

Hydrogen-desorption kinetic measurement on the Si(100)-2×1:H surface by directly counting desorption sites

Deng-Sung Lin* and Ru-Ping Chen

Institute of Physics, National Chiao-Tung University, 75 Bo-Ai Street, Hsinchu 300, Taiwan

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The desorption kinetics of hydrogen from the Si(100)-2×1:H monohydride surface was investigated by means of variable-temperature scanning-tunneling microscopy (STM) in the temperature range between 590 and 668 K. By directly counting the number of desorption sites in the STM images for various annealing time at several temperatures, an activation barrier of $E_d = 2.22 \pm 0.20$ eV and a pre-exponential factor of $\nu_d = 3.4 \times 10^{13 \pm 0.3} \text{ s}^{-1}$ for the H₂ recombinative desorption are deduced. The sequential images acquired in real times show that hydrogen desorbs in a random manner and the interaction between two neighboring paired dangling bond sites is repulsive. [S0163-1829(99)51036-9]

Thermal desorption is an important fundamental surface process.¹ When the substrate of an adsorbed layer of atoms or molecules is heated, a surface species may desorb upon receiving thermal excitation. The thermally activated nature of desorption implies that the rate equation for first-order kinetics follows an Arrhenius form: $d\theta/dt = -R_d\theta = -\nu_d \exp(-E_d/k_B T)\theta$, where R_d , θ , E_d , ν_d , and T denote desorption rate, coverage of surface species, desorption energy, pre-exponential factor, and temperature, respectively. The key kinetic parameter, E_d , is generally deduced from temperature-programmed desorption spectroscopy (TPD) used for its technical simplicity. However, the Redhead procedure used to analyze the TPD data requires assuming a value for the second kinetic parameter, ν_d , which is associated with the attempt frequency and presumably in the order of 10^{13} s^{-1} .^{1,2} Alternatively, isothermal desorption and laser-induced thermal desorption (LITD) are applied to monitor the decrease in the coverage of the surface species as a function of time.³⁻⁵ In limited applications on certain substrate/adsorbate systems, the sum-frequency generation (SFG) method or its inherent second-harmonic generation (SHG) is applied to measure accurately the relative amount of resident surface species, which may directly adsorb incident photons from a tunable laser.⁶ Because thermal desorption, LITD, and SHG data are collected under isothermal conditions, they provide more straightforward data to obtain desorption kinetic parameters than are TPD data.

Scanning-tunneling microscopy (STM) can provide atomic-scale images of a variety of adsorbate/surface systems. In particular, the variable-temperature (VT) versions enable viewing the surface as the rates of specific processes are varied by altering the sample temperature; therefore, it is ideally suited to studies of kinetic processes on surfaces. So far, many surface kinetic parameters, such as barriers of individual atom/molecule diffusion,^{7,8} dimer diffusion,⁹ kink diffusion,¹⁰ and thermal dissociation have been obtained by VT STM.¹¹

In this paper, we present the STM measurements of hydrogen isothermal desorption kinetic parameters on the Si(100)-2×1:H surface. The Si(100)-2×1:H surface has been a model system for studying the adsorption and desorp-

tion of molecules on semiconductor surfaces.^{3-6,12-14} Also, hydrogen plays an extremely important role in semiconductor processing chemistry. Many species such as H₂O, PH₃, and Si₂H₆ chemisorb dissociatively on silicon surfaces and form Si-H bonds and, therefore, hydrogen desorption is often the rate-limiting step in the chemical-vapor deposition processes because hydrogen passivates the silicon surface dangling bonds (DB's).^{15,16}

