping spots on the crystal were sequentially irradiated and the gas pulse from the irradiated spot was
monitored with the 1.75 cm diameter aperture in front of the mass spectrometer. In the isothermal desorption measurements, the H\(_2\) (D\(_2\)) partial pressure at the mass spectrometer, using the 0.3 cm diameter aperture, was monitored as a function of time after the surface reached the desired temperature.

For the LITD experiments, the 308 nm output of a XeCl excimer laser, (\(\approx 2.0 \) mJ pulse energy and \(\theta_i = 75^\circ\) with respect to the surface normal) serves to heat rapidly a 0.026 cm\(^2\) elliptical spot on the 16 x 16 mm Si(100) crystal and to desorb hydrogen from that spot. Since the hydrogen from the irradiated spot is desorbed in a single, 20 ns pulse, the signal is easily observed by the mass spectrometer, even for very low coverages. Figure 2 shows typical D\(_2\) LITD signals at relative coverages of \(\theta_D = 0.34\), 0.11, 0.06 and 0.00. Here \(\theta_D\) was measured from the amplitude of the LITD curves. The irradiated area is sufficiently large that even at a fractional coverage of \(\theta_D = 0.006\) the LITD signal is measured easily. The silicon surface was sufficiently large that 18 nonoverlapping measurements (laser shots) could be recorded for each experiment at a particular surface temperature. No damage of the surface attributable to the 2.2 mJ irradiation has been observed. We observed that the pulse energy required to ablate silicon for our optical geometry is approximately 3.2 mJ.
No evidence for diffusion of hydrogen on macroscopic length scales on the surface was observed for delay times up to 1200 seconds at 690 K. All hydrogen was removed from a spot on the surface with several laser shots. After 1200 seconds the identical spot was again subjected to a laser pulse. No signal due to refilling by diffusion was observed indicating that the LITD coverage measurements are not affected by diffusion. This procedure was performed at several different spots on the surface. This observation is consistent with the LITD studies of Koehler et al. [13] who observed the lack of H(D) diffusion on the Si(111) surface.

Care was taken to ensure that the mass spectrometric signal from a laser shot scales linearly with the surface coverage. In order to calibrate the LITD signals, a combination of LITD and TPD experiments was performed. A 0.35 K/s ramp was used to heat the surface, and a rastered sequence of D$_2$ LITD signals were measured as a function of temperature for a given initial deuterium coverage. For an identical initial deuterium coverage, using an identical heating rate, the D$_2$ TPD area was measured. The area under the TPD curve, measured from the time of the corresponding laser pulse, gives the coverage that is present at that time. This calibration was checked for three different initial coverages of deuterium on the surface. $\theta_D = 0.31$, 1.0 and 1.3. For all three coverages the LITD signals for $T > 680$ K (the temperature regime of interest) were found
to be linearly proportional to the integrated area of the remaining TPD curve. The signal-to-noise ratio was sufficient that these calibrations could be extended down to $\theta_D = 0.006$, with an error of $\pm 0.001$.

D. Isotopic Mixing Experiments

We used both LITD and TPD techniques to execute isotopic mixing experiments at low coverages. In both of these experiments the surface was initially dosed with deuterium atoms corresponding to a coverage, $\theta_D = 0.26$. The crystal was then annealed to 650K, cooled and dosed with an equivalent coverage of hydrogen atoms. LITD measurements were then made of $H_2$, HD and $D_2$ ratios. Similar experiments were carried out using the TPD technique to monitor the $H_2$, HD and $D_2$ TPD ratios.

E. Reaction of Atomic Hydrogen with a Partially Deuterated Surface

Reactions of incident hydrogen atoms with a partially deuterium atom-covered surface were studied as follows. The clean Si(100) surface was dosed with deuterium atoms to a coverage of $\theta_D = 0.5$ at 120K. The partially deuterated surface was then heated to the desired temperature and was exposed to hydrogen atoms. After the desired exposure, the surface was cooled and the isotopic composition of the remaining surface layer was determined using TPD (2.5 K/s
heating rate). These experiments were performed for a variety of hydrogen atom exposures and surface temperatures. The fraction of the deuterium atoms removed by reaction with incident hydrogen atoms was calibrated as follows. The clean surface was exposed initially to deuterium atoms and then heated to the desired temperature for a time equivalent to that for which the surface had previously been exposed to hydrogen atoms. The area under a $D_2$ TPD curve was measured to obtain the remaining coverage of deuterium in the absence of hydrogen atom dosing. This area was compared to the sum of areas of the $D_2$ and one half the HD TPD curves from the deuterated surface exposed to hydrogen atoms. The difference between the two measurements yields the fraction of deuterium atoms that had been removed by reaction with hydrogen atoms. Experiments involving the reverse isotopic exposure were performed in an analogous manner to observe the reactivity of hydrogen atoms on the surface with incident deuterium atoms.

III RESULTS

We report here results obtained in four types of experiments: (1) Hydrogen atom adsorption and the calibration of surface coverage; (2) Kinetic data from both isothermal LITD and the isothermal desorption technique.
(3) Isotopic mixing experiments; and (4) Results obtained from the interaction of hydrogen with a partially deuterated surface at various surface temperatures.

