

Desorption kinetics of hydrogen from the Si(111)7×7 surface

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The nature of the bonding and the basic electronic properties of hydrogen adsorbed on silicon surfaces have now become reasonably well understood.¹ At low coverages, hydrogen adsorbs in the monohydride Si-H state with a single hydrogen atom attached to one silicon atom via a silicon dangling bond. At higher hydrogen coverages various Si_xH_y species may also be present.¹ Despite this favorable situation with respect to most other chemisorbed species on semiconductor surfaces and despite the great technological importance of the interaction of hydrogen with silicon,² basic questions concerning the reaction kinetics remain unresolved. One of these fundamental issues concerns the reaction order for the recombinative desorption process of hydrogen from silicon surfaces.

Temperature programmed desorption (TPD) studies reveal recombinative desorption for the Si-H state with a peak of molecular H₂ appearing at about 800 K.³ However, the kinetic parameters derived from TPD have remained ambiguous for the past two decades. The data have generally been analyzed assuming second-order kinetics, in agreement with the expected behavior for an associative desorption reaction. But the observed down-shift of the desorption peak towards lower temperatures with increasing coverage, a sign of second-order kinetics, is found to be unusually small. Moreover, the inferred activation energies vary from 1.7 to 3.5 eV depending on hydrogen coverage and method of data analysis.³ Recently, isothermal desorption measurements using laser-induced thermal desorption (LITD) to monitor the hydrogen coverage have been performed.^{4,5} The data of Koehler *et al.* on Si(111)7×7 were consistent with the existing picture of second-order kinetics.⁴ With the same technique for the Si(100)2×1 surface, however, Sinniah *et al.*⁵ reached quite a different conclusion. Their data could be described by first-order behavior and a model was presented that explained this surprising finding through the existence of a band-like H* state. In this model, the rate-limiting step of desorption is the irreversible excitation of an adsorbed H atom into a delocalized band state. These H* atoms are assumed to react subsequently with localized H atoms and to undergo recombinative desorption. It was suggested that the LITD data on Si(111) of Ref. 4 were also compatible with first-order kinetics and that the model might be applicable to the desorption of hydrogen on other semiconductor surfaces.⁵ The recombinative desorption of hydrogen would thus involve a completely different mechanism from that usually present for metal surfaces.⁶

To elucidate the situation for the Si(111)7×7 surface, we have performed isothermal desorption measurements of hydrogen using surface second-harmonic generation (SHG) to monitor the hydrogen coverage.⁷ Our data extend the existing LITD data for this surface⁴ into the low coverage regime over a wide range of desorption temperatures. The high sensitivity of the SHG technique to adsorbed hydrogen permits a quantitative determination of hydrogen coverage down to 0.01 monolayer. Within the accuracy of our measurements one can easily discriminate between the predictions for different desorption kinetics. We show that the observed behavior is compatible neither with a simple first- nor second-order reaction and discuss several possible explanations for the apparent intermediate reaction order. We suggest a model that describes the desorption process in terms of conventional thermally activated recombination, but which takes into account the availability of different hydrogen adsorption sites. This model is capable of explaining the desorption kinetics of both the present work and LITD⁴ data for H/Si(111)7×7 in a consistent way.

The experiments were conducted using an ultrahigh vacuum system (base pressure below 2×10^{-10} mbar) equipped with capabilities for Auger electron spectroscopy, low-energy electron diffraction (LEED), and quadrupole mass spectrometry. The silicon samples, lightly doped with phosphorous (10 Ω cm) and cut within 1/4° of the (111) plane, were mounted on a nitrogen-cooled holder. Resistive heating was employed; the temperature was determined (with an absolute error ≤ 10 K) by means of a thermocouple bonded to the back of the sample with ceramic cement. Clean, well-ordered Si(111)7×7 surfaces were prepared by removing the native oxide from the sample at a temperature of 1300 K, followed by a slow cooling cycle. For the SHG measurements,⁸ we employed normally incident 1064 nm radiation from a Q-switched Nd:YAG laser, operating with a pulse duration of 10 ns and a repetition rate of 20 Hz. The fluence of the probe laser was kept below 0.2 J/cm². Under these conditions, the laser irradiation did not measurably affect the desorption process, as was verified by checking the results as reduced laser fluence.

