Internal-state distributions of H_2 desorbed from mono- and dihydride species on Si(100)

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Following adsorption of atomic hydrogen on Si(100)–(2×1), the surface is heated and the desorbed H_2 is detected via (2+1) resonance-enhanced multiphoton ionization (REMPI). H_2 desorption correlated with the decomposition of dihydride groups on the surface (SiH_2) is detected at a surface temperature T_s near 660 K, and with the monohydride species (SiH) near T_s=780 K. Although the H_2 rotational distributions are nearly identical for the mono- and dihydride species, the vibrational distributions differ with roughly 0.2% and 1% of the population in $H_2(v=1)$ for the monohydride and dihydride, respectively. The enhancement in the $[H_2(v=1)]/[H_2(v=0)]$ population ratio over that of a thermal distribution at T_s is, however, roughly 20 times for both mono- and dihydride species. The results are interpreted within a model that assumes desorption proceeds through a common intermediate, which is identified as the dihydride.

INTRODUCTION

Studies of recombinative desorption dynamics on semiconductor surfaces are important for developing an understanding of the role of a covalent material in surface reactions. Recently, we have performed a series of state-specific studies to probe the dynamics of hydrogen recombinative desorption from the monohydride species on silicon surfaces.[1–4] These studies reveal that the recombinative desorption process is almost totally insensitive to the silicon surface structure. Studies of H_2 desorbed from Si_2H_6-dosed Si(100)–(2×1),[1,2] Si_2H_6-dosed Si(111)–(7×7),[3] and H-atom-dosed Si(100)–(2×1)[4] have shown that the rovibrational distribution of H_2 is *the same* for each of these systems. In each case, the H_2 product desorbed rotationally cold, with an average rotational energy near 350 K, but vibrationally excited, with 1.0±0.5% of the population in the $v=1$ state, compared to 0.05% predicted for a thermal distribution at the surface temperature (T_s~780 K). It was confirmed with isotopic studies that the experiments measured the nascent H_2 product of the recombination process, unmodified by postformation events, such as collisions with the surface.

These results were interpreted in the context of a localized recombinative desorption model in which long-range surface structure (where "long range" refers to distances on the order of the silicon lattice spacing) did not play an important role in the dynamics. It was proposed that (1) the transition state was localized at a single silicon atom, with both H atoms oriented roughly symmetrically about Si and (2) the transition state was reached by migration of a H atom from a neighboring monohydride site. A similar model has also been proposed by Nachtigall *et al.*[5] It was reasoned that if the transition state is strongly associated with one Si atom and interacts only weakly with adjacent surface atoms, then the largest contribution to the rovibrational distribution will be caused by potentials near a single silicon atom. As a result, the dynamics and resulting product state distribution would be expected to be largely insensitive to surface structure, as experimentally observed. The proposed structure of the transition state resembles a dihydride species, where two hydrogen atoms are bound to a single silicon atom in the ground state configuration. A natural extension of this work is a study of desorption from the *dihydride* state on silicon.

It is well known that the adsorption of atomic hydrogen on the Si(100)–(2×1) surface can lead at high coverages to the formation of both monohydride (SiH) and dihydride (SiH_2) species.[6–13] The monohydride and dihydride surface species have been identified definitively by both electron energy loss (EEL)[7–9] and infrared[11,14] spectroscopies. The presence of the dihydride species is accompanied by several silicon surface reconstructions, such as the (3×1) and (1×1) structures. Room temperature adsorption of H atoms causes the (2×1) pattern, which is associated with both the clean surface and the monohydride phase, to convert to a (1×1) pattern at saturation, as measured by low energy electron diffraction (LEED).[6,7,13,15] However, saturation H-atom adsorption near 380 K leads to a (3×1) LEED pattern.[11,13,15]

