

Adsorption and abstraction of atomic hydrogen on the Si(110) surfaces

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The abstraction reaction of D adatoms by H atoms have been investigated on the Si(110) surfaces. The direct abstraction to form HD molecules obeys a second-order rate law in D coverage θ_D . On the other hand, the indirect abstraction to form D₂ molecules obeys a fourth-order rate law in θ_D . In addition to the direct abstraction, indirect abstraction to form HD molecules is also included due to piled H adatoms during H exposure. It is found that the indirect abstraction is promoted on the surfaces saturated with dideuterides, suggesting that dideuterides (dihydrides) play a significant role in the indirect abstraction paths. The kinetics of the abstraction reactions on the Si(110) surfaces look similar to those on the Si(100) surface. However, the delayed D₂ desorption exhibits time profiles different from those on the Si(100) surfaces.

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I. INTRODUCTION

Modern electronic device technology relies on reaction of hydrogen with silicon surfaces. Taking plasma-enhanced Si chemical vapor deposition for solar cells, for instance, it is known that H atoms in gaseous plasma play a significant role in controlling the quality of grown amorphous [1–4] or micro crystalline Si films [5, 6]. Sticking probability of H atoms onto Si surfaces is high regardless of whether the surfaces are clean or terminated with H atoms. They also abstract H adatoms, generating desorption of molecular hydrogen. By labelling surface adatoms with D atoms one can discriminate the direct abstraction of D adatoms by H atoms to form HD molecules from the indirect abstraction or H-induced recombinative desorption of D adatoms to form D₂ molecules. The former reaction has been referred to as abstraction (ABS), while the latter as adsorption-induced desorption (AID) [7].

D abstraction by H on semiconductor surfaces have been extensively studied on Si(100) [8–22] and Si(111) [7, 23]. In the detailed kinetic experiments the second- and fourth-order rate laws in D coverage have been found for the ABS and AID reactions, respectively [15, 17, 18]. To reconcile these unexpectedly higher reaction order Hayakawa et al. [17] and Khanom et al. [7] propose a hot complex (HC) mechanism rather than a hot atom (HA) mechanism [13, 23]. Here, by the HC mechanism they mean that an H atom incident to D-terminated Si surfaces is first trapped in an excited state of chemisorption potentials around a doubly occupied Si dimer DSi-SiD. In energy relaxation process, the H atom in HC recombines with one of the two D atoms of the doubly occupied Si dimer to generate HD desorption. If one of the two D atoms has been replaced with an H atom during H exposure, i.e., the core of the hot complex is HSi-SiD, D

abstraction by H is impeded in HC by the competitive H abstraction by H due to an isotope effect on the reaction [7, 15]. Thereby the observed second-order rate law can be reconciled with the HC mechanism. On the other hand, breaking of a Si dimer bond followed by formation of a dihydride is the alternative channel for energy dissipation in HC. If such a dihydride is formed at a (3×1) dihydride/monohydride domain on the (2×1) monohydride surface, the system consists of a local (1×1) dihydride phase on the (3×1) domain, which becomes thermodynamically unstable. Consequently the local (1×1) domain collapses emitting a D₂ molecule to return to the original (3×1) phase [19, 21, 22]. In this case four D adatoms in a unit cell of the (3×1) phase are related to the observed fourth-order rate law in AID [19].

D abstraction by H on Si(110) surfaces has been less studied [24], while Si(110) surfaces have attracted much attention to their clean as well as H-terminated surface structures. The bulk truncated Si(110) surface has a zigzag chain structure with a dangling bond per Si atom. Figure 1 shows such an ideal structure of H-terminated Si(110) $(1 \times 1):H$ surface. Recently, a (16×2) structure has been interested in the STM experiments [25, 26] and in the first principles calculations [27, 28], being interpreted in terms of a pair of pentagons configured with Si adatoms. Adsorption structures of H atoms on the Si(110) surface were studied by STM and IRAS [29–31]. Atomic defects on a pair of pentagons were possibly generated by H atoms [32]. Thermal desorption (TD) spectra for D₂ molecules exhibited characteristic peaks at around 700 K and 820 K [33]. The lower temperature peak was attributed to desorption from a dihydride phase, while the higher temperature peak was attributed to desorption from a monohydride phase. Both two desorption peaks were found to obey a second-order rate

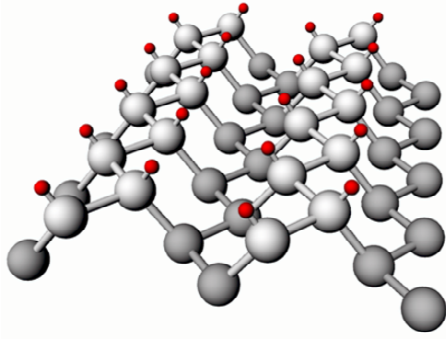


FIG. 1: Ideal bulk truncated Si(110) surface structure terminated with 1ML H (D) atoms.