In order to adsorb hydrogen on the Si(111)7×7 sample, atomic hydrogen was produced from an ambient of H₂ by a hot filament. The sample was held at a temperature of 620 K during the exposure. Under these conditions, it was found that just the Si-H monohydride species was formed, as evidenced by the presence of only the 800 K (β_1) TPD

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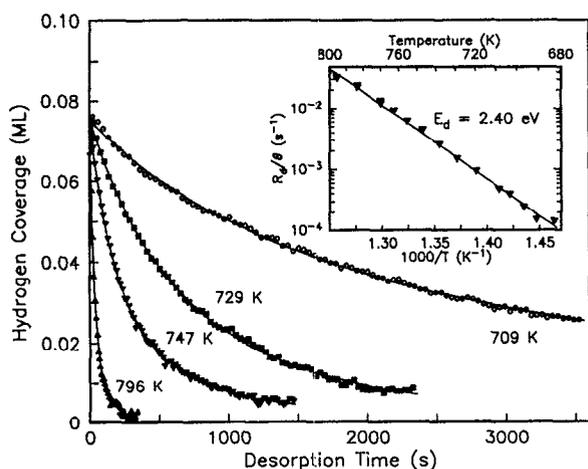


FIG. 1. Isothermal desorption of H_2 from the monohydride Si-H state on the Si(111) 7×7 surface. Symbols indicate H coverages obtained from measured SH signals at various surface temperatures; the solid lines are best fits using Eq. (1) and m between 1 and 2 (see text). The inset shows an Arrhenius plot for these and other data at 0.08 ML coverage.

peak. The calibration of hydrogen surface coverage was established by means of TPD spectra taken at selected exposures up to saturation coverage. Previous absolute calibrations have shown that the Si-H saturation coverage corresponds roughly to the number of silicon atoms in the topmost layer of the unreconstructed Si(111) surface ($0.8\times 10^{15} \text{ cm}^{-2}$).^{9,10} In the following, this coverage is referred to as one monolayer (ML). For purposes of calibration, the SH response was measured as a function of H coverage at surface temperatures slightly below the monohydride desorption temperature. The SH signal was found to be very sensitive to small coverages of hydrogen. The SH intensity, for example, decreases by a factor of ~ 100 as the H coverage rises to $\theta = 0.3$ ML, and H coverages well below 0.01 ML can be detected. In the region of $\theta < 0.15$ ML relevant for the present work, the SH field is found to vary linearly with coverage. This permits a simple and direct calibration of H coverage from observed SH signals.

A set of isothermal desorption measurements for various surface temperatures is shown in Fig. 1. The initial hydrogen coverage is 0.075 ML, except for the results for $T = 796$ K where a small amount of hydrogen desorbed while the sample was being heated from 620 K. Similar data were also obtained for an initial coverage of 0.14 ML. In these studies, the SH calibration for the clean Si surface was determined both before H adsorption and after a brief anneal at 1000 K following the measurements.

In order to derive the kinetic parameters, we have fitted the data to different theoretical curves using the Polanyi-Wigner equation for the desorption rate:¹¹

$$R_d = -\frac{d\theta}{dt} = k_m \theta^m = k_m^0 \theta^m \exp(-E_d/k_B T). \quad (1)$$

In the simplest analysis the desorption order m , the pre-exponential factor k_m^0 , and the activation energy E_d are