The (3×1) phase is believed to consist of dihydride units alternating with pairs of monohydride units that reside on a Si–Si dimer.[11] The structure of the (1×1) phase, however, has been the subject of some controversy. Although the (1×1) phase was previously thought to consist of all dihydride units,[10] both mono- and dihydride species have been found to coexist on this surface.[11] The exact structure of the (1×1) surface has been assigned variously to (1) a disordered phase of (3×1) units[11]; (2) a phase containing a mixture of mono-, di-, and trihydride (SiH_3) species;[13] and (3) a bulk-like structure with two H atoms per surface Si atom on (100) terraces, dispersed with monohydride-covered (111) facets resulting from etching.[16,17]

Accounting in part for the uncertainty in the detailed

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structure of the (1×1) phase is a lack of agreement in the literature of the H-atom coverage at saturation.[13,18] Another important parameter is the surface temperature during adsorption of hydrogen. In their work,[19,20] Uram and Jansson have emphasized that the saturation coverage and sticking coefficient of hydrogen are strongly dependent on surface temperature. The surface temperature during adsorption affects not only the saturation coverage of hydrogen, but also the resultant surface structure and the stability of a given H/Si(100) phase toward further attack by atomic hydrogen.[17] The recent scanning tunneling microscopy (STM) work of Boland[16,17] has examined in detail the interplay between surface temperature and surface structure and has brought about a better understanding of seemingly contradictory results. Boland's study indicates that the (1×1) structure is not a well-defined phase but rather an ill-defined structural manifestation of the exact H-atom exposure conditions (surface temperature and extent of exposure).

In a temperature-programmed desorption (TPD) experiment, a β_2 desorption peak associated with dihydride decomposition occurs near 660 K, whereas the β_1 monohydride desorption peak occurs near 780 K.[12,13] There is disagreement in the literature on the kinetic order of the desorption reaction. One report[14] found desorption from both the monohydride and the dihydride states to be *second order* on porous silicon, with estimated desorption activation barriers of 65 and 43 kcal/mol for the SiH and SiH_2 species, respectively. The most recent consensus, however, is that the monohydride species undergoes first-order desorption on the Si(100) surface,[21–24] calling into question the assignment of second-order kinetics for both species on the structurally related porous silicon.[14] In addition, an earlier study analyzed the dihydride desorption kinetics from Si(100) as *first order* and determined the activation barrier to be 44 ± 7 kcal/mol.[25]

In the present work, we have undertaken a study of the internal-state distribution of hydrogen desorbed from the dihydride state on Si(100) to further elucidate the desorption mechanism. Although the rotational distributions are nearly identical, H_2 desorbed from the dihydride state on Si(100) is found to have significantly less population in $v=1$ compared to $v=0$ than hydrogen desorbed from the monohydride state. This result is attributed to the difference in desorption temperatures for the two processes (660 vs 780 K). A model is presented in which desorption proceeds through a common intermediate identified as the dihydride species.

EXPERIMENT

The apparatus has been described in detail elsewhere.[1,3] It consists of an ultrahigh vacuum (UHV) chamber with low energy electron diffraction (LEED) and Auger electron spectroscopy (AES). The Si(100) crystal samples used in the experiments were cut from wafers of highly As-doped silicon; the low resistivity of the crystals (0.005 Ω cm) facilitates direct resistive heating. The details of sample preparation are described in Ref. 1. Because of the very low sticking probability of molecular hydrogen on Si(100)–(2×1), atomic hydrogen is used to dose the surface. Atomic hydrogen is produced by dissociation of H_2 gas (99.999%) by a 2000 K tungsten filament positioned a few centimeters from the surface. The H-atom flux at the surface was not calibrated; the exposures we report are therefore that of molecular hydrogen. In these experiments, the sample is typically exposed to 10^{-5} Torr of H_2 for 1 min., i.e., a 600 L dose (1 L$=10^{-6}$ Torr s), while being held at 425 K. The resulting surface contains both monohydride and dihydride species. H-atom dosing at elevated temperatures also precludes etching of the surface.[17] The LEED pattern after hydrogen exposure is (1×1) with faint streaks at the fractional order positions, possibly indicating the presence of some (3×1) domains.

