Cryogenic UHV-STM Study of Hydrogen and Deuterium Desorption from Si(100)

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A cryogenic UHV scanning tunneling microscope has been used to study the electron stimulated desorption of hydrogen and deuterium from Si(100) surfaces at 11 K. A strong isotope effect is observed, as seen previously at room temperature. Above $\sim$5 eV, the desorption yields for H and D are temperature independent, while in the tunneling regime, below 4 eV, H is a factor of $\sim$300 easier to desorb at 11 than at 300 K. This large temperature dependence is explained by a model that involves multiple vibrational excitation and takes into account the increase of the Si-H(D) vibrational lifetime at low temperature. [S0031-9007(97)05266-6]

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The ability to modify materials at the atomic and nanometer scales with the scanning tunneling microscope (STM) has been a fascinating development that is attracting strong interest. In this Letter, we focus on the STM-induced desorption of hydrogen from silicon, a system of significant scientific and technological importance. Hydrogen is not only a prototype absorbate system, but it is used extensively to chemically and electrically passivate surface and interface dangling bonds.

By varying the electron energy and current density of the STM tip-emitted electrons, it has been possible to desorb hydrogen from Si. The first such studies were performed on Si(111) [1,2], where desorption was found to occur at electron energies higher than $\sim$6 eV, and was attributed to the electronic excitation of the Si-H bond. More recent STM desorption experiments [3,4] on Si(100)-(2 $\times$ 1):H surfaces showed that, in addition to strong desorption above $\sim$6 eV, hydrogen can also be desorbed at much lower energies, in the tunneling regime. Desorption in the tunneling regime is a strong function of current and voltage [4] and is consistent with predictions of a multiple vibrational heating model proposed earlier [5]. Studies of deuterium desorption showed a very strong isotope effect [6].

Here, we present new results in which both hydrogen and deuterium desorption are studied at 11 K with a cryogenic UHV STM. Comparisons with the results of the prior 300 K studies [4,6] confirm the previously proposed desorption mechanisms and provide new insights into the dynamics of the processes involved. Specifically, no temperature dependence of the desorption yield or isotope effect is found in the higher energy electronic transition regime. In contrast, a very strong temperature effect is observed in the tunneling regime, where hydrogen is a factor of $\sim$300 easier to desorb at 11 than at 300 K. Furthermore, at 11 K, we are able to desorb deuterium in

the tunneling regime, a result we were unable to achieve at 300 K.

Hydrogen and deuterium desorption measurements were performed using a liquid-He-cooled UHV STM [7]. Highly doped *n*-type Si(100) samples (As-doped 0.005 Ω cm) were used in order to maintain good substrate conductivity at a low temperature. Passivated surfaces were prepared using standard UHV methods [3] and the STM desorption yields were determined using the threshold desorption counting method developed by Shen *et al.* [4]. This is illustrated in Fig. 1, which shows a series of sporadically depassivated lines patterned on the Si(100)-(2 $\times$ 1):H surface at 11 K. By analyzing numerous STM desorption images, we have obtained values for the desorption yield under different voltage and current conditions.
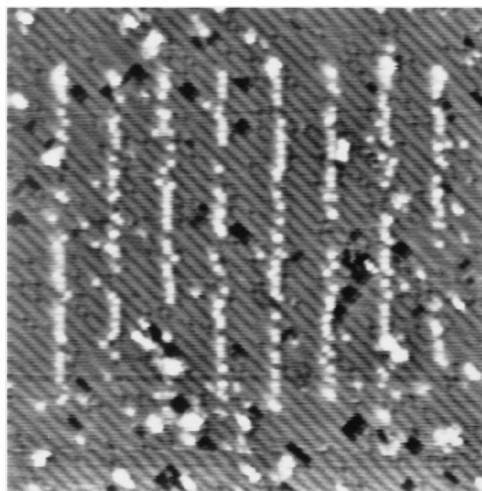

FIG. 1. A 400 Å $\times$ 400 Å image of a Si(100)-(2 $\times$ 1):H surface imaged at 11 K after threshold STM patterning of a series of parallel lines.