Temperature programmed desorption gives an overview of the binding states that are present on the surface. A typical TPD curve for saturation coverage of deuterium on Si(100) is shown in Fig. 3(a). This TPD spectrum is dominated by a large peak centered at 795 K which results from desorption of the monohydride. The smaller peak at 680 K is due to desorption of the dihydride, and the broad features below 600 K are due to the decomposition of Si$\text{D}_x$ species on the surface[10,11]. Heating the surface to 700 K and cooling removes both the Si$\text{D}_x$ species and the dideuteride without desorbing any monodeuteride, as may be seen in Fig. 3(b). Thus the area under curve (b) of Fig. 3 is proportional to the saturated monodeuteride coverage, ($\theta_D = 1$). Figure 4 shows TPD spectra of deuterium illustrating the development of the two surface deuterides as a function of exposure to D(g). Note that the monodeuteride saturates prior to the appearance of dideuteride, and that no monodeuteride is lost when dideuteride desorbs. Figure 5 shows the deuterium coverage as a function of exposure. The deuterium coverage at saturation corresponds to 1.6 monolayers, which is slightly higher than the value of 1.5 monolayers reported previously by using nuclear microanalysis [28].
Although the TPD data are somewhat ambiguous, Fig. 4 suggests that the desorption reaction for the monodeuteride phase is likely to be first order. The monohydride desorption peak has an asymmetric shape and the peak desorption temperature is nearly independent of coverage. (At coverages below $\theta_D = 0.25$ we observe an approximately 5 K upward shift in the desorption peak temperatures.) Schulze and Henzler [15] analyzed similar data for the Si(111) surface in terms of both first- and second-order kinetics, and preferred the second-order analysis. Koehler et al. [13] analyzed both TPD and LITD data for the Si(111) surface in terms of second-order kinetics. Apparently these investigators concluded that second-order desorption kinetics were appropriate because of the overall stoichiometry of the reaction, $2\text{H(a)} \rightarrow \text{H}_2(g)$. On the other hand, we have shown unambiguously that first-order desorption kinetics are appropriate for the Si(100) surface [12]. Using the method of Chan and Weinberg [29] to analyze our TPD curves assuming first-order kinetics yields an activation energy of desorption of $50\pm2$ kcal/mol and a preexponential factor of the desorption rate coefficient of $2.2 \times 10^{12}$ s$^{-1}$. These results are very similar to those of the first-order analysis of Schulze and Henzler for Si(111) [15].

Because LITD data are collected under isothermal conditions, they are more straightforward to analyze than
are TPD data. Some examples of such data, in which the decrease in the fractional coverage of chemisorbed deuterium as a function of time, parametric in temperature for two different initial coverages ($\theta_D = 1.0$ and 0.34), are shown in Figs. 6 and 7, respectively. The solid lines are calculated from the first-order rate law that is discussed below. Similar data were obtained for both hydrogen and deuterium at 13 different temperatures between 685 and 780 K using the LITD technique. Since deuterium desorption at the higher surface temperatures was rapid, the number of LITD pulses measured at these temperatures was smaller than for lower temperatures.

The direct, isothermal desorption technique provides an alternative way to measure the desorption kinetics at higher surface temperatures. Such data for surface temperatures of 760 and 790 K are shown in Fig. 8. The solid lines are again calculated from the first-order rate law obtained below. The data were quite reproducible from experiment-to-experiment.

If the desorption reaction were second order, then the time derivative of the fractional surface coverage of deuterium would be given by $d\theta_D/dt = -k_d \theta_D^2$, and a plot of $1/\theta_D(t)$ as a function of time would be linear. Here $k_d$ is the rate coefficient for desorption of deuterium. If instead the desorption reaction were first order, then $d\theta_D/dt = -k_d \theta_D$, and a plot of $\ln \theta_D(t)$ as a function of time
would be linear. As may be seen in Fig. 9, the first-order analysis gives an excellent representation of the data for a typical experiment involving deuterium desorption at $T_s = 735\,\text{K}$ obtained by the LITD technique; a second-order rate law does not fit the data, as may also be seen in Fig. 9. A similar plot for $T_s = 790\,\text{K}$ using the isothermal desorption technique is shown in Fig. 10. All desorption data in the temperature range between 685 and 790 K for both hydrogen and deuterium show similarly good agreement with a first-order rate law and similarly bad agreement with a second-order rate law.