The internal-state distributions of molecular of hydrogen desorbed from the surface are determined using $(2+1)$ resonance-enhanced multiphoton ionization (REMPI) through the $E,F\,^1\Sigma_g^+$ state. The spectroscopy[26] and optical setup[1,3] have been described previously. Briefly, the laser system includes a Nd:YAG-pumped dye laser followed by frequency doubling and mixing stages. The resulting 200–215 nm radiation propagates parallel to the crystal face inside the chamber and is focused a few millimeters above the surface. H_2^+ ions produced by REMPI are detected in a time-of-flight mass spectrometer.

The procedure for collecting internal-state distributions is as follows: the basic measurement is quantum-state-resolved temperature-programmed desorption (TPD). The mono- and dihydride-covered silicon surface is prepared by adsorption of atomic hydrogen. During the subsequent TPD, the H_2 desorption flux is intersected by the pulsed laser beam and ionized. With the laser at a set frequency, the intensity of ions resulting from a particular $H_2(v,J)$ quantum state is followed as a function of crystal temperature. The monohydride and dihydride peaks are analyzed independently and the peak areas reduced to relative rovibrational populations.

RESULTS

Two separate H_2 desorption peaks for the monohydride (β_1) and the dihydride (β_2) species are observed in temperature programmed desorption from Si(100) after a saturation dose of atomic hydrogen. Figure 1 illustrates typical TPD spectra of H_2 in both the $(v=0, J=1)$ and $(v=1, J=1)$ quantum states detected by REMPI spectroscopy after a saturation dose of hydrogen at $T_s=425$ K. Also shown for comparison is a typical desorption peak of $H_2(v=0, J=1)$ after adsorption of disilane at $T_s=375$ K. The data in Fig. 1 have been corrected for power fluctuations on a shot-to-shot basis. Note the disilane adsorption leads only to a β_1 peak, whereas both β_1 and β_2 peaks are observed with atomic hydrogen. State-specific studies of hydrogen desorption after disilane adsorption have been presented previously.[1–4] The desorption temperatures of roughly 660 and 780 K for the β_1 and β_2 peaks after H-atom exposure agree with those reported in the literature, although in the present experiments, the surface temperature reading was not calibrated carefully.

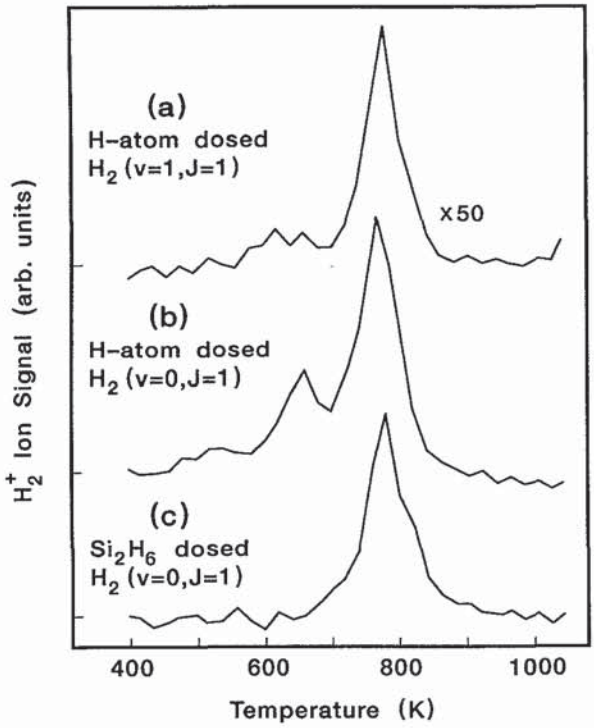

FIG. 1. Temperature-programmed desorption spectra for (a) $H_2(v=1, J=1)$ and (b) H_2 $(v=0, J=1)$ desorbed from Si(100) after a saturation dose of atomic hydrogen at $T_s=425$ K. A temperature-programmed desorption spectrum for $H_2(v=0, J=1)$ desorbed after a saturation dose of disilane at $T_s=375$ K is shown in (c) for comparison. The ion signal in (a) has been multiplied by a factor of 50. The heating rate was 10 K/s.

