Hydrogen Adsorption on and Desorption from Si: Considerations on the Applicability of Detailed Balance

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The translational energy of D_2 desorbed from Si(100) and Si(111) surfaces was measured and found roughly equal to the thermal expectation at the surface temperature T_s. Combining these results with previously measured internal state distributions, the total energy of the desorbed molecules is approximately equal to the equilibrium expectation at T_s. Thus adsorption experiments, which suggest a large energetic barrier, are at variance with desorption experiments, which exhibit a trivial adsorption barrier, and the applicability of detailed balance for this system needs to be reexamined.

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Hydrogen on silicon is the most in-depth studied of all adsorbate-on-semiconductor systems. Nevertheless, perhaps the most simple and classic of all surface science techniques, temperature programmed desorption, provoked a wave of controversy and raised questions that have required the most modern of techniques to elucidate their answers.

Sinniah *et al.* [1,2] demonstrated that H_2 desorption from Si(100) follows first-order kinetics. Confirmation of this result [3,4] combined with the observation of second-order H_2 desorption kinetics from Si(111) [3,5] and the complete description of the coverage dependence of the desorption orders [4,5] required a fundamental rethinking of the mechanism of H_2 desorption from Si surfaces. Wise *et al.* [3] proposed that pairing of H atoms on the dimers inherent to the Si(100)-(2×1) structure lies at the root of this phenomenon. This proposition is supported by other experimental [3,5,6] and theoretical [7,8] work. Finally Kolasinski, Shane, and Zare, using state-specific detection of hydrogen desorbed from Si(100) [9,10] and Si(111) [11] surfaces, demonstrated that the desorbing molecules pass through equivalent transition states on both surfaces. Thus, energetic and structural factors, namely, those leading to pairing on Si(100) and the lack of pairing on Si(111), are responsible for the kinetic differences while the dynamics of molecular formation and desorption are the same for both surfaces.

We have performed time-of-flight (TOF) measurements for D_2 desorbed from Si(100) and Si(111) surfaces. Combining these results with the internal state distributions of Kolasinski, Shane, and Zare [9,11], we are able to calculate the energy content of hydrogen thermally desorbed from Si. Hence, by invoking energy conservation and the principle of detailed balance [12,13], we are able to calculate the height of the barrier of adsorption. We conclude that the desorbing molecules do not possess an excess of energy compared to the equilibrium expectation at T_s. Thus, along the desorption trajectory, the desorbing molecules never experience a barrier with an energy significantly in excess of the zero of energy associated with the free molecule surface system. In other words, the desorbing molecules do not show any sign of having traversed a barrier that can be associated with a barrier to adsorption.

Experiments were performed in an UHV chamber with a base pressure of $< 2\times10^{-10}$ mbar. Details of this apparatus are described elsewhere [14]. Si(100) (As doped, 0.005 Ω cm, $< 0.5°$ miscut) and Si(111) (B doped, 8–10 Ω cm, $< 0.5°$ miscut) crystals were prepared as described previously [9] and yielded sharp low energy electron diffraction patterns of the appropriate symmetry. One Si(111) and two different Si(100) crystals were probed. D_2 dosing was accomplished by backfilling the chamber to 2×10^{-6} mbar while heating a W filament to approximately 1900 K. The W filament was thoroughly outgassed and the inner walls of the chamber were l-N_2 cooled prior to dosing in order to avoid contamination of the crystal. The crystal temperature during exposure was ≈ 400 K to avoid etching. In experiments involving the monohydride alone, the crystal was first annealed to desorb the dihydride. The crystal temperature was held at 600 K idle temperature during experiments. All experiments began at saturation coverage for the appropriate phase.

