

Laser-stimulated desorption of H^+ from the hydrogenated Si(100) surface

S. Vijayalakshmi,* H. T. Liu,[†] and Z. Wu

Department of Physics, Rutgers University, Newark, New Jersey 07102

(Received 16 January 1998; revised manuscript received 13 April 1998)

Desorption of H^+ ions from hydrogenated Si(100) surface is observed under the irradiation of a low-fluence 193-nm pulsed laser beam. The time-of-flight (TOF) spectra of H^+ ions on the monohydride and dihydride surfaces show little differences, both consisting of two peaks, corresponding to mean kinetic energies of 0.09 ± 0.05 and 0.38 ± 0.06 eV. The substrate temperature dependence of the TOF spectra was studied. It was found that the ratio of the 0.38-eV peak to the 0.09-eV peak increased with the substrate temperature. The experimental results are interpreted using the hydrogen pairing model on Si(100). The 0.09-eV peak and 0.38-eV peak are assumed to correspond, respectively, to the H^+ ions desorbing from doubly occupied and singly occupied dimers. The difference of 0.29 ± 0.011 eV in the kinetic energies of these two groups of H^+ ions is compared with the pairing energy on the H/Si(100) surface. Correction to the kinetic energy of H^+ ions due to the image interaction is discussed. From the kinetic energy of the H^+ ions, the hole-hole repulsion energy in the Si-H bond is estimated to be 9.4 eV, in agreement with earlier experimental results. [S0163-1829(98)08135-1]

I. INTRODUCTION

Hydrogen termination of silicon surfaces has been studied extensively in the past decade. This is a topic of great interest for both the silicon technology and fundamental science. Conceptually, H/Si(100) represents the simplest possible system of adsorption on covalently bonded surfaces. Various studies have confirmed the following picture of hydrogen adsorption on the Si(100) surface. On the unreconstructed Si(100) surface, each Si atom has two dangling (broken) bonds. Surface reconstruction causes all the broken bonds to rebond in the following fashion, lowering the energy of the surface. Silicon atoms in adjacent rows along the $[1\bar{1}0]$ direction pair up and establish a strong σ bond, forming dimers. This gives rise to a 2×1 structure.¹⁻⁵ The remaining two dangling bonds on the dimer, one from each dimer atom, form a weak π bond.⁵ The surface energy can be further lowered by allowing the symmetric dimers thus formed to buckle (Peierls distortion).^{6,7} Even though the bond in a buckled (asymmetric) dimer is not a typical π bond, we shall still refer to it as a π bond for simplicity. The buckling of dimers on the Si(100) surface has been directly observed using scanning tunneling microscopy (STM).⁷ At low H exposure, a monohydride phase is formed in which the π bond is broken and each Si atom in the dimer is bound to one hydrogen atom. Since the strong σ bond in the Si-Si dimer is not broken in this phase, the surface structure is still 2×1 .⁸⁻¹⁰ As a result of the disruption of the π bond, the dimers on the monohydride surface are symmetric. The existence of the weak π bond between the dimer atoms on the clean Si(100) 2×1 surface makes it energetically more favorable for two H atoms to be bound to the same dimer than to two separate dimers on the monohydride surface.¹¹⁻¹⁶ Direct evidence for this hydrogen pairing on H/Si(100) 2×1 was obtained using STM.¹² At high H exposure, due to the stronger bond between Si and H, dimers start to break, and the Si atoms use the newly available dangling bond to bind to a second H atom, forming a dihydride phase. The surface

structure now changes to 1×1 . A dihydride phase can be converted to a monohydride phase by annealing the sample to above 400 °C.²

Dynamic processes such as desorption of H_2 and H^+ from H/Si(100) surface provide useful information about the binding between hydrogen and surface silicon atoms. For example, thermal desorption of H_2 from the H/Si(100) surface can help identify different binding states of H on the Si(100) surface.¹⁷ Electron-stimulated desorption (ESD) and photon-stimulated desorption (PSD) of protons from a hydrogenated Si surface have been reported by several groups.¹⁸⁻²² Proton desorption is particularly interesting because the ionization potential of the hydrogen atom (13.6 eV) is much larger than that of the silicon atom (8.8 eV), and therefore nothing short of removing the two electrons in the Si-H bond, i.e., producing a two-hole state, can give rise to H^+ desorption. In both ESD and PSD studies the desorption threshold is found to be ~ 23 eV, corresponding to the threshold for producing a two-hole state in the Si-H bond via Si $L_{23}VV$ Auger decay.^{19,20} The Si $2p$ core excitation around 100 and 112 eV also leads to H^+ desorption on the H/Si(111) surface.²² The time-of-flight (TOF) spectrum of the H^+ ions resulting from the Si $L_{23}VV$ Auger decay displays a single peak corresponding to a kinetic energy of ~ 3 eV.^{18,19}

In this paper we present the results of our study of H^+ desorption from a H/Si(100) surface under the irradiation of pulsed 193-nm laser beam. When a H/Si(100) surface is irradiated by a pulsed laser beam, most of the adsorbed hydrogen atoms will thermally desorb as H_2 due to the rapid heating by the laser pulse. However, we find that a small fraction of the adsorbed H atoms will desorb as H^+ . It is important to note that the observed H^+ ions are different from the ions commonly observed in the laser ablation process. The laser fluence used in this experiment is much lower than that used in laser ablation, and, as will be described below, the kinetic energy of the ions do not depend on the laser fluence. The findings of our study are as follows. (1) To the best of our knowledge, this is the first report of PSD of H^+ ions on

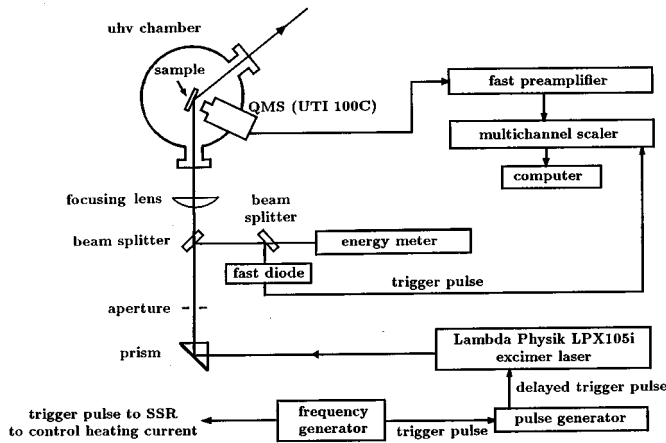


FIG. 1. Experimental arrangement.