The slopes of the straight lines in Figs. 9 and 10 are the first-order rate coefficients for desorption of $\text{D}_2$ at 735 and 790 K, respectively. Analogous rate coefficients were obtained at numerous temperatures for both $\text{H}_2$ and $\text{D}_2$ desorption, and a plot of the logarithm of the rate coefficient as a function of reciprocal temperature is shown in Fig. 11. These results show that the kinetics of $\text{D}_2$ and $\text{H}_2$ desorption fit a linear Arrhenius plot over the entire temperature range from 685 to 790 K, and that the two experimental techniques are completely in agreement with one another. Moreover Fig. 11 spans two orders of magnitude in desorption rate, and is thus quite reliable. The apparent activation energies of desorption of $\text{H}_2$ and $\text{D}_2$ obtained from the slopes of Fig. 11 are $45\pm2\,\text{kcal/mol}$ for both isotopes. The first-order preexponential factors $k_d^{(0)}$
obtained from the intercepts of the Arrhenius plots are $2.2 \times 10^{11}$ s$^{-1}$ ($10^{11.34 \pm 0.5}$ s$^{-1}$) for $H_2$ and $1.3 \times 10^{11}$ s$^{-1}$ ($10^{11.1 \pm 0.5}$ s$^{-1}$) for $D_2$, with both being accurate to within a factor of three. The error bars here represent plus or minus two standard deviations. These updated values are within the error bars quoted in our previous report [20] which employed only LITD data over a more narrow temperature range. Due to the nature of an Arrhenius plot, a small uncertainty in the value of the slope, $E_d$ results in a large uncertainty in the intercept, and in $k^{(O)}_d$. Thus the isotope effect on the preexponential factor can not be accurately determined from the present data. It is clear from figure 11, however, the $H_2$ desorption rate is approximately 1.6 times the $D_2$ desorption rate at all temperatures studied.

It is also important to note that the fact all plots such as those shown in Figs. 9 and 10 are linear over the entire range of fractional surface coverages ($0.006 \leq \theta_{H(D)} \leq 1$) implies that the rate coefficients of desorption of $H_2$ and $D_2$ are not a function of surface coverage. This does not preclude the remote possibility of a compensation effect, i.e. both $k^{(O)}_d$ and $E_d$ could be functions of surface coverage, but the individual variations are such that $k_d = k^{(O)}_d \exp(-E_d/k_BT)$ remains constant. It seems unlikely, however, that such
compensation would be so perfect over such a large range of surface temperature and coverage.

The observed first-order kinetics might appear to suggest that the hydrogen atoms are always "paired up" on the surface (independent of coverage) and do not have to diffuse across the surface to encounter one another. This could happen, for instance, when the initial dosage saturates the monohydride phase. If all desorbing hydrogen molecules are formed from atoms in adjacent positions, then it is possible that the remaining atoms occur as pairs down to very low coverage. Even though the empirical activation energy is inconsistent with this hypothesis we performed an experiment to independently test this possibility. First, the desorption kinetics were measured for low initial coverages. For example, Fig. 12 shows data acquired for an initial \( \theta_D = 0.06 \), and analyzed according to both first- and second-order rate laws. Although the signal-to-noise ratio is not so good as for the high-coverage experiments, the data are clearly in much better agreement with the first-order rate law. If the first-order kinetics were due to a propensity for the atoms to occur as pairs, then this experiment would require that the pairs form spontaneously even for sub-monolayer exposures.

An experiment to test for a propensity of atoms to pair up proceeded as follows. The surface was exposed to deuterium atoms to achieve \( \theta_D = 0.25 \). Following heating to
650 K to allow the atoms to pair up if there were a driving force to do so, the surface was cooled back to 120 K and exposed to an equivalent dose of hydrogen atoms. Finally, both LITD and TPD (in separate experiments) were used to desorb $H_2$, HD and $D_2$. Complete isotope mixing (a 1:2:1 $H_2$, HD, $D_2$ ratio) was observed. This argues against the possibility that pre-paired adsorbed hydrogen atoms represent a distinct ground state of the system, and that first-order desorption occurs due to pre-pairing.

As previously reported [20] and described in detail in the next section, we propose that the rate limiting step in the desorption of hydrogen is the irreversible excitation of a hydrogen atom from a localized Si-H bond to a delocalized intermediate state, $H^\ast$. The following experimental results help to determine the properties of this delocalized state. An important assumption in our mechanism is that the atoms in the $H^\ast$ state react with localized hydrogen adatoms bound to single silicon atoms. If hydrogen atoms from the gas phase adsorbed via the same $H^\ast$ state, then such atoms would be expected to react with atoms in the monohydride state at surface temperatures below that at which desorption normally takes place. As described in detail in section II E, the procedure was to dose the surface with deuterium atoms ($\theta_D = 0.5$) at a low temperature, then to expose the deuterated surface to atomic hydrogen at various surface temperatures. Finally,
TPD is used to measure how much deuterium is removed by the exposure to hydrogen. The decrease in the deuterium coverage due to the reaction with hydrogen atoms from the gas phase as a function of hydrogen exposure is shown in Fig. 13 for surface temperatures of 675, 450, 300 and 123 K. For $T_s = 675$ K, the predosed deuterium atoms can be removed almost completely. For lower surface temperatures, dihydride formation occurs for exposures greater than 15 units, and this appears to reduce somewhat the rate of the recombination reaction. Note that this abstraction reaction proceeds even when the surface temperature is as low as 125 K, and thus may appear to be unactivated. This observation of rapid deuterium abstraction by incoming hydrogen atoms at low surface temperatures implies that the incoming hydrogen atom is not accommodated to the surface temperature before reacting.