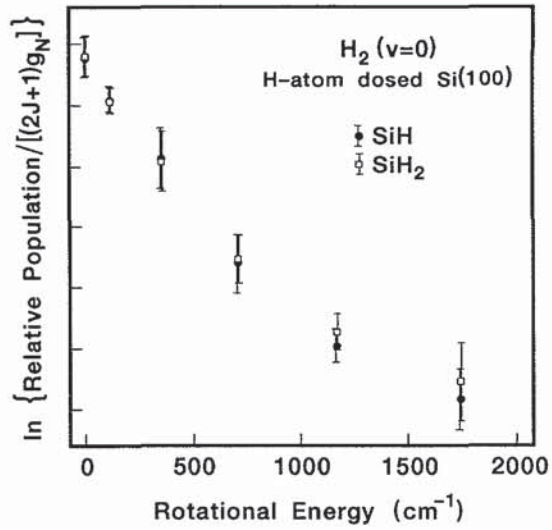

FIG. 2. The Boltzmann plot of H_2 thermally desorbed from the mono- and dihydride surface species on the Si(100) surface. Rotational distributions are shown for $H_2(v=0)$.

Integration of both the β_1 and β_2 peaks obtained for each rovibrational state, after correctly subtracting the background contribution[1] and applying the proper correction factors,[26] yields a relative population distribution. Figure 2 displays the resulting rotational distributions for the ground vibrational state in the form of a Boltzmann plot, in which the natural logarithm of the population divided by the rotational degeneracy $(2J+1)$ and the nuclear spin degeneracy (g_N) is plotted vs rotational energy (E_J). The rotational distributions of H_2 desorbed from the monohydride and dihydride species are the same within the experimental uncertainty. The distributions are non-Boltzmann, i.e., they cannot be fit by a simple thermal distribution which would appear as a straight line in a Boltzmann plot. The average rotational energy in temperature units $\langle E_{\rm rot}\rangle/k$ calculated according to $\langle E_{\rm rot}\rangle=\Sigma_J(N_JE_J)/\Sigma_JN_J$ is 320 ± 80 and 345 ± 85 K for H_2 desorbed from SiH and SiH_2, respectively. It is apparent that the average rotational energy is much lower than kT_s for desorption from both the monohydride, for which $T_s=780$ K at the maximum desorption flux, and the dihydride, for which $T_s=660$ K. Furthermore, the surface temperature appears to have no bearing on the rotational distribution, from which we conclude that the rotational distribution is dynamically, not thermally determined.

Similar TPD measurements were also made of H_2 in the $(v=1, J=1)$ quantum state, providing a measure of the degree of vibrational excitation. The vibrational population ratio between the $(v=1, J=1)$ state and the $(v=0, J=1)$ state can be converted to a total $N_{v=1}/N_{v=0}$ population ratio if the rotational distributions in both vibrational states are known. The rotational distribution in $H_2(v=1)$ was not measured in the present experiment; however, previous studies of H_2 desorption from Si_2H_6/Si(100)–(2×1) (Ref. 1) and Si_2H_6/Si(111)–(7×7) (Ref. 3), as well as of HD and D_2 desorption from Si(100)–(2×1) (Ref. 1), have shown that the rotational distribution is the same for both $H_2(v=0)$ and $H_2(v=1)$. Furthermore, because the $H_2(v=0)$ distribution is the same within error for both disilane and atomic hydrogen adsorption,[4] we assume that for the desorption following atomic hydrogen exposure the rotational distribution in $H_2(v=1)$ is the same as for $H_2(v=0)$.