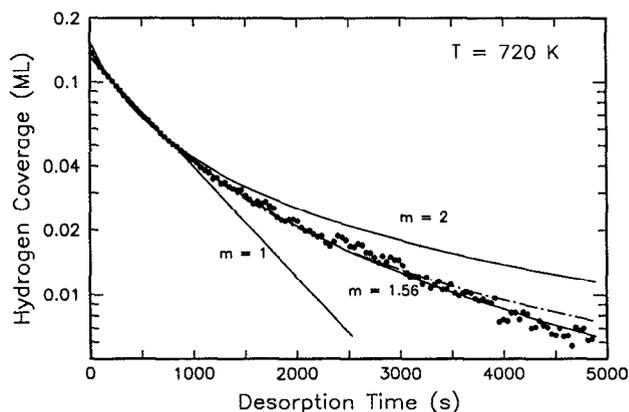


FIG. 2. Semilogarithmic plot of isothermal desorption of H_2 at a surface temperature of 720 K and an initial coverage of 0.14 ML. The results are compared with best fits to simple first- and second-order kinetics and to an effective kinetic order of $m = 1.56$. The dashed line is the prediction of the model for desorption discussed in the text.

taken to be independent of the coverage θ . For a constant temperature T , this leads to an exponential decay of θ as a function of time, $\theta(t) = \theta_0 \exp(-k_1 t)$, for $m = 1$; and to $\theta(t) = \theta_0 (1 + k_2 \theta_0 t)^{-1}$ for $m = 2$.

An example of such an analysis is given in Fig. 2. The semilogarithmic plot shows isothermal desorption data starting with a hydrogen coverage of 0.14 ML. Analytic forms for $\theta(t)$ for $m = 1$ and $m = 2$ have been fitted to the desorption behavior at early times. As is clearly demonstrated in Fig. 2, the data can be described neither by first nor by second-order kinetics assuming coverage independent parameters k_m^0 and E_d . It should also be noted that this conclusion does not require examination of the entire coverage range shown in the figure. With the available signal-to-noise of the data, it is possible to discriminate between the different analytic forms of $\theta(t)$ over a change in coverage of roughly a factor of 3. The results of Fig. 2 and of all other data taken for temperatures between 680 and 800 K show that $\theta(t)$ decreases significantly more slowly than expected for exponential decay ($m = 1$), but significantly more rapidly than required for simple second-order kinetics.

For further analysis of these data we could introduce coverage dependent parameters $E_d(\theta)$ and $k_m^0(\theta)$ and then fit the data using Eq. (1) for either $m = 1$ or $m = 2$. Alternatively, we can treat m as an adjustable parameter, which, for a given desorption temperature, is chosen to account approximately for the coverage dependence of the desorption rate R_d . Although a fractional m has no direct microscopic meaning it permits us to describe the measured quantity R_d with a minimum number of arbitrary parameters and once the θ dependence of R_d has been determined, it can then be interpreted in terms of changes in the kinetic parameters k_m and/or E_d . For the example shown in Fig. 2, the best fit is achieved with a value of $m = 1.56$. This result, displayed as a solid line in the figure, matches the measured $\theta(t)$ to experimental accuracy. We have analyzed all of our data using an adjustable m and

find values in the range between 1.4 to 1.7. No systematic trend in m either with initial coverage or desorption temperature could be established. The different m seem to reflect the accuracy with which we are able to determine this value for one set of data.

From this analysis we can obtain values for the desorption rates $R_d(\theta)$ in a model-independent fashion. The inset in Fig. 1 displays the inferred rates R_d/θ at a coverage of $\theta = 0.08$ ML in the form of an Arrhenius plot. The resulting activation energy is found to be $E_d = 2.40 \pm 0.1$ eV. For comparison with the literature we also give effective first- and second-order prefactors: $k_1^0(\theta = 0.08 \text{ ML}) = 6 \times 10^{13} \text{ s}^{-1}$ and $k_2^0(\theta = 0.08 \text{ ML}) = 0.8 \text{ cm}^2 \text{ s}^{-1}$. The activation energies for other coverages between 0.04 and 0.14 ML are the same within our accuracy of 0.1 eV. At lower coverages the experimental accuracy is poorer and somewhat larger changes may be present.