H/Si(100) surfaces, with a photon energy (6.4 eV) well below the Si *CVV* Auger decay threshold (~ 23 eV). (2) The TOF spectra of the H^+ ions show little differences on the monohydride and dihydride surfaces. They consist of two peaks, corresponding to mean kinetic energies of 0.09 ± 0.05 and 0.38 ± 0.06 eV. (3) The relative height of the two peaks was found to depend on the substrate temperature. As the substrate temperature increases, the 0.38-eV peak increases faster than the 0.09-eV peak, and eventually exceeds it. The experimental results are interpreted using the hydrogen pairing model on H/Si(100). The 0.09- and 0.38-eV peaks are assumed to correspond, respectively, to the H^+ ions desorbing from doubly and singly occupied dimers. The difference 0.29 ± 0.11 eV in the kinetic energies of the two peaks is approximately equal to the pairing energy on the H/Si(100) surface. From the kinetic energy of the H^+ ions, the hole-hole repulsion energy in the Si-H bond is estimated to be 9.4 eV, in agreement with earlier experimental results.¹⁹

II. EXPERIMENT

The experimental arrangement is shown in Fig. 1. The experiments were performed in a small ultrahigh-vacuum chamber with a base pressure of 5×10^{-10} Torr. An ArF excimer laser of wavelength 193 nm and pulse width 17 ns was used as the excitation source. Pulse energies were in the range of 150–300 mJ/cm². The pulse repetition rate was 4 Hz. The Si(100) was Czochralski grown (Wacker) and P-doped *n* type with a resistivity of approximately 5 Ω cm. Two samples of dimensions $18 \times 5 \times 0.38$ mm³ were cut from the same wafer, and a small dent was drilled in the back sample. A 0.003-in. W-26% Re/W-5% Re thermocouple was placed in the dent, and the two samples were clamped together in molybdenum holders. Resistive heating was used to heat the sample.

The samples were cleaned with methanol before being loaded into the chamber. Cleaning of the samples was carried out in two different ways. (1) They were annealed at 600 °C for 5–7 h, and then flashed to 1100 °C for 30 s. They were then rapidly cooled to 650 °C, and further cooling was done at a rate of about 1°C/s. This ensures a clean 2×1 Si(100) surface.²³ (2) The second method of cleaning involved sputtering the surface with a 2-keV Ar^+ beam for 30

min, and then annealing the sample at 650 °C for 1 h, followed by flashing and cooling down in a fashion similar to that used in the first method.¹⁷ Both methods yielded an Auger clean surface. To form a monohydride surface, the sample was kept at 320 °C and placed at 4 cm away from a tungsten filament heated to 1800–2000 °C. The chamber was then backfilled with research grade (99.9999% purity) hydrogen to a pressure of 5×10^{-6} Torr for 5 min. The dihydride surface was formed using the same procedure, except that the sample was kept at room temperature rather than 320 °C.

The vacuum chamber was equipped with a quadrupole mass spectrometer (UTI 100C), which was enclosed in a stainless-steel cylindrical tube. The cylindrical tube had an opening of 0.3-cm diameter in the front end to allow the ions to enter the mass spectrometer. The ions were detected with a filament turned off and grounded. The ion pulses from the channeltron were counted by a multichannel scaler (EG&G Ortec model T914). The laser pulse arrival time was recorded by a fast photodiode. The difference between this start pulse and the time at which H^+ ions were recorded was the flight time. The total flight length was 22 cm, of which 21.2 cm was inside the cylindrical tube.

In studying the dependence of H^+ desorption on the substrate temperature, care was exercised to make sure that the sample was grounded while the TOF spectrum was being taken. This was done as follows. The sample heating current was momentarily suspended for 2.5 ms using a solid-state relay, during which time the sample was grounded. The laser was externally triggered about 1.5 ms after the sample heating current was turned off. The collection of the TOF data was started by the laser pulse and had a duration of 0.14 ms. Thus the sample was guaranteed to be grounded while the TOF data were being taken.

III. RESULTS

Figures 2(a) and 2(b) show the typical TOF spectra of H^+ ions on the monohydride and dihydride surfaces. The monohydride spectrum was taken at a substrate temperature of 325 °C, and that of dihydride at a substrate temperature of 25 °C. Both spectra show a bimodal structure, with the two peaks being at 26 and 53 μ s, corresponding to mean kinetic energies of 0.38 ± 0.06 and 0.09 ± 0.05 eV, respectively. The uncertainty in the kinetic energy corresponds to one standard deviation of the kinetic-energy distribution. The relative height of the 26- μ s peak compared to the 53- μ s peak depends on the substrate temperature, and will be discussed in more detail later. Figures 3(a) and 3(b) are the corresponding ion kinetic-energy distributions as obtained from Figs. 2(a) and 2(b) using the formula

$$E_k = \frac{1}{2} m \left(\frac{L}{t} \right)^2, \quad (1)$$

where E_k is the measured kinetic energy of the H^+ ions, m their mass, L the flight length (22 cm), and t the flight time. Even though the spectra shown in Fig. 2 are the accumulation of 200 laser shots, the first ten laser shots are responsible for more than 90% of the H^+ signal, as shown in Fig. 4. This is consistent with studies of laser-induced thermal desorption of H_2 on Si surfaces.¹⁰ As laser fluence increased, the H^+ counts increased nonlinearly, but peak positions remained

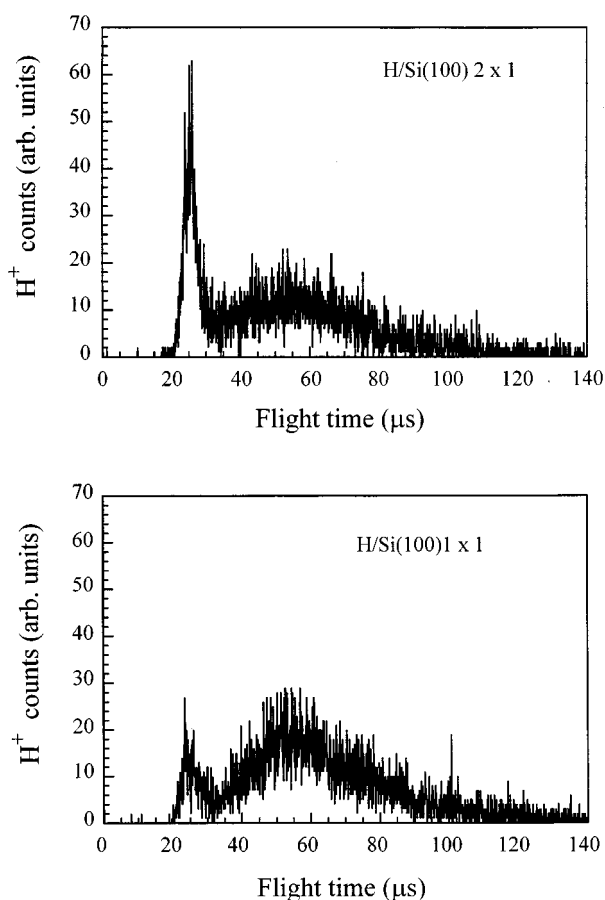


FIG. 2. Typical TOF spectra of H⁺ for (a) monohydride and (b) dihydride surfaces. The TOF spectra in this as well as in all the other figures are the accumulation of 200 laser shots.