Hydrogen desorption from the Si(100)-2×1:H monohydride surface has already been well characterized in terms of the barrier to desorption and the first-order dependence of the rate on hydrogen coverage.^{4,6,12,17} A recent STM study observed only paired DB sites on the annealed Si(100)-2×1:H surface and suggested that hydrogen desorption involved direct recombination of hydrogen atoms from the dimer units of the monohydride surface.¹² In addition, there currently exist large different reported kinetic parameters for the desorption of hydrogen from the Si(100)-(2×1):H system. Employing LITD and isothermal desorption, Siniah *et al.* measured a desorption energy of 1.96 eV and a pre-exponential factor of $2.2 \times 10^{11} \text{ s}^{-1}$.⁵ Wise *et al.*, using the same method, measured 2.53 eV with a pre-exponential factor of $5.5 \times 10^{15} \text{ s}^{-1}$.⁴ Höfer *et al.*, employing the SHG technique, reported values of E_d and the first-order pre-exponential factor to be 2.48 eV and $2 \times 10^{15} \text{ s}^{-1}$, respectively for hydrogen coverage exceeding 0.1 ML (1 ML = 6.8×10^{14} atoms/cm²).⁶ It is generally accepted that the values measured by Wise *et al.* and Höfer *et al.* are more appropriate.¹⁷ By counting the number of desorption sites on the STM images as a function of annealing time at various temperature, we obtained an activation barrier of $E_d = 2.22$ eV and a pre-exponential factor of $\nu_d = 3.4 \times 10^{13 \pm 0.3} \text{ s}^{-1}$. The sequential images acquired in real time show that hydrogen desorbs in a random manner.

In this study, experiments were performed in a vacuum chamber with a base pressure of 7×10^{-11} Torr, using a variable-temperature STM. The Si(100) samples (B-doped, 10 Ω cm) were mounted on holders made of Ta, Mo, and ZrO ceramic plates. Both the sample holders and the samples were out-gassed for 12 h at 900 K. The starting Si(100)-2×1 surfaces were prepared by direct Joule heating at ~1400 K

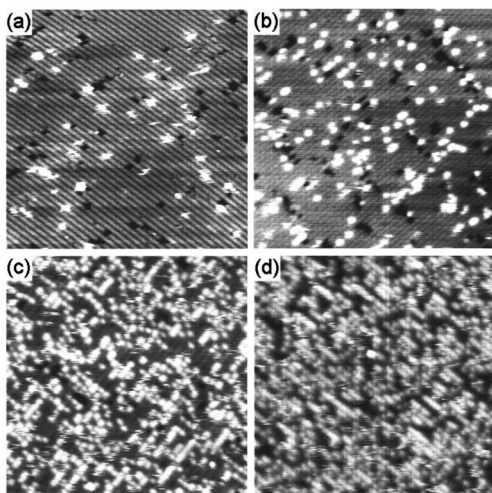


FIG. 1. (a) Filled-state STM image taken at 590 K for Si(100)-2 \times 1:H monohydride surface. (b)–(d) Filled-state STM images for thermal desorption measurement sequence after the surface shown in (a) is heated and maintained at 611 K for 50, 220, and 362 min, respectively. The scanned areas are 300 \times 300 Å². The bright features are DB sites.

with subsequent radiation quenching. An infrared optical pyrometer was used to measure the sample temperature between 525 and 1075 K. After calibrating against measurement from a thermal couple on an identical test sample, the estimated systematic error is about ± 10 K. Atomic hydrogen was produced by backfilling the chamber in the presence of an 1800-K tungsten filament, which is about 5 cm away from the sample. Typical dosing time to obtain the Si(100)-2 \times 1:H surface is 200 s at a hydrogen pressure of 1×10^{-6} Torr. To minimize interactions between the surface and the tip, the surface was normally scanned at -1.5 – -2 V sample bias and <0.3 nA tunneling current. In these tunneling conditions, the tip does not disturb the surface species in the experimental temperature range.¹³

Dosing atomic hydrogen on a clean Si(100)-2 \times 1 surface at 590 K yields a Si(100)-2 \times 1:H surface composed of symmetric monohydride dimer units [see Fig. 1(a)]. The clean Si(100)-2 \times 1 surface consists of rows of dimers, in which the two Si atoms establish a strong σ bond and a weak π interaction between their DB's.¹² Upon adsorption of hydrogen atoms, the π bond in a bare Si dimer is replaced by two strong Si-H σ bonds while the dimer structure remains intact.¹² As Fig. 1(a) shows, the Si(100)-2 \times 1:H surface prepared in the above-mentioned manner typically exhibits random apparent protrusions of less than 1%. Some bright sites appear stable and centered along the dimer rows; they can be attributed to the remaining unreacted paired Si DB sites where the π -bonded states have higher efficiency of electron transfer between the tip and the surface. In Fig. 1(a), there are also fluxional sites. The fluxional sites vary in their apparent size but are confined to a single dimer row. As shown in a previous detailed investigation by McEllistrem, Allgeier, and Boland,¹³ paired DB's may dissociate as hydrogen atoms hop to adjacent dimers at elevated temperatures; and the fluxional features are Si dimers that contain a single H atom and an unpaired DB.