TOF spectra were measured by application of laser induced thermal desorption. A KrF excimer laser (248 nm, 5 Hz repetition rate, 17 ns FWHM pulses) produced the temperature jump required for desorption. Fluences of 140–350 mJ cm^{-2} were utilized, which led to calculated peak surface temperatures of 920–1520 K using the appropriate optical constants for Si at 248 nm and suitable temporal characteristics for the excimer laser pulse [15]. No mass 4 signal was observed for laser powers which did not heat the crystal sufficiently above the desorption temperature of D_2 ($T_{des} \approx 780$ K). Flight lengths of 25–75 mm were employed and TOF spectra were corrected for ion flight times within the quadrupole mass spectrometer (Balzers QMG 311) used for detection. A typical TOF spectrum is depicted in Fig. 1. To extract a flux-weighted mean translational energy $\langle E_{trans} \rangle$, we fitted a Maxwell-Boltzmann distribution to the TOF traces [14]. In ob-

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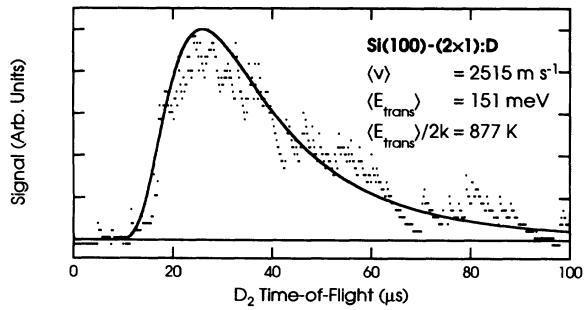

FIG. 1. TOF spectrum for D_2 thermally desorbed from the monohydride phase on Si(100)-(2×1) with $T_{max}=920$ K. The dots represent the raw data (averaged over 256 laser shots) while the solid curve represents a fit by a Maxwell-Boltzmann distribution.

taining a spectrum, 16–256 laser shots were averaged. Typically, a series of 20–40 spectra measured from 4 to 6 spots were collected for each exposure of the crystal.

The $\langle E_{trans}\rangle$ and T_{max} values are collected in Table I. T_{max} is the maximum calculated T_s induced by the laser irradiation. We see that within error bars $\langle E_{trans}\rangle/2k = T_{max}$ for monohydride-covered Si(100)-(2×1) and Si(111)-(7×7) as well as for the mixed dihydride- and monohydride-covered Si(100) surface. We note that the greatest desorption flux occurs at temperatures close to T_{max}. We conclude that D_2 desorbs with a translational energy corresponding to a temperature equal to T_s regardless of the surface or adsorbate structure. The equivalence of the $\langle E_{trans}\rangle$ values in all three cases is consistent with quantum-state-resolved measurements [9–11] in which a similar equivalence was found. Though not yet thoroughly examined, we have observed a lack of coverage dependence in the translational energy.

The measurement of the total energy of desorbed molecules represents a method of deriving the magnitude of the adsorption barrier. The energy content of an ensemble of desorbed molecules is derived from two contributions. The first contribution arises from the heat bath. For a system with a sticking coefficient this contribution imparts an equilibrium energy content to the ensemble with a temperature defined by the surface temperature. This quantity we denote $E_{eq}(T_s)$. For a system with a sticking coefficient less than unity which does not exhibit activated adsorption, dynamical corrections, i.e., those leading to rotational and/or translational cooling in desorption, can result in molecules desorbing with an energy smaller $E_{eq}(T_s)$. The second contribution to the desorbate energy arises if there is an activation barrier to adsorption. This barrier must also be crossed in desorption if the same path along the potential energy hypersurface is followed in the two reactions. A light molecule such as D_2 exchanges virtually no energy with the surface as it comes down off of this barrier; therefore, the energy from overcoming this barrier, E_{eff}^{ads}, remains in the

TABLE I. Observed values of the mean translational energy, $\langle E_{trans}\rangle/2k$, for D_2 desorbed from Si surfaces.

Desorption conditions	$\langle E_{trans}\rangle/2k$ (K)
Si(100)-(2×1):D, $T_{max}=920$ K	960 ± 200
Si(100):2D, $T_{max}=920$ K	990 ± 180
Si(111)-(7×7):D, $T_{max}=1520$ K	1300 ± 440

desorbed molecules until they are detected in the gas phase. Should there be a distribution of barrier heights as is expected, some averaging over these will occur. In this case an effective barrier height is obtained. Thus for a system which exhibits activated adsorption, the flux of desorbed molecules has an energy content, E_{flux}, given by $E_{flux}=E_{eq}(T_s)+E_{eff}^{ads}$. The energy of the desorbed molecules is given by $E_{flux}=2kT_{trans}+kT_{rot}+kT_{vib}$ and the equilibrium contribution is given by $E_{eq}(T_s)=4kT_s$. This yields

$$E_{eff}^{ads}/k = 2T_{trans}+T_{rot}+T_{vib}-4T_s \quad (1)$$

for the height of the activation barrier to adsorption. Within $\approx 5\%$, which accounts for the minimal loss of energy in the exit channel, this equality should hold as long as the barrier is in the molecular coordinates.