the same (Fig. 5). This is in contrast with the results of laser ablation studies, where the ion kinetic energy increases with laser fluence. There is some indication in our data that this nonlinearity can be described by a cubic power law. However, due to the limited range of laser fluence used in the experiment, this result is not conclusive. The upper limit of the laser fluence is determined by the damage threshold of the Si sample (~ 450 mJ/cm²) and the lower limit (~ 150 mJ/cm²) by the detectable H⁺ signal. For the data shown in Fig. 2(a), where the laser fluence was 240 mJ/cm², the H⁺ yield was $\sim 10^{-9}$ ions/photon. Due to the nonlinear dependence of H⁺ yield on the laser fluence, one has to be careful in scaling this yield to other laser fluences. Also, as will be discussed below, the H⁺ yield depends on the substrate temperature. For a sufficiently high laser fluence (>450 mJ/cm²), Si samples started to suffer damage and the spectrum obtained on these damaged spots was different [Fig. 6(c)]. This difference was used to ensure that the surface was not damaged.

Shown in Fig. 7 are the TOF spectra taken at various substrate temperatures. No visible shift in peak positions was observed. As the substrate temperature increased, the 26- μ s peak, which was initially lower than the 53- μ s peak, increased faster than the 53- μ s peak and eventually exceeded it in height. As the substrate temperature further increased both peaks started to decrease, and eventually disappeared around 650 °C. This is consistent with the result of the thermal-

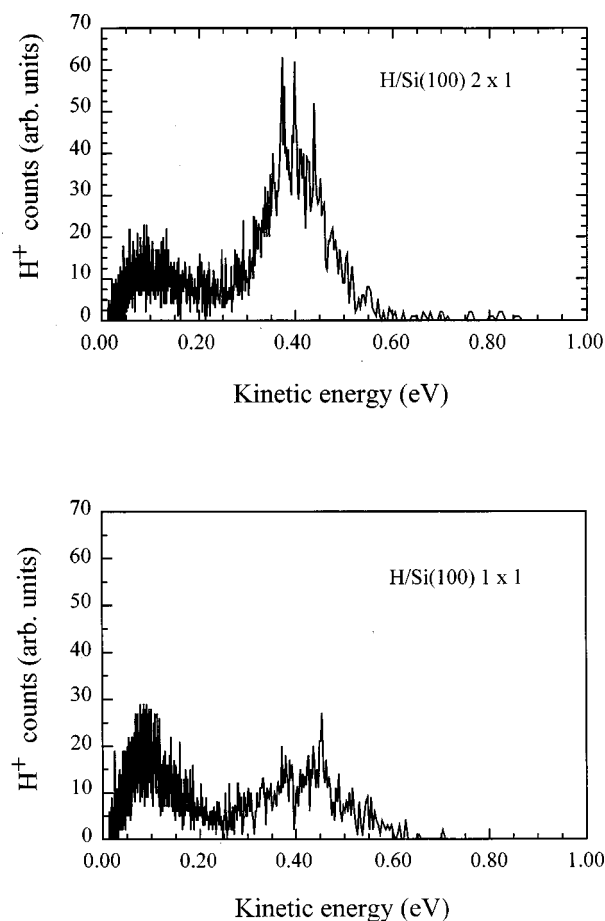
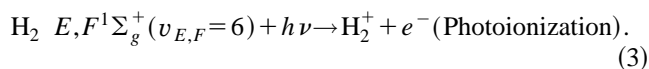
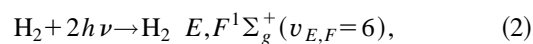


FIG. 3. Kinetic-energy distribution of H⁺ ions as derived from the data in Fig. 1.

desorption studies of H₂ molecules desorbing from H/Si(100), which shows that hydrogen atoms are completely desorbed from the sample surface at temperatures higher than 650 °C.¹⁷ It is to be noted that the ion collection efficiency, being dependent on the ion kinetic energy, is different for the 26- and 53- μ s peaks. Thus the absolute counts of each peak are not calibrated. However, this difference in the ion collection efficiency should not affect the observation that the relative height of the 26- μ s peak to the 53- μ s peak changes with the substrate temperature, since during the experiment the only variable was the substrate temperature.

In addition to H⁺, H₂⁺ signal was also observed. The H₂⁺ signal from the monohydride surface is shown in Fig. 8. The peak at 53 μ s is due to leakage from mass 1 (H⁺) and this leakage happens because of the low kinetic energy of ions.²⁴ The peak at 20 μ s, which corresponds to 1.3 eV, is the H₂⁺ signal. Unlike the H⁺ spectrum, the H₂⁺ spectrum does not depend on the surface conditions. Therefore we conclude that the H₂⁺ ions are produced in the gas-phase process. The most likely mechanism is the following. Gaseous hydrogen molecules, generated near the surface by laser-induced thermal desorption, are ionized by resonance enhanced multiphoton ionization:²⁵



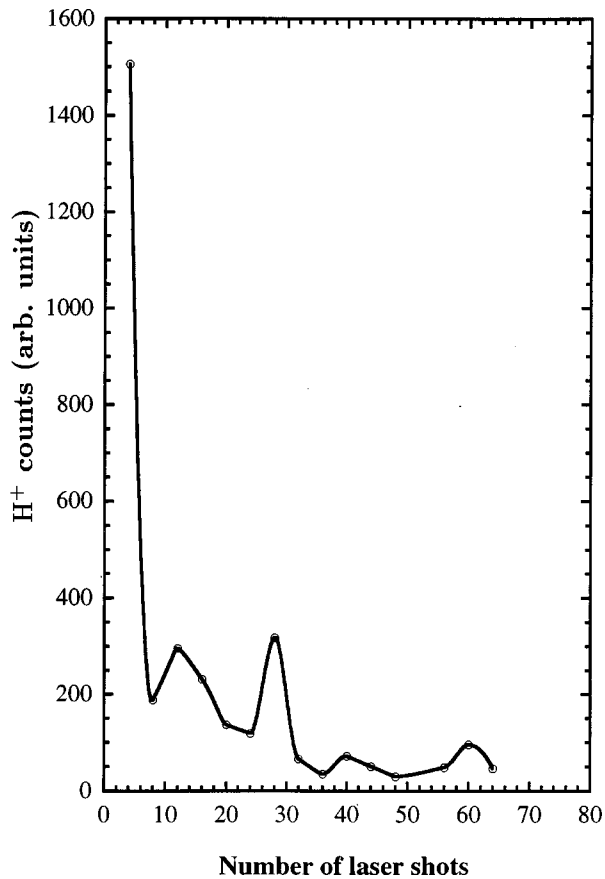


FIG. 4. The H^+ counts vs the number of laser shots.