It would be interesting to quantify the efficiency of the recombination reaction between localized adatoms and atoms incident from the gas phase. At this time, only a rough approximation can be made. If one assumes that the reaction takes place via a generalized Eley-Rideal mechanism then the expression $-d\theta_D/dt = F_H \cdot \sigma \cdot \theta_D$ will yield the cross section for the reaction. Here $F_H$ is the flux of the hydrogen atoms impinging upon the surface (estimated as described in footnote 27). $\sigma$ is the $H^* + D(a)$ reaction cross section, and $\theta_D$ is the fractional coverage of
deuterium present on the surface. A plot of $-\ln \theta_D$ as a function of exposure is illustrated in Fig. 14 for $T_s = 123, 325, 450, 675$ K. The data are roughly consistent with a first-order dependence on the hydrogen atom flux, and, within the scatter of the data, there is no dependence of the initial rate (in the regime of monohydride coverage) on the surface temperature. Using the average initial slope of the four plots results in an estimated cross section of $5 \times 10^{-16}$ cm$^2$. Thus if the initial sticking coefficient is near unity, an assumption in our estimate of the hydrogen flux, $F_H$, then the cross-section implies a concomitantly large probability of Eley-Rideal like abstraction.

It can also be qualitatively confirmed that the probability of removal of $D(a)$ by $H(g)$ is of the same order as the sticking probability by comparing Figs. 5 and 13. We estimate that for an incident $H(g)$ atom the ratio of the probability that $H^*$ reacts with the localized deuterium atom to the sticking probability is 0.4. A surprising result was obtained when the order of dosing the two isotopes was reversed. The efficiency of hydrogen atom removal due to reaction with incoming $D^*$ atoms is only 20 percent of that of $H^* + D(a)$.

IV. DISCUSSION

The experimental results presented above show clearly that the recombinative desorption of hydrogen from $Si(100)$
follows a rate law that is first order in the coverage of atomic hydrogen. This result was verified over a temperature range from 685 to 790 K and a coverage range from $\theta = 0.006$ to 1.0. A second important result is the low value of the measured activation energy of desorption, $45 \pm 2$ kcal/mol. This activation energy appears to be constant over the full range of temperature and surface coverage. The ratio of the rates of desorption of $H_2$ and $D_2$ is consistent with a normal kinetic isotope effect, i.e., $k_d(H)/k_d(D) \approx 1.8$. Reaction of incident hydrogen atoms with a partially deuterated surface at various surface temperatures suggests that the efficient reaction between hydrogen atoms from the gas phase and localized deuterium atoms appears not to be activated. Although hydrogen on silicon is one of the more extensively studied systems in the surface chemistry of covalently bonded solids, these results were completely unanticipated.

The experimental results reported here require a new model for the dynamics of recombinative desorption from covalently bonded surfaces. In this section, we will (1) interpret our results in terms of our recently proposed mechanism for hydrogen desorption from Si(100) [20]; (2) describe briefly the shortcomings of alternate mechanisms; (3) discuss how the present results compare to those obtained previously for the hydrogen/silicon system; and
(4) briefly suggest directions for further studies of the dynamics of atoms interacting with covalent surfaces.

The formulation of a model to describe the kinetics behavior observed for hydrogen desorption from Si(100) requires an estimate of the Si-H bond energy for the monohydride phase. When an Si-H bond at the surface is cleaved, both the silicon atom and the hydrogen atom go from a coordinatively saturated configuration to one with a half filled valence orbital. The best molecular analogue that one can use to estimate the energy of such a bond cleavage is the cleavage of a \((\text{Si} \text{H}_2\text{H}_{n+1})_3\)Si-H bond. Typical bond strengths in various silane molecules are the following: \(D(\text{H-SiH}_3) = 90.3 \text{ kcal/mol}\), \(D(\text{H-SiH}_2\text{CH}_3) = 89.6 \text{ kcal/mol}\), \(D(\text{H-SiH}_2\text{H}_5) = 86.3 \text{ kcal/mol}\), and \(D(\text{H-SiH}_2\text{C}_6\text{H}_5) = 88.2 \text{ kcal/mol}\) [30]. We choose to use a value of 90 kcal/mol because this approximates the Si-H bonding energy in many silanes [30]. In agreement with our point of view, the monohydride Si-H stretching frequency [31] is very similar to that of fully saturated silanes. Other investigators have tended to choose lower values for the Si-H bond strength. A value of 70 kcal/mole has been suggested [1]. One justification for such a low value is the average Si-H bond energy in SiH\(_4\) [1, 32-34]. This lower value is not appropriate because it incorporates bond energies for SiH\(_{1,2,3}\) radicals whose bonding configurations are unrelated to those of the monohydride Si-H bond.
A. Proposed Mechanism

We have recently proposed a mechanism which is consistent with all data concerning the recombinative desorption kinetics of hydrogen on Si(100) [20]. In this mechanism the activated $H_2$ desorption reaction proceeds via an irreversible excitation of a covalently bound hydrogen adatom from a localized Si-H bond (monohydride) to a two-dimensional delocalized state, $H^*$. The $H^*$ state is 45 kcal/mol higher in energy than the Si-H bond but is itself bound to the surface by 45 kcal/mol. We assume that the reverse process, quenching of $H^*$ to form a localized Si-H bond, is slow due to momentum conservation constraints analogous to those that are effective in selective adsorption scattering [35,36]. The final step in the recombinative desorption reaction is the reaction of a $H^*$ atom with a localized hydrogen adatom (Si-H) leading to $H_2$ desorption.