Kolasinski, Shane, and Zare [9] have reported $T_{rot}=330\pm50$ K and $T_{vib}=1700\pm330$ K for D_2 desorption from monohydride-covered Si(100) at $T_s=780$ K. Hence, we have to extrapolate $\langle E_{trans}\rangle/2k$ to this T_s. Within error bars we observe $\langle E_{trans}\rangle/2k=T_s$ at the two values of T_s probed experimentally. However, the exact nature of the scaling cannot be clearly established. Hence, in order to be on the safe side, we assume that $\langle E_{trans}\rangle/2k$ would have at $T_s=780$ K the same value as observed experimentally at higher T_s. Substituting these values into Eq. (1), we obtain $E_a^{ads}=7\pm8$ kJ mol^{-1} (77 ± 80 meV) and $E_a^{ads}=12\pm12$ kJ mol^{-1} (130 ± 135 meV) for the Si(100) and the Si(111) faces, respectively. Note that we would have to measure a $\langle E_{trans}\rangle/2k$ of ca. 6500 K to obtain a 1 eV barrier. Therefore, small corrections to Eq. (1) and the exact dependence of $\langle E_{trans}\rangle$ on T_s are immaterial. Consequently, desorption experiments show no evidence for a substantial barrier to adsorption.

A simplistic model to calculate the magnitude of an adsorption barrier states that when a crystal is exposed to a gas with a thermal energy distribution, the fraction of molecules which stick is that fraction of the impinging distribution which has an energy greater than the barrier height. Thus to calculate the barrier height, one needs only to calculate the energy which corresponds to a Boltzmann factor equal to the sticking coefficient. The sticking coefficient [16] of H_2 on Si is $<10^{-8}$; thus within this model, we must solve $\exp(-E_{eff}^{ads}/kT) < 10^{-8}$. This yields $E_{eff}^{ads} > 46$ kJ mol^{-1} (0.48 eV).

An accurate method for determining the adsorption barrier height is to measure directly the sticking coeffi-

cient as a function of molecular energy. Ho and coworkers [17] attempted this; however, they observed no sticking even at the highest available energies. They concluded that the adsorption barrier must be 100–200 kJ mol^{-1} (1–2 eV). Recent theoretical work yields adsorption barriers of 1.2 (Ref. [18]) and 1.15 eV (Ref. [19]). These values clearly stand in contradiction to the results reported herein. We are thus left with the task of trying to explain the discrepancies between the reported values.

A model in which defects, which present no adsorption barrier, mediate ad- and/or desorption can be ruled out. Should adsorption take place only on very special defects, these would have to occupy about 10^{-8} of all available sites in order to explain the low sticking coefficient. Equivalent sites in equivalent numbers would have to be present on Si(100) and Si(111) surfaces in order to explain the low sticking coefficient and identical internal state distributions on both surfaces. However, it is known [20] that Si(100) surfaces appear intrinsically to have many more defects than Si(111) surfaces. Furthermore, if a defect-mediated process is active on both Si(100) and Si(111) surfaces, the desorption kinetics should be the same because they would be determined by the hunt for these sites on both surfaces. Such a model contradicts the known kinetics vs coverage behavior [4,5] on these surfaces.

Three possible explanations may account for the inconsistency between adsorption and desorption experiments. First, recent calculations from the Brenig group [21] have shown that translationally cool molecules may be observed in desorption even in the presence of an activation barrier to adsorption if desorption is tunneling dominated. Were tunneling to dominate desorption, one would expect difference in the behavior of H_2, HD, and D_2. In contrast, the internal state distributions of H_2, HD, and D_2 are equivalent [9] and the rates of desorption for H_2 and D_2 exhibit no anomalous isotope effects [2]. While we cannot as yet exclude this model completely, there is no experimental evidence aside from the roughly thermal translational distributions measured here to support it.