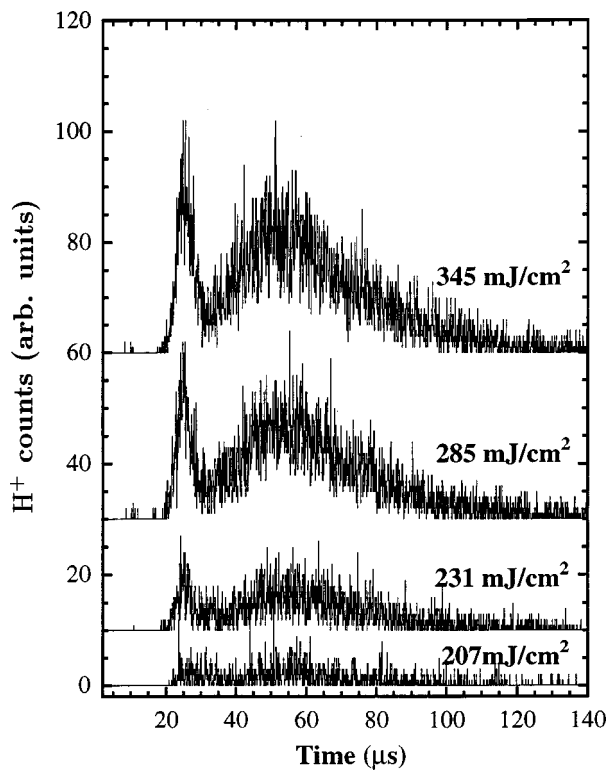


FIG. 5. The laser fluence dependence of the H^+ signal.

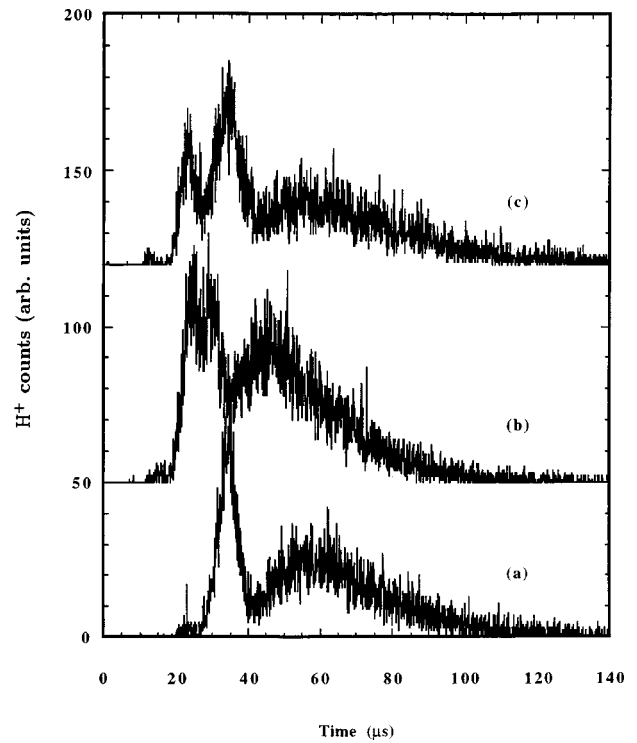


FIG. 6. TOF spectrum of H^+ from an Ar^+ bombarded Si(100) surface [(a) and (b)] and a laser-damaged spot (c).

The most conclusive evidence for the surface origin of the H^+ ions is that the TOF spectra of H^+ ions depend on the surface condition. For example, the spectra obtained on samples which were cleaned by Ar^+ sputtering without an-

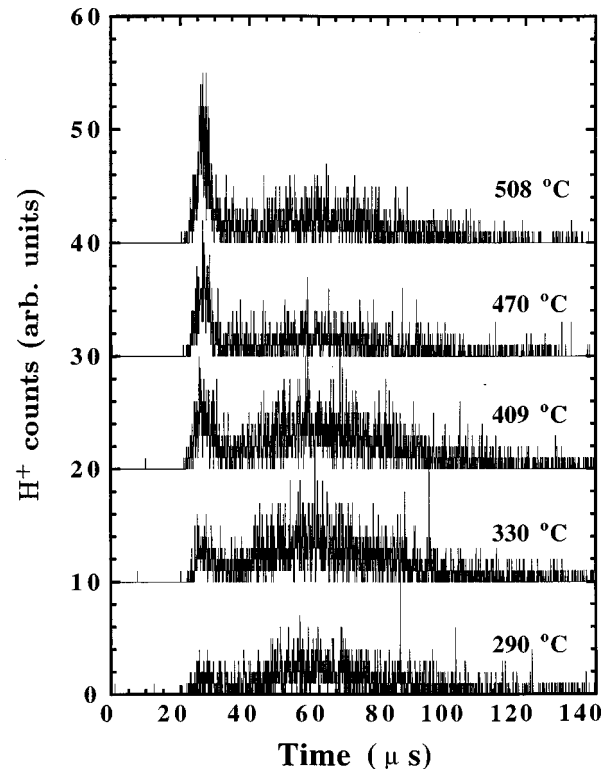


FIG. 7. Substrate temperature dependence of H^+ ion desorption. The laser fluence is 150 mJ/cm^2 .