This mechanism can be represented by two elementary steps, namely,

$$H(a) \overset{k_1}{\longrightarrow} H^*(a), \quad (1)$$

and

$$H^*(a) + H(a) \overset{k_2}{\longrightarrow} H_2(g). \quad (2)$$

The surface coverage of $H^*$ is always small if the first step is rate limiting. This implies that $\theta_{H^*} \approx k_1/k_2$ and that the rate of desorption is $R_d = k_1 \theta_H$. This mechanism
gives a clear explanation for both the order of the reaction and the low activation energy. The 45 kcal/mol activation energy to reach the \( \text{H}^* \) state is a result of the extreme corrugation of the H-Si(100) potential energy surface, as would be expected for surfaces of covalent solids with highly directed dangling bonds. The delocalized \( \text{H}^* \) species itself is located further from the surface-Si plane than required for formation of a Si-H bond, and therefore the \( \text{H}^* \) species experiences only a slight effective corrugation as it translates across the surface.

Figure 15 presents a potential energy diagram that illustrates the relative energies of the Si-H bond, the \( \text{H}^* + \text{Si-H} \) state, 2\( \text{H}^* \) adatoms, and gas phase \( \text{H} \) and \( \text{H}_2 \). Relative to an \( \text{H}_2 \) molecule in the gas phase as the energy zero, two localized hydrogen adatoms on the silicon surface lie at -75 kcal/mol; one delocalized adatom and one localized adatom lie at -30 kcal/mol; and two delocalized adatoms lie at +15 kcal/mol. The dotted curve shows the barrier which \( \text{H}_2(g) \) must overcome in order to chemisorb dissociatively. The energy values used in the diagram are based on our experimental measurements and the assumption that the Si-H bond energy of the monohydride is 90 kcal/mol. From this diagram, it is clear that the activation energy for dissociative adsorption of \( \text{H}_2 \) is less than 15 kcal/mol. While a value for the Si-H bond energy different from 90 kcal/mole will change the quantitative
values used in Fig. 15, the qualitative picture will not be affected.

In order to verify the existence of a relatively long-lived H* state, the reactivity of localized deuterium atoms with hydrogen atoms incident from the gas phase was studied. As shown in Fig. 13, first the surface at 120 K was exposed to atomic deuterium. The surface temperature was then maintained at values in the range 123-675 K for which deuterium desorption from the monodeuteride phase is negligible. The surface was then exposed to hydrogen atoms. If the H* species exists in the mechanism for desorption, H(g) atoms incident upon the surface would be expected to pass through the H* state before becoming localized in a Si-H bond [37]. The incident gaseous hydrogen atoms were found to react and to efficiently remove the adsorbed deuterium atoms. For example, when a surface with 0.5 monolayer coverage of deuterium at 675 K was exposed to hydrogen atoms with an exposure that would have produced 0.5 monolayer of hydrogen if the surface had been at 130K, 30% of the deuterium atoms were removed as HD, and the final coverage of hydrogen and deuterium was 0.70. In the absence of H(g), θD would have decreased by less than 1% during the same period of time at this temperature. Since H* atoms react with Si-D bonds at a temperature below the thermal desorption temperature, this strongly suggests that a long-lived H* species exists and,
when the H* species is supplied from the gas phase, that the activation energy of H* + Si-D → HD(g) is less than that of excitation of a ground state deuterium adatom to the D* state. This rules out the hypothesis that the second step in the desorption is the recombination of two H* atoms.

As shown in Fig. 13, deuterium-atom removal is efficient when reacting with H* atoms from the gas phase. Since the initial slopes of the depletion plots are not a strong function of surface temperature, cf. Fig. 14, the H* + D(a) reaction superficially behaves as if it is not an activated process. According to the energy level diagram presented in Fig. 15, however, an activation energy between 30 and 45 kcal/mole would be expected if the incoming hydrogen atom were thermalized within the H* manifold of states without deexciting into a localized site. The apparent lack of an activation energy for the H* + D(a) reaction thus implies that energy accommodation for the incoming hydrogen atoms with the surface is slow compared to the reaction time, and some of the kinetic energy of the incident hydrogen atom remains available for the D(a) atom abstraction reaction.

There is an interesting isotopic effect in the reaction of gas-phase atoms with those localized on the surface. Gas-phase deuterium atoms are less effective at removing localized hydrogen atoms than gas-phase hydrogen
atoms are at removing localized deuterium atoms. To the extent that the first collision of a gas-phase atom with the surface is impulsive, an incoming D(g) atom will lose a greater fraction of its kinetic energy to the surface than a hydrogen atom and hence would be expected to be less effective in activating an Si-H bond compared to the converse process. Clearly, it will be very interesting to perform more quantitative dynamical studies of this phenomenon.