A second possibility is that adsorption and desorption do not follow the same potential energy hypersurface. In such a case, adsorption and desorption are not directly related by microscopic reversibility and the principle of detailed balance. This explanation, however, goes against chemical intuition and many years of cumulative experience which suggest that adsorption and desorption can be directly related by the principle of detailed balance [12,13]; therefore, such a line of argumentation should not be made without good cause.

The third explanation is that the barrier to adsorption is not solely energetic in nature but also entropic. In other words, only a very small portion of configuration space contains favorable adsorption trajectories while all others experience a high (1–2 eV) barrier. Calculations on H/metal systems show that molecular orientation [22–24] and lattice impact parameter [24] play a role in determining the effective barrier height. These effects may be accentuated in the H/Si system because of the requirement for a highly symmetric transition state in desorption and because of the highly localized interactions in the H/Si system [9–11]. While molecular orientation and impact site play a role in determining the sticking coefficient, it is difficult to imagine that they alone can account for a sticking coefficient of $< 10^{-8}$, especially since almost all configurations encounter a barrier of up to 2 eV, yet a fraction of the configurations encounter no barrier whatsoever.

The final and decisive contribution to the restricted configuration space model arises from surface atom motion. Motion (reconstruction) of Si atoms is inherent to the adsorption process of hydrogen on Si [25–32]. The barrier to adsorption is, as shown by Wu, Ionova, and Carter [18], sensitive to the surface atom geometry. In adsorption, the Si atoms may have to move into approximately the final state geometry for an incident H_2 to complete successfully a dissociative trajectory. On the time scale of the interaction (the H_2-surface collision time), Si atoms rarely attain this configuration because thermal vibrations of the clean surface rarely present the proper geometry and Si atoms do not have sufficient time to react under the influence of the impinging H_2 molecule. Furthermore, in an impulsive collision an incident H_2 cannot force the Si atoms to assume the proper positions because the large mass mismatch prohibits an efficient transfer of energy to the lattice. As a consequence, impinging H_2 experiences only the large barrier configurations and adsorption experiments yield results indicative of such a large barrier.

In desorption, the system starts out with a relaxed lattice which should also have a lower Debye temperature than the clean surface. Calculations show that the vibrational amplitude of the Si(100) dimer atoms is sensitive to the strength of the coupling in the dimer bond [33]. Because adsorption destroys the π-bond or Peierls-distortion-induced stabilization of the clean dimer, H adsorption leads to greater thermal vibrational amplitudes of the dimer atoms. On the Si(111) surface, adsorbed H atoms weaken the bonding of Si adatoms to the underlying surface, as evinced by the greater mobility of these atoms [25,26], which also leads to greater vibrational freedom. Other evidence for considerable lattice relaxations induced by H adsorption has been observed both experimentally [27–32] and theoretically [8,34,35]. Additionally, Alerhand and Mele [36] demonstrated an intrinsic coupling between phonons and electronic structure on Si surfaces. Such coupling provides a mechanism for producing an activation barrier that is not only sensitive to the surface geometry but also to surface vibrational excitations. By starting with a relaxed and softer lattice, a different and wider range of surface atom configurations is presented to the H atoms which attempt to recombine than can be presented to an impinging H_2 molecule. As a

result, the recombining atoms experience a lower barrier as they desorb from the surface than they would have seen in adsorption. Even though these low barrier configurations may be improbable, simple argumentation based on the Arrhenius behavior of the desorption reaction shows that the smallest barrier process will make the greatest contribution to the desorption rate.

As a consequence of a surface geometry sensitive barrier, the processes of adsorption and desorption appear to follow two different potential energy hypersurfaces, rendering the usual application of detailed balance invalid. When examined more closely, however, we see that this apparent violation of detailed balance results from the high dimensionality of the adsorption/desorption process. The much different initial conditions of the two processes lead to different parts of the potential energy hypersurface playing decisive roles in the respective processes. That is, the great modification of the lattice properties due to hydrogen adsorption enables the system to gain access to parts of the potential energy hypersurface during the desorption event that are effectively closed channels during the adsorption event. This is in stark contrast to the H/Cu system where trajectory studies have successfully modeled the adsorption/desorption process by considering desorption trajectories that started at a common transition state [37] or by performing calculations for adsorption alone [38]. Our results for the D_2/Si system demonstrate that higher dimensionality, specifically the inclusion of lattice degrees of freedom, is critical for a description of the adsorption/desorption phenomenon.

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