The $N_{v=1}/N_{v=0}$ vibrational population ratio is significantly different between the monohydride- and dihydride-desorbed H_2. This can be seen easily by comparing in Fig. 1 the relative β_2 and β_1 TPD peak intensities for the $H_2(v=1, J=1)$ level with that for the $H_2(v=0, J=1)$ level. In the $v=0$ state, the β_2 peak is roughly 30% of the β_1 peak, whereas in $v=1$, the β_2 peak is much smaller. The calculated vibrational population ratios are $N_{v=1}/N_{v=0}=0.0099 \pm 0.005$ for the monohydride and 0.0023 ± 0.0009 for the dihydride, i.e., roughly 1.0% and 0.2% of the hydrogen population is found in $H_2(v=1)$ for desorption from the mono- and dihydride, respectively.

The vibrational distribution of H_2 desorbed from Si(100)–(2×1) is not at equilibrium with the surface temperature. Hydrogen desorbs from both the SiH and SiH_2 species with a population in $H_2(v=1)$ significantly greater than that expected for a thermal distribution at the surface temperature of desorption. The vibrational ratio expected from Boltzmann statistics at T_s of desorption is $(N_{v=1}/N_{v=0})_{\rm Boltz}=\exp(-\nu_{01}/kT_s)$, where ν_{01} the vibrational en-

ergy spacing is 4164 cm^{-1} for H_2. Thus $(N_{v=1}/N_v=0)_{Boltz}$ is 0.000 465 during the monohydride desorption, using a surface temperature of 780 K, and 0.000 115 for the dihydride desorption, using $T_s=660$ K. Although the absolute $N_{v=1}/N_{v=0}$ population ratios differ by a factor of ~ 5 between the mono- and dihydride, the relative enhancement over the thermal prediction at T_s is approximately 20 times in both cases.

DISCUSSION

The results above allow us to compare the internal-state distributions of H_2 desorbed from the dihydride state on Si(100) at $T_s \approx 660$ K with H_2 desorbed from the monohydride state at $T_s \approx 780$ K. The data show clearly that the relative population in $H_2(v=1)$ is significantly smaller in the case of dihydride than for the monohydride, but that in both cases, it exceeds what would be expected for a Boltzmann distribution at the surface temperature. The rotational distributions, on the other hand, are the same within error for both species and are significantly lower than either surface temperature.

The interpretation of the data is not straightforward. Because we perform a TPD experiment, we are constrained by nature to study desorption from the dihydride at temperatures near 660 K, and desorption from the monohydride near 780 K. These are the temperatures at which the desorption flux reaches a maximum if the surface coverage of hydrogen is not replenished. Therefore, in comparing the two distributions, we must take into consideration the fact that both the *identity* of the initially adsorbed species (SiH vs SiH_2) and the *temperature of the surface* differ.

Our goal is to compare directly the H_2 desorption dynamics from the dihydride species with that from the monohydride species. To accomplish this, we must first deconvolute the surface temperature effects. This requires a knowledge of the surface temperature dependence of the rovibrational distribution. Although no such experimental measurement has been made for the H_2/Si(100) system, a recent theoretical calculation by Sheng and Zhang[27] on H_2 desorbed from the monohydride state on Si(100)–(2×1) has examined the effect of surface temperature on the internal state distribution. We note that this theoretical model predicts H_2 rovibrational state distributions at 780 K in good agreement with what we measure. In addition to the theoretical work, surface temperature effects have been studied experimentally for some cases of hydrogen recombinative desorption on metal surfaces.[28,29] In these cases, the hydrogen was supplied continuously to the surface by atomic permeation through the bulk, allowing the surface temperature to be varied independently.