The ability of hydrogen and deuterium atoms from the gas phase to react with atoms localized on the surface is similar to recently observed "Eley-Rideal" behavior for hydrogen atom reactions on metal surfaces [18,19]. Also, the H\(^*\) state on Si(100) may have similar properties as the "hot precursors" proposed to explain the behavior of the reaction of H\(_2\) with oxygen atoms on Pt surfaces [38,39]. By comparison, the mechanism that we have proposed for H\(_2\) desorption from Si(100) may be best considered to be a generalization of the "Eley-Rideal" mechanism for reactions on surfaces. Rather than requiring a direct collision between an impinging gas-phase atom and a localized adatom, our mechanism proposes that the incoming hydrogen atom enters the long-lived H\(^*\) state from which it is able to react with localized hydrogen adatoms.
B. Alternative Mechanisms

The fact that the proposed mechanism is both plausible and agrees with a wide variety of different experimental data is not, of course, proof of its validity. One possible explanation for the observed first-order desorption reaction is that the hydrogen atoms are always "paired up" on the surface and do not have to diffuse across the surface to encounter one another. Due to the anisotropic nature of the surface, there are several ways that one could imagine a propensity for the atoms to form pairs. We will focus on the possibility that the pairing is due to a preference for populating both silicon atoms of a Si-Si dimer before populating another randomly selected site. Similar arguments can be applied to the other possible pairing mechanisms. Fig. 12 shows a comparison between an analysis based on first- and second-order desorption kinetics for deuterium at an initial coverage of 0.06 monolayer. Even at such a low initial coverage, the desorption kinetics still follow the first-order rate law that applies to the high-coverage data. Thus if pre-pairing is the explanation for the first-order kinetics, it takes place even at very low initial coverages. The most obvious argument against a driving force to pair up the hydrogen atoms is that if the rate-limiting step for the desorption reaction were a concerted desorption from pre-formed pairs, the expected activation energy would be greater than 75
kcal/mol, i.e. $2D(Si-H)-D(H-H)$. Since this argument rests on an estimated Si-H bond energy, however, we seek independent experimental evidence against the "pre-paired" hypothesis. First, such a hypothesis is inconsistent with the infrared data of Chabal [40], which shows that there is no propensity to populate both sides of the dimer as opposed to randomly filling in the available sites. When both sites on a silicon dimer are occupied, a splitting between the symmetric and anti-symmetric combinations of the Si-H stretch is observed. This splitting is absent at low coverage and gradually develops as the monohydride phase is saturated. Secondly, we have performed isotopic mixing experiments, as described above, which argue against a preference for the hydrogen atoms to be paired up at low coverage. The evidence rules out unambiguously the possibility that pre-paired hydrogen atoms represent a distinct ground state of the system.

C. Comparisons to Previous Results

In general, recombination reactions on metal surfaces involve the "hopping" of adsorbate atoms between surface sites until adjacent atoms combine and desorb. This produces second-order desorption kinetics. Although exceptions to this mechanism for hydrogen recombination on metal surfaces have been found recently [18,19], a first-order mechanism is so unusual that even though
Schulze and Henzler [15] observed that the thermal desorption peak temperature remained nearly constant with increasing coverage for hydrogen recombination on the Si(111) surface, a phenomenon that indicates first-order kinetics, they still preferred to interpret their data in terms of a second-order mechanism. Koehler et al. [13] also analyzed LITD data for hydrogen desorption from the Si(111) surface in terms of second-order kinetics. In the LITD experiments of Koehler et al., the laser desorption mechanism appeared to change below a surface coverage of $\theta_H = 0.2$ in such a way that the surface coverage could not be measured for lower values of the coverage. This made it impossible for them to distinguish between first- and second-order kinetics, which are equally consistent with their data. Reinterpreting their data in terms of first-order desorption kinetics yields activation energies and preexponential factors of 43 kcal/mol and $3.3 \times 10^{10}$ s$^{-1}$ for $H_2$, and 47 kcal/mol and $3.6 \times 10^{11}$ s$^{-1}$ for $D_2$. Thus the experimental results of Koehler et al. [13] are consistent with the mechanism we propose. The data of Gupta et al. [14] for hydrogen desorption from the monohydride phase on porous silicon surfaces, measured using Fourier transform infrared (FTIR) spectroscopy, also can be reanalyzed using first-order kinetics. An activation energy of 50 kcal/mol and a preexponential factor of $1 \times 10^{12}$ s$^{-1}$ are obtained. It thus appears that
the first-order kinetics are consistently applicable over a wide range of temperatures, coverages and surface morphologies, and that the kinetic parameters are relatively constant as long as the hydrogen coverage is in the monohydride range. Further studies will be necessary to confirm the generality of these conclusions for these and other surfaces of covalently bonded solids.

D. Remaining Issues

The recombinative desorption of hydrogen is one of the most intensively studied problems in surface science. In 1912 Langmuir investigated the interaction of hydrogen with tungsten [41], and subsequently there have been a host of studies carried out concerning hydrogen recombination on metal surfaces and more recently on covalent solids [42]. It is thus somewhat surprising that the mechanism for recombinative desorption from Si(100) is still a matter of controversy. In retrospect, it is not so surprising that the mechanism of such a simple reaction on a covalent surface should be quite different from that on a metallic surface. Both the magnitude and the anisotropy of the barriers to migration across the surface are much greater for the highly oriented dangling bond orbitals of a covalent surface than for the more isotropic projected density of electronic states on a metallic surface. It will be very interesting to determine if the conclusions reached
here will apply to a wide variety of covalent surfaces, or if hydrogen desorption kinetics are sensitively dependent on the adatoms and surface under study.