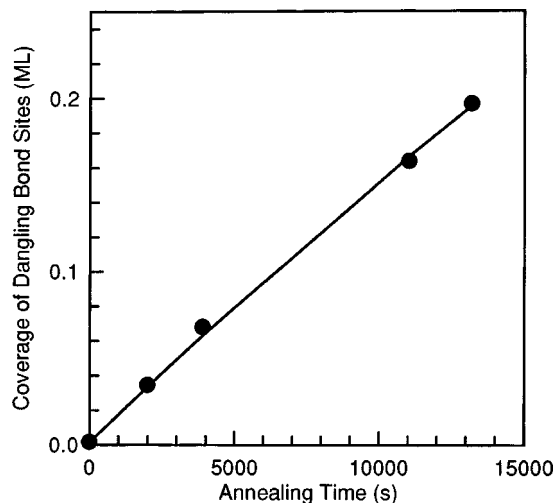


FIG. 2. Coverage of DB sites counted from STM images as a function of annealing time at 611 K. The desorption rate R_d is obtained by fitting the data to $1 - \exp(-R_d t)$.

At 590 K, either on the same areas or different ones, the coverage of DB sites remained about the same over several hours of STM observation, indicating that the scanning does not induce H₂ desorption; the desorption rate is insignificant at this temperature. As the substrate temperature was stepped up to 611 K, the DB (desorption) sites increased their population as shown in Figs. 1(b), 1(c), and 1(d). The number of DB sites on the surface as a function of annealing time for each scan was then counted. The corresponding coverage of the DB sites was plotted in Fig. 2. Only data points for low coverage are shown in Fig. 2 because a ball-like feature of a DB site in the STM image covers an area of nearly three monohydride dimers, causing difficulty in accurately site counting at high coverage. Following the first-order rate equation and Poisson statistics, the data in Fig. 2 is fit to $1 - \exp(-R_d t)$, where t is the annealing time. The only fitted parameter is R_d . For higher temperatures, significant coverage of desorption takes place before the thermal drift resulting from raising sample temperature is much reduced; therefore, real-time imaging is inappropriate for accurate statistics. To observe H₂ desorption, the H-terminated surface is typically heated up from room temperature to a certain temperature for a period of time; STM is then performed after the sample cools back to room temperature. In this conventional preparation, the sample experiences a large temperature ramp. Thus the annealing time for the “isothermal” desorption cannot be precisely determined. To resolve these difficulties, the substrate is first maintained at $T_i = 590$ K for a period of time (0.5 h typical), heated to various desorption temperatures, T_f (622–668 K) for time t , and cooled back down to T_i for imaging. Because of the small difference between T_i and T_f , the uncertainty in annealing time t for high temperature is significantly reduced. As an example, Fig. 3 shows an image obtained at T_i after 210 s anneal at $T_f = 668$ K. Again, the desorption rate was determined at temperatures ranging from 622 to 668 K by counting desorption sites. Figure 4 shows the plot of $\ln(R_d)$ as a function of reciprocal temperature and its linear fit. Based on Fig. 4, the apparent activation energy E_d is 2.22 ± 0.20 eV and the pre-exponential factor ν_d is $3.4 \times 10^{13 \pm 0.3} \text{ s}^{-1}$. These values are

