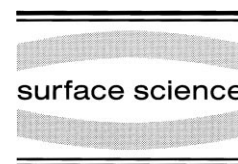




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Temperature suppression of STM-induced desorption of hydrogen on Si(100) surfaces

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Abstract

The temperature dependence of hydrogen (H) desorption from Si(100) H-terminated surfaces by a scanning tunneling microscope (STM) is reported for negative sample bias. It is found that the STM induced H desorption rate (R) decreases several orders of magnitude when the substrate temperature is increased from 300 to 610 K. This is most noticeable at a bias voltage of -7 V where R decreases by a factor of 200 for a temperature change of 80 K, whilst it only decreases by a factor of 3 of at -5 V upon the same temperature change. The experimental data can be explained by desorption due to vibrational heating by inelastic scattering via a hole resonance. This theory predicts a weak suppression of desorption with increasing temperature due to a decreasing vibrational lifetime, and a strong bias dependent suppression due to a temperature dependent lifetime of the hole resonance. © 1999 Elsevier Science B.V. All rights reserved.

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Desorption of hydrogen (H) from a H-terminated silicon (Si) surface has recently been studied actively [1–10], because of its potential applications to construct novel optical and electronic devices. For positive sample bias, Shen et al. [4] have shown that <4 V the STM induced H desorption is related to vibrational heating [11,12] by inelastic scattering of tunneling electrons with the Si–H $6\sigma^*$ resonance, and >4 V it is related to direct electronic excitation of the Si–H bond. At negative sample bias, the desorption

mechanism has recently been explained by the authors [10] to be due to inelastic scattering of tunneling holes with the Si–H 5σ hole resonance and quantitative agreement between experimental desorption data and first principles calculations was obtained.

The present paper focuses on the temperature (T) dependence of the STM induced H desorption rate (R) from Si(100)-H(2×1) surfaces in ultra high vacuum (UHV) at negative sample biases from -10 to -4 V and temperatures from 300 to 610 K. For a given sample bias (V_b) and tunnel current (I) we measure a decreasing R with increasing T . The effect is most pronounced at

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$V_b = -7$ V, where R decreases by a factor 200 for an increase in T of 80 K, whilst it only decreases by a factor of 3 at $V_b = -5$ V upon the same temperature change. Previous studies of the T dependence of R have been carried out for positive sample bias and at $T = 11$ K, where R was reported to increase by a factor of ~ 300 compared to room temperature [9]. The lower R with increasing T was explained by a decreasing vibrational life time of the Si–H stretch mode with increasing T [13,14].

In the present study the T dependence of R has been modelled using a first principles model [15] of inelastic scattering of tunneling holes with the Si–H 5σ hole resonance. Two temperature effects, which are based on the T dependence of the lifetime of vibrational excitations and electronic excitations, respectively, are included in the model. At $V_b = -5$ V, the T dependence of R is related to the lifetime of the vibrational excitation, which is similar to the result for positive V_b reported previously by Foley et al. [9]. At $V_b = -7$ V the T dependence from this effect is too weak to explain the experimental data. The strong T dependence of R in this case is mainly caused by the T dependence of the lifetime of the 5σ hole resonance, which gives rise to an additional strongly bias dependent temperature effect. The combination of a T dependent vibrational lifetime and a T dependent electronic lifetime accounts very well for the experimental data in the whole bias range from -10 to -4 V.

The experiments were performed at a base pressure of $\sim 7 \times 10^{-9}$ Pa using n-type Si(100) ($N_D = 1 \times 10^{18} \text{ cm}^{-3}$) samples and a JEOL JSTM-4000XV microscope with electrolytically sharpened tungsten (W) tips. Samples were heated using a direct current flowing between two contacts at each end of the samples, the STM tip being positioned in the middle of the two contacts. A change in V_b caused by the current flow was corrected for in the STM bias circuit, and the absolute value of V_b was verified by measuring the zero point in current–voltage curves. The Si(100)-H(2×1) surfaces were prepared by standard procedures [3]. The surfaces are constructed by an array of parallel ‘dimer rows’, where the dimer consists of two dimerized Si atoms each bonded to a single H atom. If one of the H atoms is

desorbed, a Si dangling bond appears and is observed as a bright spot in filled-state STM images. The desorption rate (R) of H atoms is determined by the following STM parameters: the scanning speed (s) of the STM tip, V_b , I and T . The experiments were carried out at negative V_b between -10 and -4 V and at T between 300 and 610 K. Increasing T above 610 K caused an excessively large thermal desorption of H atoms and the study is therefore limited to $T < 610$ K.