There are two essential features of the proposed mechanism that are responsible for the observed rate law. First, the barriers for migration between surface sites is a large fraction of the bond energy. Second, dissipation of kinetic energy from a hydrogen atom traversing across the surface is relatively inefficient. Since neither the interaction potentials nor the dynamics for atoms and molecules interacting with covalent surfaces are well known, it is clearly necessary to obtain more data relating to these aspects of surface reactions. One can surmise that chemisorption on surfaces of all covalently bonded solids will be characterized by highly localized bond sites. Also, it seems likely that the relaxation rate from excited surface states will scale upward with increasing mass of the adatom. Thus one would expect that hydrogen recombination may occur by the proposed mechanism for a variety of surfaces, while the site-to-site hopping of heavier atoms may tend to be less unusual. In this respect we should point out that for any appreciable coverage of adatoms the diffusion length necessary to find a reactive partner is not very great. Thus the fact that formation of the H state appears to be irreversible may not be so difficult to understand.
Perhaps the most important property that remains to be determined for the monohydride phase on Si(100) is the Si-H bond energy. The present results indicate that the activation energy for excitation into a delocalized state is independent of coverage up to saturation of the monohydride phase. This suggests that there is no substantial change in the Si-H bond energy as a function of coverage. This conclusion is supported by the infrared stretching frequencies [31] which are nearly independent of coverage except for the development at high coverages of the symmetric stretch – asymmetric stretch splitting of 12 cm$^{-1}$ [9]. The mechanism we propose indicates that there is no direct relationship between the Si-H bond energy and the activation energy for desorption, and hence the bond energy cannot be inferred from kinetic studies.

Because it is possible for incoming H and D atoms to react with atoms already on the surface, careful absolute sticking probability measurements as a function of surface coverage should be performed for all mixtures of isotopes. Such data would give a direct measurement of the branching ratio between sticky and reactive collisions, and would be a great help in defining the detailed dynamics for the system. In particular, such measurements would help define the rate of relaxation of H* atoms into localized positions, a process that is too slow to be inferred from the recombinative desorption kinetics.
V. SUMMARY

The recombinative desorption kinetics for the monohydride phase of hydrogen on Si(100) were found to be first order in the hydrogen coverage over a wide range of temperatures and coverages. This was interpreted in terms of a mechanism for recombinative desorption which involves an irreversible excitation of a hydrogen adatom into a delocalized $H^*$ state that subsequently reacts with a Si-H species to produce $H_2(g)$. This mechanism is supported by sequential dosing experiments with D(g) and H(g) which show that the adsorption of hydrogen atoms proceeds through an $H^*$ precursor state that is capable of reacting with Si-D surface species to produce HD(g) at temperatures below that at which thermal desorption of hydrogen normally takes place. Further, we have shown that this $H^*$ state is weakly coupled to the surface. The proposed mechanism is consistent with the accepted Si-H bond energy of 90 kcal/mol, and predicts that the activation energy for dissociative adsorption of $H_2$ is less than 15 kcal/mol. It seems likely that this proposed mechanism will be applicable to hydrogen desorption from other crystallographic orientations of silicon and from the surfaces of other covalent solids.
ACKNOWLEDGMENTS

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REFERENCES


27. In all the figures, the dosage of hydrogen or deuterium atoms are given in arbitrary units. We have approximated the conversion of arbitrary units of exposure to hydrogen atom flux by assuming the probability of adsorption of hydrogen atoms on a Si(100) surface to be unity at zero coverage and that a monolayer coverage consists of $6.8 \times 10^{14}$ monohydride species/cm$^2$ of the silicon surface.


37. Although microscopic reversibility does not require that atoms adsorb via the $H^*$ state, it seems highly likely that they would do so.


40. Chabal observes a single Si-H stretching mode in the IR spectrum of the monohydride phase at low coverages. With increasing hydrogen atom exposure to the surface, two IR peaks are observed.
corresponding to the symmetric and asymmetric stretch of the doubly occupied dimer, H-Si-Si-H. This is consistent with a statistical population of monohydride sites rather than a propensity to form pairs of H atoms on the Si dimers[31].


Figure Captions

Fig. 1. Schematic diagram of the apparatus used in the LITD experiments. M = mirror, BS = beam splitter, BST = beam stop, A = aperture, F = quartz windows used as neutral density filters to adjust the laser intensity at the surface, PM = power meter.

Fig. 2. The D₂ mass spectrometric output for a single laser shot is shown for several values of the coverage. The rise and decay times are due to the time it takes the gas pulse to fill the volume around the mass spectrometer and to be pumped away. No dynamics can be inferred from the time dependence. The signals are intense and reproducible to very low coverages. Because a more sensitive mass spectrometer scale is used for lower coverages, the effective time constant of the electronics is longer and the signal to noise ratio remains large.

Fig. 3. Temperature programmed desorption curves of D₂ for two representative exposures to atomic deuterium. Curve (a) was recorded immediately after dosing and shows a monodeuteride peak at 795 K, a partially developed dideuteride peak at 680 K and a broad distribution of lower binding energy desorption process associated with deuterium induced surface etching. Curve (b) was recorded after annealing the deuterium-covered surface to 700 K. The annealing removes all of the low binding energy deuterium without affecting the coverage of the monodeuteride. For lower exposures only the monodeuteride desorption process is observed.