In general, the surface temperature is found to have little or no effect on the *rotational* distribution. Sheng and Zhang[27] predict with their theoretical model very little change in the average rotational energy of H_2 desorbed from Si(100)–(2×1) as a function of surface temperature. Experimentally, Kubiak, Sitz, and Zare[28] observed no systematic differences in the rotational distribution of H_2 desorbed from Cu(110) and Cu(111) at 850 and 960 K, respectively. Schröter, David, and Zacharias[29] found only a very weak change in the rotational temperature of H_2 desorbed from Pd(100) when the surface temperature is varied from 325 to 740 K.

The surface temperature does, however, affect the *vibrational* distribution. The strength of the temperature dependence for vibrational excitation can be illustrated by recent results of Schröter *et al.*[30] on the H_2/Pd(100) system. State-specific measurements of H_2 desorbed recombinatively from the Pd surface over a temperature range of 325–740 K showed both superthermal vibrational excitation and a nearly exponential dependence of the $N_{v=1}/N_{v=0}$ ratio on the inverse surface temperature. Schröter *et al.*[30] were able to fit the form of their data well using a theoretical reaction path model. Furthermore, calculations by Darling and Holloway[31] demonstrate more generally that Arrhenius-like behavior is to be expected in such a system even though the apparent activation energy for the process might not correspond to the gas-phase vibrational frequency of the desorbed species. As a result, the vibrational distribution can be superthermal yet appear to be thermally activated, i.e., follow an exponential dependence on $1/T_S$.

The theoretical model by Sheng and Zhang also predicts hyperthermal vibrational excitation with a nearly exponential dependence on $1/T_s$ for the specific case of H_2/Si(100)–(2×1).[27] In their model, H_2 desorption results from a bound–free transition between initially bound Si–H states and a final continuum state consisting of H_2 and the Si surface. The state-to-state desorption rate is given by a thermally averaged golden-rule expression. The hyperthermal vibrational population of H_2 results directly from the Franck–Condon integral for the bound-continuum transition, where the initial H–H separation on the surface (modeled as two H–Si species on the same silicon dimer) is much greater than for free H_2. At 780 K, they predict for H_2 desorbed from the monohydride a vibrational enhancement over the thermal prediction of 33.5, relatively close to the value of 21 ± 10 that we measure. At 600 and 700 K, they find *approximately the same enhancement* relative to a thermal prediction at those temperatures. The model of Sheng and Zhang contains several key approximations and simplifications that will affect the absolute values of the results, but it is expected that the observed trends in the calculated internal-state distributions as a function of surface temperature are less dependent on the details of the model.

Although we have data at only two surface temperatures, we find that from *both* the mono- and dihydride species, the enhancement in the $N_{v=1}/N_{v=0}$ population ratio over that of a thermal distribution at the respective surface temperatures is approximately a factor of 20. In the context of the models of Sheng and Zhang,[27] Darling and Holloway,[31] and Schröter *et al.*,[29] the difference in vibrational distribution between the dihydride species at 660 K and the monohydride at 780 K is accounted for by the difference in surface temperature. This suggests that the dynamics of desorption from the dihydride is similar to, if not the same as, that from the monohydride.

This interpretation of our result leads us to propose

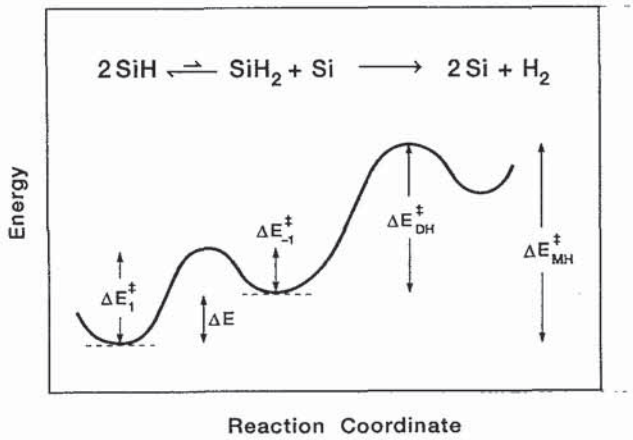

FIG. 3. A schematic diagram of the potential energy along the reaction coordinate for hydrogen desorption from silicon.