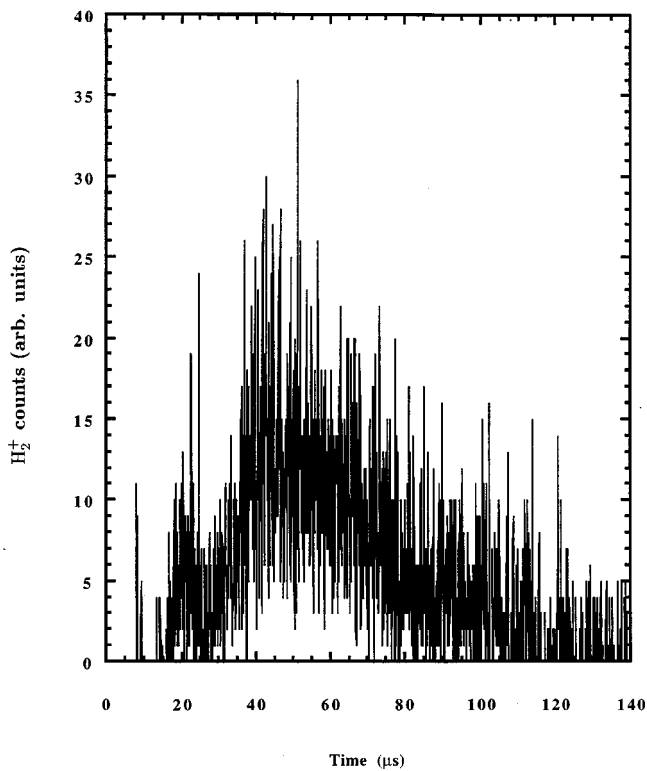
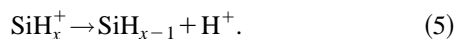
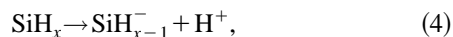


FIG. 8. Typical TOF spectra for H₂⁺. The peak at 53-μs is leakage from the H⁺ signal (see Ref. 24).

nealing display a wide variety both in terms of the number of peaks and peak positions. Some of these spectra are shown in Figs. 6(a) and 6(b). The difference between these spectra and those in Fig. 2 is probably due to the large number of defects created on the surface by Ar⁺ sputtering. The H⁺ spectrum at laser damaged spots [Fig. 6(c)] is also different from that in Fig. 2. Because the H⁺ spectrum depends on the surface condition and that of H₂⁺ does not, we conclude that H₂⁺ or H₂ cannot be the origin of the H⁺ signal.

We also observed a small signal corresponding to mass 29, 30, 31, and 32 ions, i.e., the silicon hydride SiH_x (x = 1, 2, 3, and 4) ions. No higher silicon hydride (Si₂H_x) ion signal was observed at the laser fluence used in the experiment. The existence of these signals suggest the possibility that the H⁺ ions might be produced in the gas phase from photoionization and/or photodissociation of SiH_x (x = 1, 2, 3, and 4) species:



We rule out Eq. (4) because no negative silicon hydride ions were detected. Since the H⁺ ions produced in process (5) should carry most of the kinetic energy because of its small mass, one expects the kinetic energy of H⁺ to be larger than that of SiH_x⁺. Experimentally, the kinetic energies of the SiH_x⁺ species are between 3 and 5 eV, much larger than the kinetic energy of H⁺. Therefore, we believe that silicon hydride was not the source for the H⁺ ions.

Another question we need to address is whether it is possible that the H⁺ ions originate from some impurities on the

surface rather than from the Si-H bond. The small amount of impurities were presumably deposited on the surface during hydrogen dosing. The following observation seems to rule out this possibility. The H⁺ signal was also observed on samples which were cleaned by Ar⁺-ion bombardment but not exposed to hydrogen dosing. The H⁺ TOF spectra on these surfaces vary considerably depending on the Ar⁺ bombardment conditions. They look similar to the TOF spectra in Figs. 6(a) and 6(b). However, after the samples were annealed, the TOF spectra of H⁺ would always look the same as those in Fig. 2. Since no hydrogen dosing was involved, the impurities on these annealed Si(100) surfaces are expected to be negligible. Therefore, from the fact that the TOF spectra on these surfaces are the same as those in Fig. 2, we conclude that the H⁺ signal from the monohydride and dihydride surfaces does originate from the Si-H bond rather than from the impurities on the surface. Our observation of a H⁺ signal from a clean Si surface which was not exposed to hydrogen dosing is similar to that reported by Knotek *et al.*,²⁰ who observed H⁺ desorption from cleaved Si(111) surface using photon energies near the Si K excitation threshold. The H⁺ signal was attributed to the H surface segregation from the bulk.

IV. HYDROGEN PAIRING AND DESORPTION OF H⁺ ON H/Si(100)

As mentioned in Sec. I, due to the weak π bond between the dimer atoms on the clean Si(100)2×1 surface, it is energetically favorable for dimers to be doubly occupied by hydrogen atoms on the H/Si(100) surface. In removing the second hydrogen atom from a doubly occupied dimer, a certain amount of energy (π bond energy) is recovered by allowing the two dimer atoms to reestablish their weak π bond. Therefore, it requires less energy to remove the second hydrogen atom than to remove the first hydrogen atom from a doubly occupied dimer, the difference in energy being approximately equal to the π bond energy. The difference in energy required to remove the first and second H atoms from a doubly occupied dimer is also equal to the pairing energy E_{pair} , which is defined as the energy required to convert a bare dimer and a doubly occupied dimer into two singly occupied dimers.¹³ Several attempts have been made to calculate the pairing energy. The calculated values range from 0.08 eV (Ref. 14) to 2.2 eV.¹⁵ Experimentally, the pairing energy has been determined to be 0.25 ± 0.05 eV in a study of isothermal desorption of H₂ on H/Si(100) using second-harmonic generation technique.¹⁶

The results of the present experiment will be interpreted in the framework of the hydrogen pairing model on the H/Si(100) surface. We make the following assumptions.

(1) Since there are no visible differences in the TOF spectra from the monohydride and dihydride surfaces, we assume that the H⁺ desorption occurs *only* on the monohydride surface. The desorption of H⁺ on the dihydride surface occurs only after the dihydride surface is locally converted into the monohydride surface by laser heating. This can be understood as follows. On the dihydride surface, the distance between the two hydrogen atoms from the neighboring Si atoms is only 1.64 Å, whereas on the monohydride surface it is 3.49 Å.²⁶ The two neighboring H atoms on the dihydride surface, being so close to each other, are more likely to de-

sorb as H_2 due to laser-induced thermal desorption.

(2) As in all previous ESD and PSD studies of hydrogen ions from the hydrogenated Si surface, we assume that the H^+ desorption results from the creation of a two-hole state in the Si-H bond.^{19,20,27} Since the photon energy in this study is only 6.4 eV, the only way to create a two-hole state in the Si-H bond is by multiphoton excitation. We assume the two-hole state is created in the D_1 band of Si-H bond, which is located at 3 eV below the valence-band maximum.^{8,28} This is a well-defined energy state, and therefore the kinetic energy of the H^+ ions is fixed. This explains why the peak positions are independent of laser fluence (Fig. 5).