Fig. 4. Temperature programmed desorption curves as a function of coverage. For each curve, the deuterated surface was preannealed to 500 K to allow the low binding energy deuterium to either migrate to dideuteride sites or desorb. The monodeuteride peak temperature is nearly independent of coverage. The θ_D = 0.26 peak is shifted approximately 5 K to higher temperatures compared to the higher coverage peaks.

Fig. 5. Coverage of deuterium as a function of exposure to atomic deuterium. The saturation coverage of 1.6 times that of the saturated monodeuteride is slightly higher than expected if there are an equal number of monodeuteride and dideuteride sites at saturation. (a - where ever this letter appears in figures see ref. 27.)
Fig. 6. Variation in fractional surface coverage with time for the isothermal desorption of D$_2$ from Si(100) measured with the LITD technique. The initial coverage was $\theta_D = 1.0$.

Fig. 7. Same as that of Fig. 6 with the initial coverage being $\theta_D = 0.34$.

Fig. 8. Deuterium coverage as a function of time measured by the overall change in pressure in the mass spectrometer. The initial coverage was $\theta_D = 1.0$, but significant desorption occurred before the surface temperature reached the desired value. Again, the solid curves are calculated from the first order rate law as in Fig. 6 and 7.

Fig. 9. Comparison of first- and second-order kinetics of D$_2$ desorption from Si(100) using the LITD method at 735 K. The linear fit demonstrates that the desorption reaction is first-order in $\theta_D$.

Fig. 10. The same plot as in Fig. 9 except that the data was acquired by measuring the ambient D$_2$ pressure for $T = 790$ K and initial coverage $\theta_D = 1.0$. All plots of this type for the range of temperature and coverage that we were able to explore showed a clear preference for first-order kinetics.

Fig. 11. Arrhenius plots for the desorption of H$_2$ (open triangles) and D$_2$ (open circles for LITD data, closed circles for isothermal desorption data) from Si(100). The implied activation energies and pre-exponential factors of the desorption rate coefficients are 45±2 kcal/mol and $2.2 \times 10^{11}$ s$^{-1}$ for H$_2$, and 45±2 kcal/mol and $1.3 \times 10^{11}$ s$^{-1}$ for D$_2$.

Fig. 12. A comparison of first- and second-order kinetics of D$_2$ desorption at an initial coverage of $\theta_D = 0.06$. The plot extends to $\theta_D = 0.004$. Although the signal-to-noise ratio is not so large as for the higher coverage data, there is still a clear preference for the first-order rate law.

Fig. 13. The change in the deuterium coverage due to exposure to H atoms from the gas phase at surface temperatures of 123, 300, 450 and 675 K. Note that for
H exposures above 12 units the surface coverage is entering the dihydride range.

Fig. 14. Plot of $-\ln(\theta_D(t)/\theta_D(0))$ as a function of hydrogen atom exposure showing that in the low coverage limit the reaction between incoming H atoms and D adatoms is roughly first-order in exposure to H atoms and within the scatter of the data, there is no dependence of the rate (in the monohydride phase) on the surface temperature.

Fig. 15. Schematic potential-energy diagram for the interaction of hydrogen with the Si(100) surface. The main diagram is for movement along the desorption "reaction coordinate" while the upper left hand corner shows the barriers for H migration over the surface. A Si-H bond energy of 90 kcal/mol is assumed. A 45 kcal/mol minimum barrier to diffusion across the surface is inferred from the activation energy of the desorption reaction. This implies that diffusing adatoms can be bonded to the surface by up to 45 kcal/mol even though they are not localized at a particular site. The energy required to cause two hydrogen atoms to diffuse is higher than the $H_2$ desorption energy.
UHV System for Laser Desorption Experiment

Laser Optics

Ion Gauge

To collimated-array doser, calibrated flux

LEED + Auger

Si (100) crystal

View Port

Quadrupole mass spec.

Excimer Laser Beam (XeCl, 308 nm)
\[ \frac{dT}{dt} = 2.5 \text{ K/s} \]

\[ T_{\text{ads}} = 123 \text{ K} \]

\[ 1 \times 10^{-10} \text{ Torr} \]

- \[ \frac{\theta_D}{f} = 1.60 \]
- \[ \frac{\theta_D}{e} = 1.47 \]
- \[ \frac{\theta_D}{d} = 1.31 \]
- \[ \frac{\theta_D}{c} = 0.95 \]
- \[ \frac{\theta_D}{b} = 0.57 \]
- \[ \frac{\theta_D}{a} = 0.26 \]

Temperature, K
\[ \theta_D(\text{initial}) = 0.34 \]
$D_2 (735 \text{ K})$

$\theta_D(t=0) = 0.31$

\[ \frac{(0)\theta}{(t)\theta} \]

- 1st order
- 2nd order
\[ D_2(715 \text{ K}) \]

\[ \theta_D(t=0) = 0.06 \]

\[
\left[ \frac{(0)\theta}{(t)\theta} \right]_{\text{unlabeled}}
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\[ \text{Time, s} \]

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