In order to establish the relationship between R , I , V_b and T , the surface was scanned by the STM tip at various conditions, and R could be determined from s and the number of desorbed H atoms identified from the STM images. Two different kinds of experimental methods were employed. In one method the STM tip raster scanned areas of $20 \text{ nm} \times 20 \text{ nm}$ on the Si(100)-H(2×1) surface using a fixed value of V_b , while I and s were adjusted to yield a suitable countable number of desorbed H-atoms (typically 100–200 atoms). This method was used to determine R as function of I for constant V_b . In another method, line scans with a fixed $s = 2 \text{ nm s}^{-1}$ were performed at various V_b , and I was adjusted to yield desorption of 50% of the H atoms along a line scan on the surface. This method was used to determine the relationship between V_b and I for constant R .

Fig. 1 shows a filled state STM image recorded at $T = 530$ K after desorption of H from the Si(100)-H(2×1) surface. The bright line running from the top right to the bottom left is a chain of Si dangling bonds created by scanning the tip along a line with $s = 2 \text{ nm s}^{-1}$, $V_b = -7.0$ V and $I = 8.0 \text{ nA}$. The width of the line is approximately equal to the width of one dimer row and the resolution is similar to that obtained for lithography at room temperature [10].

Fig. 2 shows R plotted as function of I for $V_b = -7$ V (Fig. 2a) and $V_b = -5$ V (Fig. 2b) and for temperatures $T = 300$ (\square), 380 (\times) and 450 K (\triangle). We have made least squares fits to the data of a power-law dependence of R upon I , $R = R_0 (I/I_{\text{des}})^\alpha$, where I_{des} is the tunnel current corresponding to $R_0 = 4 \text{ s}^{-1}$. At $V_b = -7$ V the least-squares fitted parameters are: $\alpha = 5.7 \pm 0.7$, 4.7 ± 0.5 and 4.6 ± 0.7 , and $I_{\text{des}} = 0.85$, 2.0 and 3.3 nA for $T = 300$, 380 and 450 K, respectively.

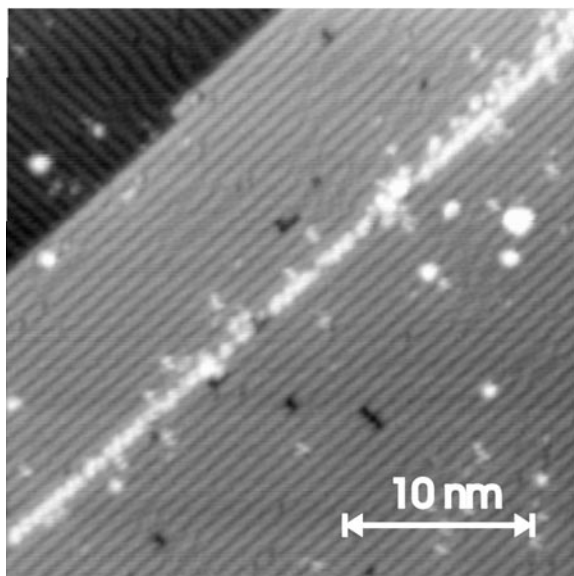


Fig. 1. Scanning tunneling micrograph of exposed silicon dangling bonds as a result of hydrogen (H) desorption on a H terminated Si(100)-(2 × 1) reconstructed surface of the n-type sample at a substrate temperature of 530 K and a line scan with a speed of 2 nm s⁻¹, a sample bias (V_b) of -7 V and a tunnel current (I) of 8.0 nA. The filled-state image was recorded at $V_b = -1.7$ V and $I = 0.2$ nA.