(3) We assume that the 0.09- and 0.38-eV peaks originate from doubly and singly occupied dimers, respectively. The difference in the kinetic energies of these two groups of H^+ ions corresponds approximately to the pairing energy E_{pair} .

V. DISCUSSION

A. Image interaction and contact potential difference

The measured kinetic energy of H^+ ions can be affected by the image interaction and the contact potential difference between the sample and the cylindrical shielding tube around the mass spectrometer, both of which were grounded. The contact potential difference creates an electric field, which accelerates or decelerates the ions. It is important to note that the contact potential difference shifts the 0.09- and 0.38-eV peaks by the same amount, and therefore does not affect the energy difference between these two peaks. To eliminate or minimize this contact potential difference, we coated the front end of the cylindrical shielding tube with the same type of Si as our Si sample, using the laser ablation technique. The image interaction correction to the kinetic energy of H^+ ions can be estimated as follows.²⁹⁻³¹ To a first-order approximation, the measured kinetic energy E_k is given by

$$E_k = E_k^{(0)} - |V_I|, \quad (6)$$

where $E_k^{(0)}$ is the kinetic energy of the ion in the absence of the image potential energy V_I . The image potential energy V_I is given by

$$V_I = -\frac{e^2}{4s_0} \frac{\epsilon - 1}{\epsilon + 1}, \quad (7)$$

where s_0 is the distance from the surface where the ion is formed,^{29,31} and $\epsilon=12$ is the dielectric constant of the Si sample. We have neglected the Thomas-Fermi screening because the electron number density in our n -type Si sample is more than six orders of magnitude lower than in the metal, and the Thomas-Fermi screening length scales as the inverse of the square root of the electron density. Therefore, the screening is negligible.

To determine the distance s_0 for desorption from singly and doubly occupied dimers, we note that a doubly occupied dimer is a completely symmetric dimer unit, and, for a singly occupied dimer, the buckling is significantly less (if at all present) than that of the bare (unoccupied) dimer because H chemisorption destroys the mechanism which causes the buckling of bare dimers. Therefore, we assume that the distance s_0 at which the H^+ ions are formed is the same for

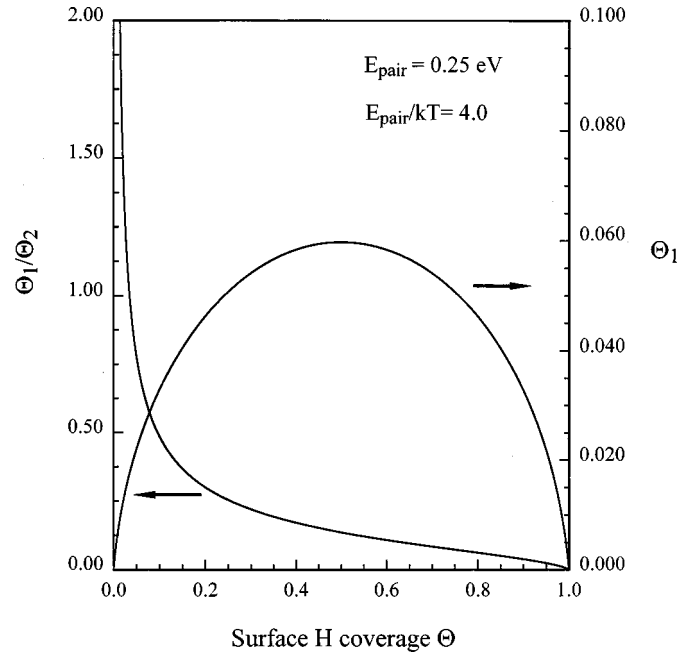


FIG. 9. Calculated hydrogen coverage in singly occupied dimers and the ratio of the hydrogen coverage in singly occupied dimers to that in doubly occupied dimers as a function of H coverage.

desorption from singly and doubly occupied dimers. If for s_0 we use the calculated equilibrium position of the hydrogen atom on the monohydride surface,²⁶ then we have $s_0 = 1.4 \text{ \AA}$ and $V_I = -2.1 \text{ eV}$. Therefore, taking into account the image interaction correction, the 26- and 53- μs peaks correspond to kinetic energies of 2.48 and 2.19 eV, respectively. The uncertainty in the value of s_0 is expected to be the main source of uncertainty in the ion kinetic energy $E_k^{(0)}$.²⁹

B. Population of singly and doubly occupied dimers

In the first-order approximation, the hydrogen coverage in singly occupied dimers Θ_1 and that in doubly occupied dimers Θ_2 can be calculated using a simple lattice gas model.¹³ Assuming the H pairing energy $E_{\text{pair}}=0.25 \text{ eV}$ (Ref. 16) and $E_{\text{pair}}/kT=4.0$, which corresponds to the typical temperature used in the temperature dependence study, the calculated hydrogen coverage in singly occupied dimers Θ_1 and the ratio Θ_1/Θ_2 are shown in Fig. 9 as a function of the surface H coverage Θ . Starting from full coverage $\Theta=1$, the coverage of singly occupied dimers first increases, reaches a maximum value ~ 0.06 at $\Theta=0.5$, and then decreases as Θ further decreases. Also we note that the ratio Θ_1/Θ_2 increases monotonically as Θ decreases.

C. Dependence of the desorption of H^+ on the H coverage

The substrate temperature dependence of the H^+ signal is depicted in Fig. 7. Since the surface H coverage decreases as the substrate temperature increases, the data also show the H coverage dependence of the H^+ signal. Using the results of Sec. V B, the data can be understood as follows.