Figure 2 compares the desorption yield for hydrogen and deuterium at 11 K with the 300 K hydrogen desorption yield data of Shen *et al.* [4]. The H desorption yield shows a threshold at a sample bias (i.e., electron energy) of about 6 V. Moreover, both the threshold and the desorption yield itself show no significant dependence on temperature. The desorption threshold was ascribed to the onset of an electronic transition [4,6]. Electron energy loss spectra of the Si(100)-(2 × 1):H surface [8] show a hydrogen related electronic excitation with a peak at 8 eV and an onset at about 6 eV. Cluster model calculations [6] also find an Si-H derived excitation at the same energy. These calculations show that a $\sigma \rightarrow \sigma^*$ transition is involved resulting in a repulsive excited state. In our experiments, the electric field produced by the tip is estimated to be ≤ 0.5 V/Å, too weak to induce field desorption [9]. Finally, the fact that the yield is essentially constant at energies >7 eV (Fig. 2) eliminates desorption mechanisms involving resonant electron capture [10]. On the basis of these observations, we conclude that the desorption involves an electronic excitation. Given the high frequency of the Si-H oscillator, the excitation spectrum should be weakly dependent on temperature.

One would expect that electronic excitation of surface Si-H groups by the tip-emitted electrons would populate this unbound (repulsive) state and lead to direct desorption. The low desorption yield argues against this simple picture. Competing with H desorption is a quenching process involving the tunneling of the excited electron into conduction band states [11]. Molecular dynamics calculations [6] indicate that this quenching dominates the desorption process. The desorbed H atoms are those atoms that managed to acquire enough kinetic energy on the repulsive excited state potential energy curve to enable them to overcome the residual binding energy in the ground state after quenching. Since the excited state lifetime is not a strong function of the temperature, we should
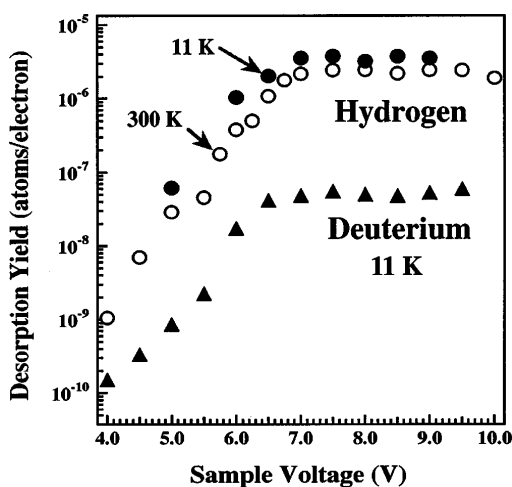
not expect a significant temperature dependence of the desorption yield. This is in agreement with the results shown in Fig. 2.

The desorption process also displays a large isotope effect. Substitution of hydrogen by deuterium leads to a D desorption yield at 300 K, which is about a factor of ~50 lower than that of H [6]. As Fig. 2 shows, the same ratio of 50 is also observed at 11 K. The magnitude of the isotope effect is unusually high. Kinetic isotope effects are usually <10. A number of different mechanisms can give rise to an isotope effect [12]. The simplest cause is the higher thermal activation barrier for deuterium due to its lower zero-point energy. However, this is ruled out by the observed independence of the desorption yield on temperature. Similarly, while an isotope effect can arise by H(D) tunneling through a barrier, the lack of temperature dependence of both the yield and the isotope effect negates such a mechanism. A different mechanism that involves the quenching of an excited state and can, in principle, lead to large isotope effects was first discussed by Menzel and Gomer [13]. In this mechanism, the isotope effect is due to the larger mass of deuterium and its influence on the extent of quenching. Both H and D feel the same repulsion moving on the excited state potential energy curve. However, D moves more slowly, and, as a result, it stays in the vicinity of the surface longer so that the corresponding excited state is more heavily quenched. Again, if the isotope effect is the result of an allowed electronic transition and no thermal activation is needed, no dependence on temperature should be expected, in agreement with our findings here. Finally, we note that the extremely short electronic lifetime (on the order of 10^{-15} s) [6] minimizes the temperature effect on the desorption yield that may arise from phonon-assisted energy transfer processes that tend to delocalize the excitation from the originally excited site to neighboring sites [14].

Excitation of the Si(100)-(2 × 1):H system by electrons with energies below those needed for electronic excitation can still lead to H desorption, albeit with a much reduced yield. The characteristics of the desorption process are, however, very different from those for excitation above the electronic threshold. As shown in Fig. 3, the desorption yield is now a strong function of the tunneling current, and, unlike the case of electronic excitation, there is a remarkably strong enhancement of the yield, ~300×, upon cooling from 300 to 11 K.