At $V_b = -5$ V, the corresponding parameters are: $\alpha = 6.3 \pm 1.3$, 4.6 ± 0.5 and 6.4 ± 0.9 , and $I_{\text{des}} = 4.5$, 4.2 and 6.4 nA. The data follow the power law very well at all temperatures and the slope is almost independent of T . The temperature effect is largest at -7 V; for example at $I = 2$ nA, R decreases from 700 to 3 s⁻¹ when T is increased from 300 to 380 K, while at -5 V and $I = 8$ nA, R only decreases from 120 to 40 s⁻¹ upon the same temperature change.

The relationship between I_{des} and V_b , corresponding to a fixed desorption rate of $R_0 = 4$ s⁻¹ or 50% desorption of H along a line scan with $s = 2$ nm s⁻¹ is depicted in Fig. 3 for T ranging from 300 to 610 K. At a given T and V_b , $R > 4$ s⁻¹ for values of $I > I_{\text{des}}$. At all T , the data show a minimum in I_{des} at $V_b = -7$ V, and therefore a maximal desorption yield at this voltage.

Previously we have shown that the room temperature data can be explained by vibrational heating of the Si-H stretch mode due to inelastic scattering with the Si-H 5 σ hole resonance, and

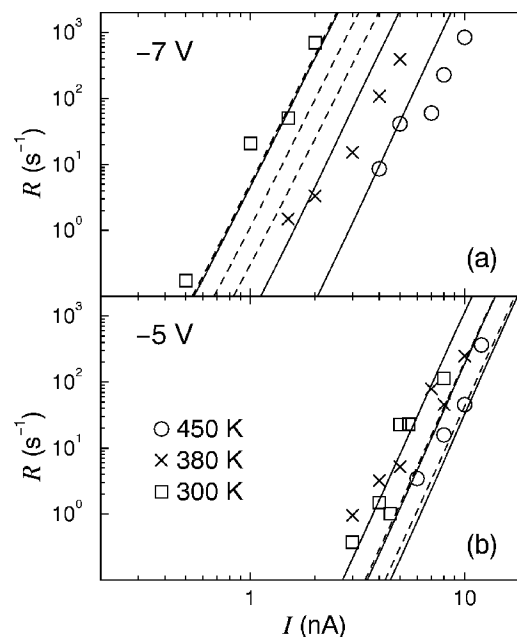


Fig. 2. STM induced desorption rate (R) as function of tunnel current (I) for temperatures 300, 380 and 450 K for sample biases of (a) -7 V and (b) -5 V. Curves show theoretical calculations of R using only a temperature dependent vibrational lifetime (---) and combined with a temperature dependence of the electronic lifetime (—).

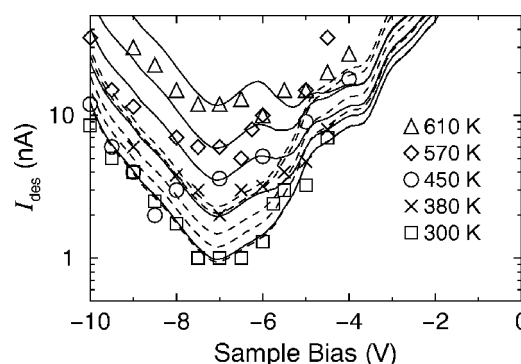


Fig. 3. The tunnel current (I_{des}) as function of sample bias (V_b) which gives rise to 50% desorption of H from a Si(100)-H(2 × 1) surface along a line scan of 2 nm s⁻¹ by an STM tip. Results are plotted for temperatures between 300, 380, 450, 570 and 610 K. Curves show theoretical calculations (see caption of Fig. 2).

first principles calculations of R due to this mechanism are in quantitative agreement with the experimental data [10]. In the following we use this

method to calculate the T dependence of R and compare it with the experimental data.