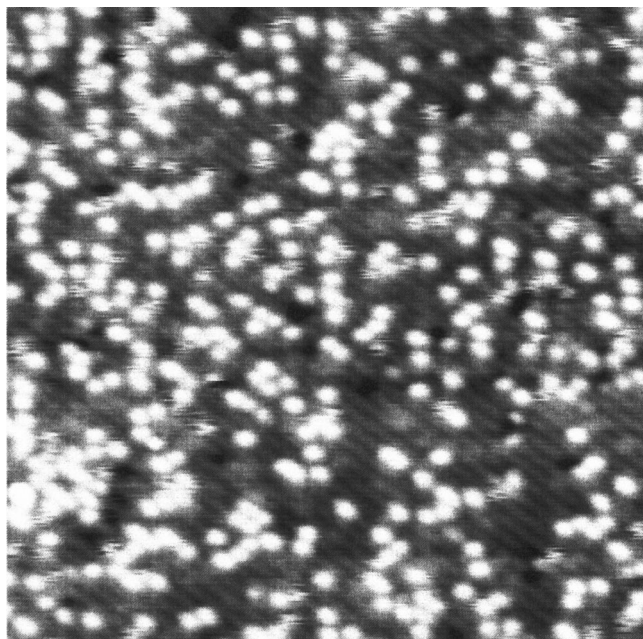


FIG. 3. Filled-state STM image of the Si(100)-2 \times 1:H obtained at $T_i=590$ K after 210 s of H₂ desorption at $T_f=668$ K. Area shown is 300 \times 300 Å².

smaller than that obtained in recent measurements.^{4,6} The desorption rates achievable by STM measurement (Fig. 4) span two orders of magnitude. The number of sampling in an STM image of typical 300 \times 300 Å² size is large (about 3000), yielding excellent statistics. Therefore, the errors of E_d and ν_d resulted primarily from the relatively large temperature uncertainty, which resulted from large resistivity change of our silicon samples with temperature around 600 K.

In a previous STM investigation, delineated DB regions of the monohydride surface following 5-min desorption of

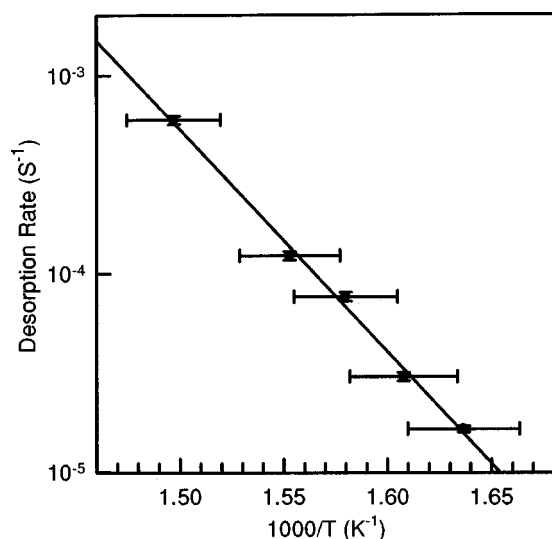


FIG. 4. Arrhenius plot of the H₂ desorption rate for the Si(100)-2 \times 1:H surface in the temperature range between 611 and 668 K. The solid line is a linear fit; its slope determines the energy barrier E_d and the intercept is the pre-exponential factor ν_d for the thermally activated H₂ desorption. The horizontal error bars indicate the estimated temperature uncertainty.