It has been argued [5] that, because of the large STM tunneling current densities and the long vibrational lifetime of the Si-H mode [15], inelastic tunneling can lead to multiple vibrational excitation and, thus, break the Si-H bond. A simple truncated harmonic oscillator model was used to describe the process. In this model, transitions between vibrational levels are induced by inelastic electron tunneling and by energy exchange with the substrate. The transition rate from level $|n\rangle$ to level $|n + 1\rangle$ is given by $R_{\mathrm{up}} = (n + 1)[f_{\mathrm{in}}(I/e) + w_{\mathrm{vib}}\exp(-\hbar\omega/kT_s)]$, while

FIG. 2. The desorption yield for hydrogen and deuterium at 11 K compared with the 300 K hydrogen desorption yield. The 300 K data are from Ref. [4].
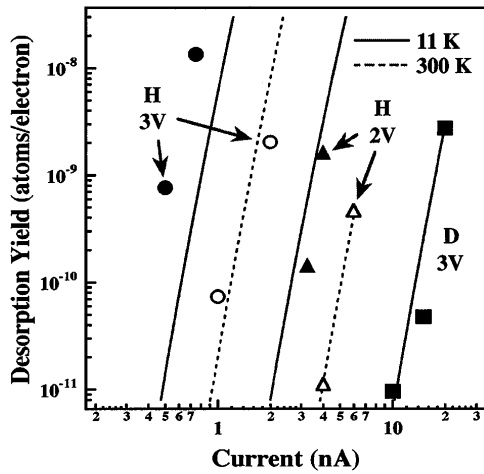
FIG. 3. Current dependence of the desorption yield for hydrogen at 11 and 300 K at 2 and 3 V, and deuterium at 11 K and 3 V. The lines are predictions based on the truncated harmonic oscillator model using the following values of inelastic fraction: $f_{in} = 7.6 \times 10^{-4}$ at 2 V and 2.8×10^{-3} at 3 V. For details on how these inelastic fractions were determined, see Ref. [9]. The 300 K data are from Ref. [4].

the downward transition from $|n\rangle \rightarrow |n - 1\rangle$ is given by $R_{down} = n[w_{vib} + f_{in}(I/e)]$, where f_{in} is the fraction of the electrons that tunnel inelastically (typically 10^{-3}–10^{-4}), I is the tunneling current, w_{vib} is the vibrational decay rate (inverse of vibrational lifetime τ_{vib}), $\hbar\omega$ is the vibrational energy, and T_s is the substrate temperature. Using these rates, one can write a set of master equations whose solution gives the populations of the different vibrational levels [5]. Competing with the local vibrational excitation process is vibrational energy transfer away from the originally excited site in the form of vibrational excitons or incoherent (so-called Foerster) energy transfer. From the study of the dispersion of the vibrational bands [16] of Si(111)-(1 × 1):H, it is known that coherent energy transfer is very efficient with the Si-H excitation delocalizing within 10^{-13} s. A similar behavior is expected for the monohydride of Si(100). Recently, it has been argued [14] that energy transfer in the STM is influenced by the local electric field produced by the tip. This field induces an energy shift of the vibrational excitation energy (Stark shift) of the species under it. When this shift is larger than the bandwidth of the vibrational excitation, the excitation is localized at the original site. First principles calculations of the Stark shifts [9,17] showed that, indeed, these shifts are large enough at our experimental conditions ($F \approx 0.5$ V/Å) to induce the localization of the exciton at the originally excited site. The efficiency of incoherent phonon-assisted energy transfer is also reduced but not eliminated. This process could lead to a temperature dependence of the desorption yield. Taking into account the above considerations, the desorption rate R_{des} can be written as

$$R_{des} = \lambda w_{vib} \frac{\Delta E}{\hbar\omega_F}$$
$$\times \left[\frac{(I/e)f_{in} + w_{vib}\exp(-\hbar\omega_F/kT_s)}{(I/e)f_{in} + w_{vib}} \right]^{\Delta E/\hbar\omega_F}. \quad (1)$$

In Eq. (1), λ accounts of the effects of energy transfer [18], and $\hbar\omega_F$ is the quantum of vibrational energy in the presence of the tip-induced electric field F. The solid and dashed lines shown in Fig. 3 are the predicted desorption yields based on Eq. (1). The observed good agreement with the experiment gives confidence in using the same model to account for the large increase, ~300×, of the yield upon cooling to 11 K. In Eq. (1), both λ, the phonon-assisted energy transfer rate, and w_{vib}, the energy decay rate, are functions of the temperature. Calculations of the energy transfer rate [18] show that, for an expected ~50 cm^{-1} Stark shift of the Si-H frequency, λ will change by less than a factor of 2 upon cooling. The main factor that controls the desorption rate is the vibrational energy decay rate w_{vib}. The stretching frequency of the Si-H mode is very high, ~2000 cm^{-1}, so the only way this excitation can decay is by a multiphonon process. As a rule, the preferred relaxation channel would involve the lowest possible number of vibrational quanta. It is, therefore, expected that the Si-H stretch would couple to the Si-H bending mode, which has a frequency of ~600 cm^{-1}. In the case of Si-H relaxation on Si(111), it was found that, indeed, the decay involves three quanta of the Si-H bending mode and a 200 cm^{-1} Si phonon [19]. An analogous situation should prevail in the monohydride of Si(100). The decay rate w_{vib} is given by