The first principles method for calculating the inelastic current is based on a high voltage extension [16] of the Tersoff–Hamann model [17] for the STM tunnel junction, and has been described in detail elsewhere [10,15]. We include inelastic scattering events with energy transfer $\pm\hbar\omega_0$, $\pm 2\hbar\omega_0$ and $\pm 3\hbar\omega_0$, where $\hbar\omega_0=0.26$ eV is the energy of the Si–H stretch mode. Energy relaxation due to coupling with silicon phonon modes is described by a current independent energy relaxation rate, γ_T , which we determine from experiment [18] in a manner similar to Ref. [9]. To obtain R , we solve the Pauli master equation for the transitions among the vibrational levels of the H potential well, and assume that desorption occurs when the energy of the H atom exceeds the desorption energy $E_{\text{des}}=3.36$ eV, corresponding to a truncated harmonic potential well with 13 levels

In the calculation of the inelastic current a correction is made for the difference in the Fermi level, ϵ_F^s and the band bending, Φ , between the slab and the sample. This is carried out using an offset between the sample bias of the slab model V_b and the experimental \tilde{V}_b [16]

$$eV_b = e\tilde{V}_b + \tilde{\epsilon}_F^s - \tilde{\Phi} - (\epsilon_F^s - \Phi), \quad (1)$$

where the values with a tilde are slab quantities. Both ϵ_F^s and Φ depend on the sample temperature. However, since the changes in Φ and ϵ_F^s nearly cancel each other, the offset, $V_b - \tilde{V}_b = 0.30 \pm 0.05$ V, is almost constant for the temperatures considered in this work. The dependence of the inelastic current on T due to changes in Φ and ϵ_F^s can therefore be neglected.

We first consider the effect of a T dependence of γ_T . The relaxation of the Si–H stretch mode due to phonon–phonon interaction is expected to involve three quanta of the Si–H bending mode, $\hbar\omega_b=0.078$ eV, and a Si phonon $\hbar\omega_{\text{Si}}=0.026$ eV [9,19]. The T dependence of this interaction is described by [14]:

$$\gamma_T = \gamma_0 \{ [1 + n_T(\omega_b)]^3 [1 + n_T(\omega_{\text{Si}})] - n_T(\omega_b)^3 n_T(\omega_{\text{Si}}) \}, \quad (2)$$

where $n_T(\omega) = 1/[\exp(\hbar\omega/kT) - 1]$ is the Bose–Einstein occupation number. Using the experimental room temperature relaxation rate, $\gamma_{300}=10^8$ s $^{-1}$ and Eq. (2) the relaxation rate at $T=0$ K is determined to be, $\gamma_0=5 \times 10^7$ s $^{-1}$. At 600 K the relaxation rate obtained from Eq. (2), $\gamma_{600}=3 \times 10^8$ s $^{-1}$, which is three times larger than the value at room temperature.

We note that lateral diffusion of the excitation into the H overlayer through incoherent exciton motion is not important for the present system. This is due to the fact that inelastic scattering with an energy transfer of $2\hbar\omega_0$ dominates the desorption process and the lateral diffusion rate for excitations with $n > 1$ is very low due to the anharmonicity of the Si–H bond potential [14,20].

The dashed curves in Fig. 2 show the result of this model for the dependence of R on I for $V_b = -7$ V and $V_b = -5$ V and $T=300, 380$ and 450 K. We note that there are no adjustable parameters in the model. For the present system inelastic scattering events with energy transfer $2\hbar\omega_0$ give the dominant contribution to R in the temperature and voltage range investigated. Since there are 13 levels in the truncated harmonic potential well of the H atom [10] it can be shown that $R \propto (I_2/\gamma_T)^{13/2}$ [24] where I_2 is the inelastic current with energy transfer $2\hbar\omega_0$. From Eq. (2) we have $\gamma_T=1, 1.3$ and 1.7×10^8 s $^{-1}$ at $T=300, 380$ and 450 K, respectively. From this model we obtain $R(300)/R(380) \sim 1.3^{6.5} \sim 5$ and $R(300)/R(450) \sim 30$. At $V_b = -5$ V this is in good agreement with the measured T dependence, whilst the measured T dependence is almost two orders of magnitude larger at $V_b = -7$ V. The dashed curves in Fig. 3 show the calculated bias dependence of I_{des} for temperatures, 300, 380, 450, 570 and 610 K. The minimum in I_{des} occurring at -7 V is reproduced by the model and is related to the position of the energy level of the 5σ hole resonance [10]. For all voltages R decreases with T . For $V_b > -5$ V there is quantitative agreement between the theoretical model and the experimental data. However, for $V_b < -5$ V there is an additional temperature dependence not accounted for by the T dependence of γ_T .