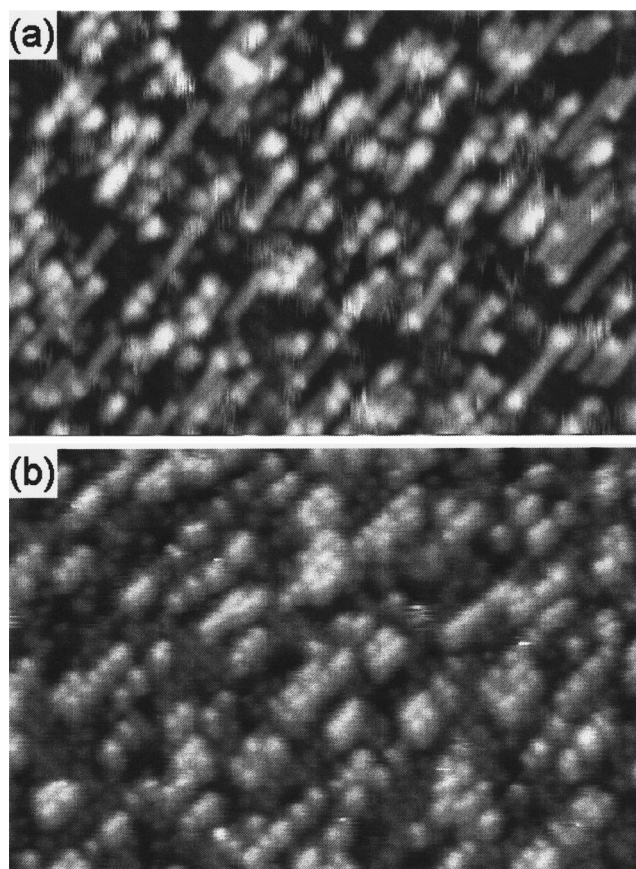


FIG. 5. STM images obtained at 622 K for (a) the H-terminated surface with 1D monohydride trains prepared by exposing a clean Si(100)-2 \times 1 surface to 15-L disilane at 643 K to form 1D 2 \times 1:H trains and (b) the same surface after 230-min annealing at 622 K. Note that the paired DB's on the 1D trains are prevalently separated by two lattice units. Areas shown are 300 \times 200 Å². The image (a) has been rotated by 90° so that its dimer row direction is aligned with that in (b) for easier comparison.

about 60% of surface hydrogen at 710 K were observed to be separated from hydrogenated ones. This observation led to speculation whether the spatial distribution of DB sites depends on the desorption rate, if the hydrogen desorbs in a regular fashion, or whether desorption occurs in a random manner followed by a rearrangement to yield the observed structure. In our real-time desorption experiment, however, regular distribution of paired DB's has never been observed at low DB coverage (<0.25 ML). Therefore, it is likely that hydrogen desorbs in a random manner, at least in the low coverage regions. As mentioned above, paired DB's are quite mobile at >590 K and could nucleate and form clusters or islands. Nevertheless, paired DB sites such as those in Figs. 1(b) and 3 remained randomly distributed over the surface without apparent nucleation throughout prolonged real-time observation. This suggests two possibilities: (1) There is a small attractive interaction between two individual paired DB's. As suggested by Boland, a paired DB may induce a nonlocal strain field which effectively attracts another nearby paired DB.^{12,13} However, entropy at high temperature drives paired DB's to separate. (2) There is repulsive interaction between two paired DB's. This possibility seems evident since, as suggested in the STM observation,

paired DB's do not accommodate each other upon encountering. However, the spatial distribution of paired DB's on Si(100)-2×1:H alone offers no conclusion about the nature of the interaction of paired DB's in that they are free to move over the entire surface. If the entropy factor can be largely eliminated by limiting the freedom of paired DB's, the nature of the interaction between paired DB's can be determined. This can be accomplished by partially desorbing H₂ from one-dimensional (1D) 2×1:H monohydride trains, as demonstrated in Fig. 5. The 1D 2×1:H trains can be obtained on a Si(100) surface by dosing 15-L disilane at 643 K, as shown in Fig. 5(a). A recent STM study by Wu and Lin showed that the surface prepared in this manner is H terminated with 1D 2×1:H monohydride trains running perpendicular to the dimer rows of the substrate.¹⁵ Obtained after annealing this H-terminated surface for 230 min at 622 K, as Fig. 5(b) shows, those paired DB's on the 1D trains are prevalently separated by more than two lattice units at this coverage. In contrast, two paired DB's immediately adjacent to each other are rare. This micrograph strongly suggests that the interaction between two paired DB's on the same dimer row is, in fact, repulsive. This behavior is not unexpected, because the electrons between two neighboring paired DB's intuitively have steric repulsive Coulomb interaction. De-

spite their subtle differences, the conclusion drawn here for 1D dimer trains is likely applicable to those on the flat surface since DB interaction on the flat Si(100) surface involves predominantly the same dimer row. When the desorption of surface hydrogen exceeds 50% on the Si(100)-2×1:H surface, clusters and/or patches of DB pairs will certainly form for obvious statistical reasons, as confirmed in Ref. 12. However, the exact thermodynamically favorable spatial distribution of DB pairs at high coverage, complicated by possible effect of nonlocal strain fields,¹² is unclear.

In summary, we have investigated the desorption of H₂ molecules of the Si(100)-2×1:H surface at temperatures from 590 to 668 K using VT STM. Simply by counting the number of desorption (DB) sites in the STM images as a function of time, we extracted the key parameters of the H₂ desorption kinetics. In this method, the number of sampling sites is large (several thousands) and measured desorption rates span more than two orders of magnitude, yielding excellent statistics. The VT STM measurement reported here demonstrated that the kinetic process of desorption can be quantitatively studied in real space and real time.

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*Electronic address: dslin@cc.nctu.edu.tw

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