In agreement with the more recent literature, the activation energy of $E_d = 2.40 \pm 0.1$ eV is considerably higher than the results of the earlier TPD measurements at low coverage³ ($E_d \approx 1.8$ eV). Our value is somewhat lower than that obtained by Schulze and Henzler⁹ using TPD ($E_d = 2.54$ eV) and by Koehler *et al.*⁴ using LITD ($E_d = 2.65$ eV). In both studies simple second-order kinetics was assumed. On the other hand, our value is larger than what has been reported for data analyzed in terms of first-order kinetics. Schulze and Henzler deduced $E_d = 2.1$ eV under this assumption, similar to what Greenlief *et al.*¹² find from secondary ion mass spectrometry both for Si(111) and Si(100) surfaces and to the value that Sinniah *et al.*⁵ determined by LITD for Si(100) ($E_d = 2.05$ eV). This situation probably arises from the assumption of a simplified coverage dependence of the desorption rate in the previous studies [$R_d(\theta) = k_1\theta$, or $R_d(\theta) = k_2\theta^2$]. Our analysis, on the other hand, is able to determine R_d at a given θ quite precisely. The inferred activation energy should therefore be more accurate for the coverages that we have investigated. Finally, it is worth noting that our measured activation energy and second-order prefactors are similar to those predicted by Raff *et al.*¹³ with Monte Carlo techniques ($E_d = 2.41$ eV, $k_2^0 = 0.2 \text{ cm}^2 \text{ s}^{-1}$), although this agreement may be accidental since the calculations did not consider the 7×7 reconstruction of the Si(111) surface.

The desorption rate determined in our isothermal measurements deviates appreciably from the second-order behavior expected for a simple associative desorption reaction. For reasons that will be given below, we propose that the observed coverage dependence results from the existence of different sites for hydrogen adsorption on the reconstructed Si(111) 7×7 surface. To account for the observed kinetic behavior, we have developed an elementary model of a conventional recombinative desorption process occurring on a surface with two distinct adsorption sites. Limiting cases of such a model have been mentioned previously in the literature in conjunction with desorption from metal surfaces.¹¹ Let us denote the two types of binding sites as A and B , which might correspond to different

sites on the ideal Si(111) 7×7 surface or, possibly, to defect or step sites. Now, for a moment, suppose that at some temperature the hydrogen atoms in the A sites (H^A) have a finite hopping rate, but those in the B sites (H^B) are trapped. Suppose further that desorption occurs only by recombination at the B sites. If the reaction $H^A + H^B \rightarrow H_2^{\text{des}}$ is followed by a conversion $H^A \rightarrow H^B$ (as would happen for B sites with higher binding energy), then the concentration H^B would stay constant until all of the H^A species are depleted. Consequently the desorption reaction would appear to be approximately first order up to this point and would then stop. Upon raising the temperature, the H^B would become mobile and desorption would resume with second-order behavior. In a more realistic case, the surface mobilities and recombination rates of hydrogen atoms at the two sites may be similar, leading to more complex behavior. The observed reaction order m may then lie between 1 and 2 over a wide range of adsorbate coverage.