As already discussed for the present system there are no significant temperature effects due to

band bending and lateral diffusion of the vibrational excitation, and calculations of the tunnel current using the appropriate Fermi–Dirac occupation factors show that the thermal current is negligible. At the elevated temperatures we still have atomic resolution for imaging and lithography (see Fig. 1), implying that the temperature does not affect the tip shape. At elevated temperatures the deposition of H atoms from the tip to the surface becomes important [21], but this effect is not large enough to change R by a factor of 100.

Instead we consider the effect of a T dependent lifetime of the 5σ hole resonance. The time evolution of the wave function, $\phi_{5\sigma}$, is given by:

$$\phi_{5\sigma}(t) = \sum_{\mu} \langle \mu | 5\sigma \rangle \psi_{\mu}(0) e^{-i\epsilon_{\mu}t/\hbar} e^{-t/2\tau_{\text{ph}}}, \quad (3)$$

where ψ_{μ} are eigenstates of the adsorbate + substrate system with eigenvalue, ϵ_{μ} , and due to electron–phonon couplings they have a finite lifetime, τ_{ph} , which we take to be independent of μ . If the 5σ resonance is approximated by a Lorentzian line shape we obtain

$$\phi_{5\sigma}(t) = \phi_{5\sigma}(0) e^{-i\epsilon_{5\sigma}t/\hbar} e^{-(1/2\tau_e + 1/2\tau_{\text{ph}})t}, \quad (4)$$

where, $\epsilon_{5\sigma}$, is the resonance energy and τ_e is the lifetime due to electronic coupling with substrate eigenstates. The lifetime of the resonance may now change with temperature due to a T dependence of both τ_{ph} and τ_e . The T dependence of τ_{ph} for different eigenstates of Si has been measured in Refs. [22,23], and $\hbar/2\tau_{\text{ph}} \sim 0.1$ eV at room temperature and $\hbar/2\tau_{\text{ph}} \sim 0.2$ eV at 600 K [22,23]. We also expect a T dependence of τ_e , since the electronic coupling between H and the Si surface depends on the displacements of the Si atoms from their equilibrium positions.

The energy dependent probability of inelastic scattering, $P_n(\epsilon)$, with transfer of energy, $n\hbar\omega$, is for a Lorentzian resonance given by [24]:

$$P_n(\epsilon, \Delta_T) \propto \frac{\Delta_T}{[(\epsilon - \epsilon_{5\sigma})^2 + \Delta_T^2]^{n+1}}, \quad (5)$$

where $\Delta_T = \hbar/2\tau_{\text{ph}} + \hbar/2\tau_e$ is the half width at half

maximum (HWHM) of the resonance at temperature T . From P_n the T dependent inelastic currents can be calculated using

$$I_n(\epsilon, T) = I_n(\epsilon, 0) \frac{P_n(\epsilon, \Delta_T)}{P_n(\epsilon, \Delta_0)}, \quad (6)$$

where $I_n(\epsilon, 0)$ is the first principles value for the $T=0$ K contribution to the inelastic current of tunneling holes with energy ϵ , and $\Delta_0 = 0.6$ eV, $\epsilon_{5\sigma} - \epsilon_F^s = -6$ eV (including band bending) are the parameters at $T=0$ [10].