At high H coverage, the desorption of H^+ from singly occupied dimers (the 26 μs peak) is small due to the small population of singly occupied dimers. As the surface H coverage decreases due to substrate heating, the population of

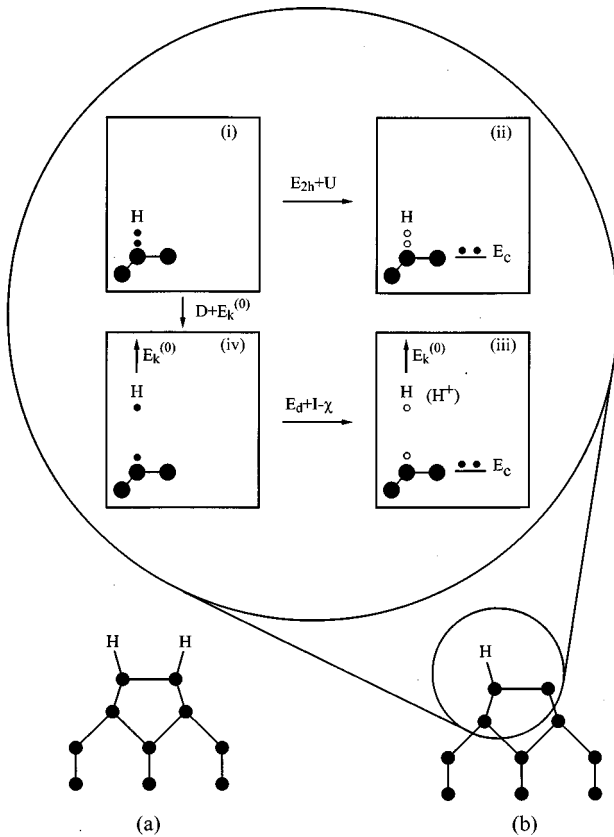


FIG. 10. Desorption of H⁺ from doubly (a) and singly (b) occupied dimers. The filled circles represent Si atoms. Inset: the energy cycle during H⁺ desorption. A hydrogen atom just before (ii) and right after (iii) its desorption as H⁺. The small open circles in (ii) represent localized holes in the Si-H bond. The small open circle on the Si atom in (iii) represents a hole in the dangling bond, and that on the departing H atom indicates a missing electron, i.e., a H⁺. The small filled circles in (ii) and (iii) represent electrons at the bottom of the conduction band.

singly occupied dimers increases, and therefore the 26- μ s peak increases. Also, as H coverage decreases, the ratio of Θ_1/Θ_2 monotonically increases (Fig. 9), which implies that the ratio of the 26- μ s peak to the 53- μ s peak increases with the substrate temperature. This provides a simple qualitative explanation for the data in Fig. 7.

D. Hole-hole interaction in the Si-H bond

The kinetic energy $E_k^{(0)}$ of the H⁺ ion right after its formation on the surface is related to the hole-hole interaction U in the Si-H bond. To a first-order approximation the relationship between $E_k^{(0)}$ and U can be derived from the energy cycle as follows. Consider the desorption of a H⁺ ion from a singly occupied dimer [Fig. 10(b)]. The configurations just before and right after desorption are depicted in insets (ii) and (iii) of Fig. 10. The main electronic relaxation processes during desorption are (1) the hole left on the surface Si atom becomes a dangling-bond hole, and (2) the hole on the departing H atom corresponds to ionization of the H atom. Therefore, if we assign the dangling-bond energy to the hole left on the surface Si atom and ionization energy to the departing H atom in inset (iii), configurations (ii) and (iii) will have approximately the same energy. Configuration (ii) can

be obtained from (i) by providing energy $E_{2h} + U$, where E_{2h} is the energy required to create a two-hole state in the Si-H bond in the absence of hole-hole interaction U . The energy needed to convert (i) to (iii) is $D + E_k^{(0)} + E_d + I - \chi$, where $D = 3.40$ eV is the energy required to remove the H atom from a singly occupied dimer,¹⁵ $E_d = 1.9$ eV is the energy required for exciting an electron from the surface Si dangling bond to the bottom of the conduction band,³² $I = 13.6$ eV is the ionization energy of a H atom, and χ is the local electron affinity of the Si surface. By equating the energies of (ii) and (iii), we obtain

$$E_k^{(0)} = E_{2h} + U - D - E_d - I + \chi. \quad (8)$$

Since the D_1 band is 3 eV below the valence-band maximum, $E_{2h} = 8.2$ eV. The electron affinity χ of the monohydride surface is 3.7 eV,³³ which is 0.37 eV lower than that of the clean Si(100)2 \times 1 surface.³⁴ This is because on the clean Si(100)2 \times 1 surface dimers are buckled, with the up-atom having more electronic charge than the down-atom. This gives rise to a surface dipole moment, which accounts for the increase in the electron affinity. Hydrogenation removes the buckling and therefore lowers the electron affinity. As will be discussed later, for desorption of H⁺ from the monohydride surface, the local electron affinity χ as “seen” by the H⁺ ions is 3.7 eV. Using $E_k^{(0)} = 2.5$ eV in Eq. (8), we find $U = 9.4$ eV, which lies within the estimated range of 8–10 eV for U in Ref. 19.

E. Comments

According to our model, one sees from Eq. (8) that the difference in the kinetic energies $E_k^{(0)}$ of the two groups of H⁺ ions is equal to the difference in the energy D required to remove the first and second H atoms from a doubly occupied dimer, only if we can assume that the local electron affinity χ as seen by the desorbing H⁺ ions is the same for desorption from singly and doubly occupied dimers. We have made use of this assumption in identifying the difference of 0.29 ± 0.11 eV in the kinetic energies of the two groups of H⁺ ions as the pairing energy on the H/Si(100) surface. The basis of our assumption is that, as mentioned before, both singly and doubly occupied dimers are symmetric. For desorption from a doubly occupied dimer, the dimer is symmetric both before and after the desorption. The same is true for desorption from a singly occupied dimer, because a hole is left on the dimer atom from which the desorption of H⁺ occurs, and as a result no π bond is formed during desorption and the dimer will remain symmetric. Therefore, we assume that the local electron affinity is the same for desorption from doubly and singly occupied dimers and is equal to that of the monohydride surface. This argument, however, may not be entirely correct because it does not take into account the nearby bare dimers which might be buckled and possess a dipole moment, leading to an increase in the local electron affinity. This will affect the kinetic energy of the desorbing H⁺ ions, as well as the width of their kinetic-energy distribution. In this sense, the energy difference 0.29 ± 0.11 eV between the two groups of H⁺ ions is probably not as good a measure of the pairing energy E_{pair} as the value obtained in the study of

H₂ desorption,¹⁶ where the kinetic energy of the neutral H₂ molecules is not affected by the surface electron affinity.

VI. CONCLUSIONS

In conclusion, we have made an observation of laser stimulated desorption of H⁺ from H/Si(100) surfaces with a photon energy (6.4 eV) well below the Si CVV Auger decay threshold (~23 eV). The mean kinetic energies of the H⁺ ions are 0.09±0.05 and 0.38±0.06 eV, and are the same on the monohydride and dihydride surfaces. A model based on

hydrogen pairing on the H/Si(100) surface is used to interpret the experimental data. More studies are needed to understand fully the desorption of H⁺ ions from the H/Si(100) surface.