To show that these concepts can indeed describe the experimental results with reasonable parameters, we outline a specific model calculation of the desorption process, details of which will be published elsewhere.¹⁴ In the calculation, each of the two adsorption sites is characterized by its binding energy, density of states, and residence time for the monohydride species. The net flux of hydrogen atoms leaving the A and B sites can be calculated from statistical mechanics as a function of the total adsorbate coverage. The desorption rate is found by considering recombination occurring at both sites, with the rate at each site taken as proportional to the incident flux of diffusing hydrogen atoms and an appropriate reaction probability for recombinative desorption. For definiteness, we have neglected phase-space factors in describing the hopping of hydrogen atoms from the A and B sites. At a given surface temperature, the variation of the desorption rate with adsorbate coverage is then determined by three parameters: the ratio of residence times for hydrogen atoms trapped in each site (τ_B/τ_A), the ratio of recombination probabilities at each site (p_B/p_A), and the fraction of A and B sites on the surface (N_B/N_A). Figure 2 illustrates that this simple model can reproduce the observed intermediate-order desorption kinetics. The parameters used in this fit are $\tau_B/\tau_A = 13$ ($E_B - E_A \approx -0.15$ eV), $p_B/p_A = 23$, and $N_B/N_A = 0.06$. Thus only small differences in the binding energies for the two sites and a modest propensity for recombination at the B sites are required to explain the experimental data. The latter could arise either through a lowered barrier for the recombinative desorption process or through more favorable phase-space factors. Although various parameters are compatible with the current measurements, reasonably small values for τ_B/τ_A and p_B/p_A are achieved only if the available number of B sites is in the order of 5–10% of a monolayer. In this instance, our model predicts a θ dependence of the desorption rate close to θ^2 in the high θ limit, a behavior consistent with the LITD results of Koehler *et al.*⁴

These predictions of the model certainly do not constitute a proof of our explanation. Since many unknown factors enter the desorption process, it is generally difficult

to distinguish between different models. Other possible factors contributing to the observed intermediate kinetic order could include a decrease of the prefactor $k_2^0(\theta)$ with θ , caused, e.g., by changes in the surface reconstruction induced by hydrogen adsorption.¹⁵ Alternatively, a relatively small increase in the activation energy for desorption $E_d(\theta)$ could also account for the observed behavior. This might arise from an attractive (substrate-mediated) interaction of the adsorbed hydrogen atoms. In this instance, the possibility of island formation would also need to be considered. An appropriately modified model along the lines suggested by Sinniah *et al.*⁵ for H/Si(100) could also give rise to the required intermediate kinetic order.

Although it is difficult to preclude a particular model from the available desorption data, there are several independent arguments that suggest the importance of different surface sites in the desorption process. First, it is clear that on the Si(111)7×7 surface there are indeed different adsorption sites for the monohydride species, as has been demonstrated by infrared spectroscopy.¹⁶ Also several recent experiments relying on scanning tunneling microscopy and photoelectron spectroscopy have provided evidence that the different dangling bonds of the Si(111)7×7 surface¹⁷ show differing reactivities for various adsorbates.¹⁸ It is possible, for example, that H atoms adsorbed on the adatoms of the 7×7 surface are more mobile than those bound to rest atoms, but that the desorption occurs predominantly at the rest atoms. This scheme would be roughly compatible with the parameters chosen for the fit of our model discussed above. Lastly, in related studies of H/Si(111)7×7 we have been able to determine the surface diffusivity of the adsorbed hydrogen.¹⁴ The measurements yield an activation energy for diffusion that is significantly lower than that for desorption and a pre-exponential factor of the same order of magnitude as is usually found for classical hydrogen diffusion on metal surfaces. These results strongly favor a conventional diffusion mechanism associated with thermally activated hopping from site to site.

In conclusion, we have examined the process of recombinative thermal desorption of the Si-H monohydride species adsorbed on Si(111)7×7 surfaces. Isothermal measurements obtained for coverages below 0.2 ML show unambiguously that the desorption rate departs significantly from the second-order kinetic behavior usually expected for a simple recombinative desorption process. The data also fail to conform to the predictions of simple first-

order kinetics recently reported for Si(100) surfaces. It is found that the results for coverages below 0.2 ML over a range of temperatures of 680 K < T < 800 K can all be adequately characterized by an intermediate reaction order of $m = 1.5 \pm 0.2$. An activation energy for desorption of 2.40 ± 0.1 eV is observed. At a coverage of ≈ 0.1 ML, the effective prefactors for first- and second-order kinetics are $6 \times 10^{13} \text{ s}^{-1}$ and $0.8 \text{ cm}^2 \text{ s}^{-1}$, respectively. The observed kinetic behavior can be explained using a simple model in which two sites with different binding energies and recombination rates are considered.

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