We determine the T dependent width, Δ_T , by relating R calculated using $I_n(\epsilon, T)$ and γ_T to the measured values at $V_b = -7$ V. The fitted values of Δ_T are plotted as function of T in Fig. 4, and solid curves in Fig. 2 show the corresponding T dependent values of R as function of I for $V_b = -5$ V and $V_b = -7$ V. At $V_b = -5$ V the dashed curves and the solid curves coincide, and the T dependence of R mainly stems from γ_T , whilst there is a strong additional T dependence of R from Δ_T at $V_b = -7$ V. This behaviour can be understood using $R = (I_2/\gamma_T)^{6.5}$ and taking into account the T dependence of I_2 from Eq. (6). Using Eq. (5) it is observed that $I_2 \propto \Delta_T$ for $|V_b| \ll |\epsilon_F^s - \epsilon_{5\sigma}|$ and $I_2 \propto \Delta_T^{-5}$ for $|V_b| \gg |\epsilon_F^s - \epsilon_{5\sigma}|$. At $V_b = -7$ V this gives a T dependence of $R(300)/R(380) = (1.3 \times 1.13^5)^{6.5} \sim 10^2$ and $R(300)/R(450) = 10^4$ in good agreement with the measured data. At $V_b = -5$ there is a weak T dependence of R upon Δ_T since $|V_b| < |\epsilon_F^s - \epsilon_{5\sigma}|$ causes I_2 to be nearly independent of T and the T dependence of

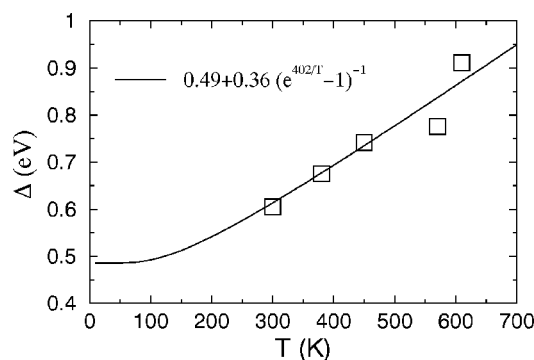


Fig. 4. □, Temperature dependent values of Δ obtained by fitting theoretical desorption rates to the experimental values. The solid curve shows a least-squares fit of Eq. (7) to the data points.

R therefore mainly stems from γ_T . The solid curves plotted in Fig. 3 as obtained from the present model are in good agreement with the experimental data for the whole bias range from -10 to -4 V. It is observed that the curves become flatter with increasing temperatures in good agreement with experimental data. At positive bias inelastic scattering with the Si–H $6\sigma^*$ is the dominant desorption mechanism for $|V_b| \leq 3$. In this bias regime $|V_b| \ll |\epsilon_F - \epsilon_{6\sigma}^*| = 6$ eV and at this condition the main T dependence of R must come from γ_T in good agreement with Ref. [9].

In order to investigate the origin of the T dependence of Δ_T we model Δ_T by [22]

$$\Delta_T = \Delta_0 + a(e^{\Theta/kT} - 1)^{-1}. \quad (7)$$

From a least-squares fit to the data in Fig. 4 we obtain $\Delta_0 = 0.49$ eV, $a = 0.36$ eV and $\Theta = 402$ K. The T dependence of Δ_T is quite strong and almost linear for $T > 300$ K with the slope $a/\Theta = 1$ meV K $^{-1}$. The measured dependence upon T of Δ_{ph} for silicon is in the range 0.1 – 0.4 meV K $^{-1}$ [22,23], and a major part of the T dependence must therefore come from Δ_e . This dependence must be related to a change in the electronic coupling between the adsorbate and the surface upon excitations of phonons with frequency $\hbar\Omega = \Theta$. However, the fit in Eq. (4) is quite insensitive to the value of Θ and from the present data we can only state that $\hbar\Omega < 0.1$ eV. It is therefore not possible to distinguish whether the T dependence of Δ_e is from Si phonons or Si–H transverse vibrations.

In summary we have presented experimental data of the desorption rate of STM induced desorption of H from the Si(100)–H(2×1) surface as a function of temperature, and found a decreasing desorption rate as function of the temperature. The desorption mechanism is related to vibrational heating of the H atom by holes inelastic scattering with the Si–H 5σ hole resonance, and the temperature dependence is explained by both a decreasing vibrational life-time of the Si–H stretch mode and a decreasing electronic life-time of the Si–H 5σ hole resonance with increasing temperature.

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