that *desorption from the monohydride state occurs through a dihydrade species*

$$2\mathrm{SiH} \rightleftarrows \mathrm{SiH_2} + \mathrm{Si}, \tag{1}$$

$$\mathrm{SiH_2} \rightarrow \mathrm{Si} + \mathrm{H_2}. \tag{2}$$

With this mechanism, the dynamics of H_2 desorption from the monohydride and dihydride states would be the same. Based upon our previous work on monohydride desorption from different silicon surfaces, we have proposed that the reaction occurs through a transition state localized near a single silicon atom, i.e., through a dihydride-like intermediate.[3] This model was also proposed by other authors.[5] The above scheme in which desorption occurs through an actual dihydride species is a natural extension of our model for desorption from the monohydride state.

Interestingly, it is known from previous kinetic measurements that the dihydride is actually unstable with respect to the monohydride in the presence of dangling bonds.[32] This just implies that there is an equilibrium between the mono- and dihydride that is strongly biased toward the monohyride when unoccupied silicon atoms are present. The interplay between this equilibrium and the proposed desorption can be seen in a schematic potential energy diagram shown in Fig. 3.

The reaction scheme illustrated in Fig. 3 agrees with the known kinetic relationships between the monohydride and dihydride for this system. There will be a pre-equilibrium between the mono- and dihydride characterized by a small activation barrier for the reverse of reaction (1). Therefore, the dihydride state will be present only in very low concentration if unoccupied silicon atoms are available. However, if no dangling bonds are available, the reverse of reaction (1) cannot occur and the dihydride species will be stable, as observed experimentally at high hydrogen coverages.[6–13] It can be shown easily that the rate of desorption is the same whether the monohydride desorbes directly or proceeds through the dihydride if an equilibrium between the two species exists. The activation barrier for desorption from the monohydride $\Delta E^{\ddagger}_{\mathrm{MH}}$ is then just the sum of $\Delta E + \Delta E^{\ddagger}_{\mathrm{DH}}$, where $\Delta E^{\ddagger}_{\mathrm{DH}}$ is the activation barrier for desorption from the dihydrice and ΔE is the energy difference between the monohydride and the less stable dihydride. Experimental values for the activation barriers are $\Delta E^{\ddagger}_{\mathrm{MH}} \sim 60$ kcal/mol and $\Delta E^{\ddagger}_{\mathrm{DH}} \approx 45$ kcal/mol.[14,25]

The monohydride-to-dihydride conversion mechanism proposed here for recombinative hydrogen desorption from Si(100) may also apply to Si(111). Both the rate constants and the dynamics for desorption on these two surfaces are the same.[3] Although the kinetic orders for hydrogen desorption from these surfaces do differ [first order on Si(100)–(2×1)[22–24] and second order on Si(111)–(7×7)[23,25,33]], these different reaction orders are not inconsistent with the common dihydride intermediate that we propose. We show this below by amending reactions (1) and (2) to distinguish between the monohydride-to-dihydride conversion steps on these two surfaces.