$$w_{vib} = 1/\tau_{vib} = w_D - w_U, \quad (2)$$

where w_D is then given by [20]

$$w_D = \frac{2\pi}{\hbar} G(q_1 \ldots q_4)(1 + \langle n_{q1}\rangle)(1 + \langle n_{q2}\rangle)$$
$$\times (1 + \langle n_{q3}\rangle)(1 + \langle n_{q4}\rangle)\delta(\omega_0 - \omega_{q1}\ldots - \omega_{q4}) \quad (3)$$

and w_U by

$$w_U = \frac{2\pi}{\hbar} G(q_1 \ldots q_4)\langle n_{q1}\rangle\langle n_{q2}\rangle\langle n_{q3}\rangle\langle n_{q4}\rangle$$
$$\times \delta(\omega_0 - \omega_{q1}\ldots - \omega_{q4}). \quad (4)$$

In Eqs. (3) and (4), $\langle n_{qi}\rangle = 1/[\exp(\hbar\omega_i/kT) - 1]$ is the Bose-Einstein factor, $\omega_{q1} = \omega_{q2} = \omega_{q3} = 600$ cm^{-1}, and $\omega_{q4} = 200$ cm^{-1}.

Equations (2)–(4) allow us to evaluate the temperature dependence of the vibrational lifetime. At room temperature, the measured lifetime shows some variation from sample to sample, a fact that is attributed to the presence of efficient energy transfer processes among surface sites and the presence of defects that can act as excitation sinks [15]. The best estimate of the intrinsic lifetime is 10 ns. This value is used to obtain the decay rate at other
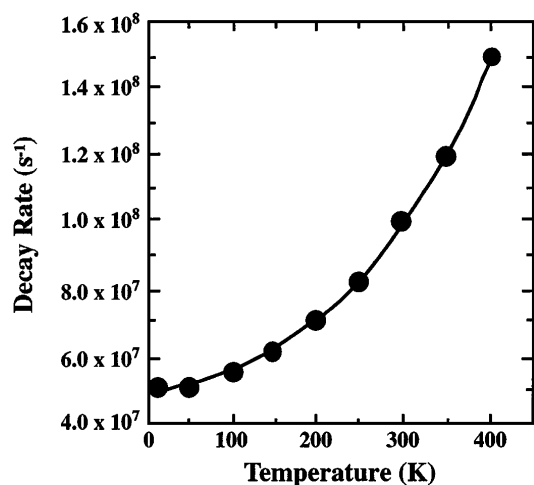
FIG. 4.   Calculated decay rate for the Si-H oscillator showing an exponential temperature dependence.

temperatures, and the results are shown in Fig. 4. We find that the decay rate decreases essentially exponentially (the solid line is an exponential fit) over this temperature range. Most importantly, w_{vib} is found to decrease by about a factor of 2 as the temperature decreases from 300 to 11 K. From Eq. (1), we find that this change in the decay rate should lead to a 300× increase in the desorption rate, in very good agreement with the experimental findings shown in Fig. 3.

Finally, we note that substituting D for H changes the nature and/or number of phonons involved in the vibrational relaxation, and this, in turn, affects the efficiency of the vibrational up-pumping process [6,21]. The frequencies of the Si-D modes are lower than those of Si-H by a factor of $\sqrt{2}$. Although the decay path of the Si-D vibration is not known, it is likely to involve only three phonons and this would lead to a shorter lifetime. Indeed, the Si-D lifetime at 300 K was measured and found to be 0.2 ns at 300 K [15]. As we saw above, due to the nonlinear character of the excitation process [Eq. (1)], a change in lifetime by only a factor of 2, as a result of cooling, can lead to a more than hundred times change in the H desorption yield. The much larger change in lifetime induced by deuteration should lead to a D yield many orders of magnitude lower than the H yield (already very low in the vibrational regime). Thus, the D yield at room temperature should be too low to be observable, as we find to be the case [22]. At 11 K, the Si-D lifetime should be increased because of the variation of the corresponding Bose-Einstein factors [Eqs. (2)–(4)] to the point that D desorption becomes detectable (Fig. 3). Comparison of the three V, H, and D yields shows that the isotope effect in the vibrational regime is much larger than the isotope effect in the electronic excitation regime.

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