ACKNOWLEDGMENTS

We acknowledge discussions with Sue Raynor on the H₂ gas-phase process. This work was supported by NSF Grant No. DMR-9408779.

-
- *Present address: Department of Electrical and Computer Engineering, New Jersey Institute of Technology, Newark, NJ 07102.
[†]Present address: Department of Physics, University of Science and Technology of China, Hefei, Anhui, China.
- ¹D. J. Doren, in *Advances in Chemical Physics*, edited by I. Prigogine and S. A. Rice (Wiley, New York, 1996), Vol. XCV, p. 1, and reference therein.
 - ²T. Sakurai and H. D. Hagstrum, *Phys. Rev. B* **14**, 1593 (1976).
 - ³R. E. Schlier and H. E. Farnsworth, *J. Chem. Phys.* **30**, 917 (1959); J. J. Boland, *Phys. Rev. Lett.* **65**, 3325 (1990).
 - ⁴R. M. Tromp, R. J. Hamers, and J. E. Demuth, *Phys. Rev. Lett.* **55**, 1303 (1985); R. J. Hamers, R. M. Tromp, and J. E. Demuth, *Phys. Rev. B* **34**, 5343 (1986).
 - ⁵J. A. Applebaum, G. A. Baraff, and D. R. Hamann, *Phys. Rev.* **14**, 588 (1976).
 - ⁶D. J. Chadi, *Phys. Rev. Lett.* **43**, 43 (1979); J. Pollmann, P. Krüger, and A. Mazur, *J. Vac. Sci. Technol. B* **5**, 945 (1987).
 - ⁷R. A. Wolkow, *Phys. Rev. Lett.* **68**, 2636 (1992).
 - ⁸S. Ciraci, R. Butz, E. M. Oellig, and H. Wagner, *Phys. Rev. B* **30**, 711 (1984).
 - ⁹Y. J. Chabal and K. Raghavachari, *Phys. Rev. Lett.* **53**, 282 (1984).
 - ¹⁰K. Sinniah, M. G. Sherman, L. B. Lewis, W. H. Weinberg, J. T. Yates, Jr., and K. C. Janda, *Phys. Rev. Lett.* **62**, 567 (1989); *J. Chem. Phys.* **92**, 5700 (1990).
 - ¹¹M. L. Wise, B. G. Koehler, P. Gupta, P. A. Coon, and S. M. George, *Surf. Sci.* **258**, 166 (1991).
 - ¹²J. J. Boland, *Phys. Rev. Lett.* **67**, 1539 (1991).
 - ¹³M. P. D'Evelyn, Y. L. Yang, and L. F. Sutcu, *J. Chem. Phys.* **96**, 852 (1991).
 - ¹⁴C. J. Wu and E. A. Carter, *Chem. Phys. Lett.* **185**, 172 (1991); C. J. Wu, I. V. Ionova, and E. A. Carter, *Surf. Sci.* **295**, 64 (1993).
 - ¹⁵P. Nachtigall, K. D. Jordan, and K. C. Janda, *J. Chem. Phys.* **95**, 8652 (1991); P. Nachtigall, K. D. Jordan, and C. Sosa, *Phys. Chem.* **97**, 11 666 (1993).
 - ¹⁶U. Höfer, L. Li, and T. F. Heinz, *Phys. Rev. B* **45**, 9485 (1992).
 - ¹⁷C. C. Cheng and Y. T. Yates, *Phys. Rev. B* **43**, 4041 (1991).
 - ¹⁸K. Ueda, S. Kodama, and A. Takano, *Appl Surf. Sci.* **60/61**, 178 (1992); K. Ueda and A. Takano, *Surf. Sci.* **287/288**, 506 (1993).
 - ¹⁹H. H. Madden, D. R. Jennison, M. M. Traum, G. Margaritondo, and N. G. Stoffel, *Phys. Rev. B* **26**, 896 (1982).
 - ²⁰M. L. Knotek, G.M. Loubriel, R. H. Stulen, C. E. Parks, B. E. Koel, and Z. Hussain, *Phys. Rev. B* **26**, 2292 (1982).
 - ²¹H. Akazawa, *Phys. Rev. B* **51**, 7314 (1995).
 - ²²L. Hellner, L. Phillippe, G. Dujardin, M. J. Ramage, M. Rose, P. Cirkel, and P. Dumas, *Nucl. Instrum. Methods Phys. Res. B* **78**, 342 (1993).
 - ²³J. J. Boland, *Phys. Rev. B* **44**, 1383 (1991).
 - ²⁴This was verified as follows. We biased the sample by 5 V and found the 20- μ s peak (1.25 eV) to move to 6.24 eV, whereas the 53- μ s peak disappeared. This is in contrast to the H⁺ spectrum, where the sample bias shifted both 26- and 53- μ s peaks to higher-energy positions.
 - ²⁵J. D. Buck, D. H. Parker, and D. W. Chandler, *J. Phys. Chem.* **92**, 370 (1988); E. Xu, A. P. Hickman, R. Kachru, T. Tsuboi, and H. Helm, *Phys. Rev. A* **40**, 7031 (1989).
 - ²⁶W. S. Verwoerd, *Surf. Sci.* **108**, 153 (1981).
 - ²⁷Two-hole final states were also evoked in the ESD studies of H⁺ ions from Ni surface [C. F. Melius, R. H. Stulen, and J. O. Noell, *Phys. Rev. Lett.* **48**, 1429 (1982)].
 - ²⁸The Si-H bands that have higher local density of states than *D*₁ are located at ~5 eV below the valence-band maximum. To create a two-hole state in these bands would require 4–5 photons. One possible reason that the H⁺ desorption is not likely to originate from these Si-H bands is that when the laser fluence is high enough for these multiphoton process to be efficient, all the hydrogen atoms on the surface will have desorbed in the form of H₂ due to laser heating of the surface.
 - ²⁹W. L. Clinton, *Surf. Sci.* **112**, L791 (1981).
 - ³⁰Z. Miskovic, J. Vukanic, and T. E. Madey, *Surf. Sci.* **141**, 285 (1988).
 - ³¹J. W. Gadzuk, *Phys. Rev. B* **14**, 2267 (1976).
 - ³²M. Schmeits, A. Mazur, and J. Pollmann, *Phys. Rev. B* **27**, 5012 (1983).
 - ³³P. Koke and W. Monch, *Solid State Commun.* **36**, 1007 (1980).
 - ³⁴R. M. Broudy, *Phys. Rev. B* **1**, 3430 (1970).