Si(100):

$$\mathrm{H{-}Si{-}Si{-}H} \rightleftarrows \mathrm{Si{-}SiH_2}, \tag{1a}$$

$$\mathrm{Si{-}SiH_2} \rightarrow \mathrm{Si{-}Si} + \mathrm{H_2}. \tag{2a}$$

Si(111):

$$\mathrm{SiH} + \mathrm{SiH} \rightleftarrows \mathrm{Si} + \mathrm{SiH_2}, \tag{1b}$$

$$\mathrm{SiH_2} \rightarrow \mathrm{Si} + \mathrm{H_2}. \tag{2b}$$

In both cases, desorption occurs from a dihydride structure which gives rise to the same dynamics. The different reaction orders result from the way in which the dihydride species is reached. On the Si(100) surface, we have assumed what is called the *prepairing mechanism*[34] and have written reaction (1a) as occurring from a single H–Si–Si–H entity; this reaction is therefore analogous to an isomerization and hence is first order as observed experimentally. On Si(111), the monohydride units are not correlated with one another and the necessity of random diffusion for two H atoms to meet leads to a second-order coverage dependence for reaction (1b), again consistent with experiment. It therefore seems highly probable that the monohydride-to-dihydride conversion proposed here for Si(100) is also operative on Si(111).

This model of desorption occurring via a dihydride species is especially appealing if one considers the reverse reaction of dissociative adsorption. Dissociative adsorption of H_2 on silicon surfaces is an extremely low probability process. Thus, when H_2 does stick, it might be only at very specific sites on the surface that have a preferred geometry for H_2 adsorption. A likely site for adsorption is a Si atom with two dangling bonds. This is just the reverse of reaction (2). Detailed balance in fact predicts that H_2 would desorb from these same minority sites.[35,36] Surface silicon atoms with two dangling bonds are expected to be present in very low concentration, and such "defect" atoms may be produced by thermal fluctuations through a disfavored equilibrium analogous to reaction (1).

In the above model, desorption from the dihydride occurs by association of both H atoms in a single dihydride unit [reaction (2)]. We note that a different dihydride de-

sorption scheme, in which H atoms in adjacent dihydride units recombine, has received more support in the literature[6,9,10,13,14]

$$2SiH_2 \rightarrow 2SiH + H_2. \quad (3)$$

In reaction (3), desorption leaves behind two monohydride units on the surface. Two experimental results have generally been cited as evidence for this model—the assignment by Gupta *et al.*[14] of second-order desorption for the dihydride species from porous Si, and the observation that desorption of the dihydride phase leaves behind a monohydride phase.[6] The latter observation is based on spectroscopic evidence that the SiH stretch intensity increases upon desorption of the SiH_2 species,[9,14] and also upon stoichiometric calculations using the relative ratios of H_2 desorbing from the mono- and dihydride.[13]

The support for reaction (3), is however, not conclusive. First, it has not been determined definitively whether first-[25] or second-order[14] kinetics describe the dihydride desorption. Furthermore, although much evidence points to the fact that a (2×1) monohydride-covered surface is formed by desorption of the dihydride, this does not necessarily mean that the monohydride phase is the *direct* product of the dihydride elimination reaction, as in reaction (3). The possibility exists that *surface rearrangement during or after desorption* could occur.

As discussed above, the dihydride species is unstable in the presence of empty sites (i.e., dangling bonds) undergoing a decomposition reaction

$$SiH_2 + Si \rightarrow 2SiH \quad (4)$$

that competes with desorption.[32] Reaction (4) is just the reverse reaction in equilibrium (1). It follows that were the primary desorption mechanism to occur "intramolecularly" as we propose in reaction (2), some of the dihydride species would undergo decomposition into monohydride species on adjacent, newly unoccupied silicon sites. The net result would be a monohydride-covered silicon surface, as observed. The stepwise combination of reactions (2) and (4) yields reaction (3), and we do not believe that the experimental data available at present can distinguish between the stepwise and direct processes. Thus, the present experimental data does not necessarily imply reaction (3), but could just as well be interpreted as being consistent with the model we have proposed.

In conclusion, we have interpreted the experimental observations in terms of a model in which desorption from the monohydride species occurs via a dihydride formed in a pre-equilibrium reaction. Furthermore, the desorption from the dihydride occurs via self-association of both H atoms on a single silicon atom. Although other interpretations of the present results are possible, the model we propose does explain all the data available at present.

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