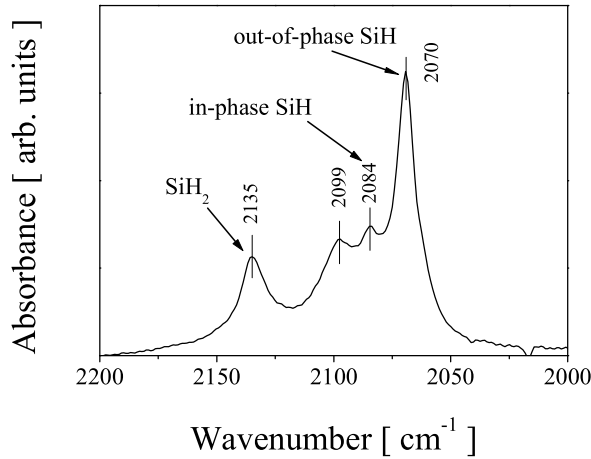


FIG. 2: Infrared absorption spectra in the Si-H stretching vibration region of the Si(110) surface recorded after 3000 L H₂ exposure at room temperature.

law. Desorption activation energies were evaluated to be 2.68 eV and 2.22 eV for β_1 and β_2 TD, respectively [33].

In this paper we study kinetic mechanism of D abstraction by H on the Si(110) surface. Surface entities that are responsible for ABS and AID reactions are elucidated by FTIR and TD spectroscopies. In detailed analysis of measured HD and D₂ rate curves, we find that the H-induced desorptions from D/Si(110) surfaces are quite nonlinear with respect to D coverage. Mechanisms of the ABS and AID reactions on the Si(110) surface are comparatively discussed with those on Si(100) surfaces.

II. EXPERIMENT

Infrared (IR) spectra of H-terminated Si(110) surfaces were obtained with an FTIR absorption spectrometer in an ultra high vacuum chamber equipped with an RHEED. IR light was introduced to the chamber through

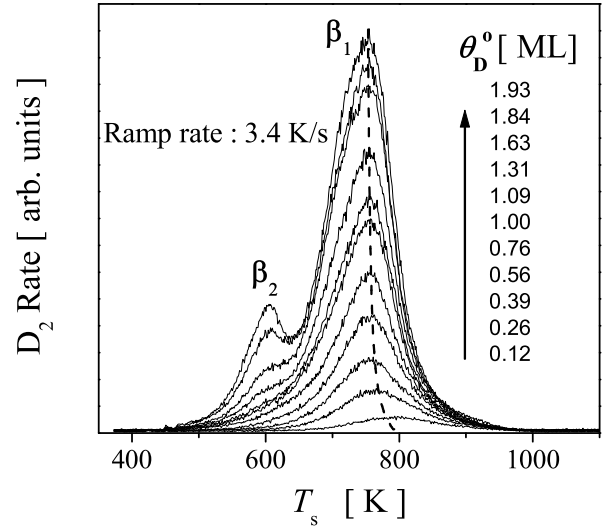


FIG. 3: D₂ thermal desorption (TD) spectra from the Si(110) surfaces as a function of initial D coverage θ_D^0 . β_2 : TD arising from the di-deuteride phase. β_1 : TD arising from the monodeuteride phase. The dashed line shows the systematic peak shift which suggests a second-order desorption kinetics. The D/Si(110) surface is prepared at 373 K.

a BaF₂ window, and was focused onto one of bevel-polished edges of the sample. The light then underwent about 70 times internal reflections until it emerged from the other end of the sample, and was finally focused onto an InSb IR detector. The resolution of the FTIR spectrometer was 2 cm⁻¹ after averaging 600 interferograms. IR spectrum measured for the clean Si(110) surface was used as a background. Deposition of H atoms onto the sample was done through thermal cracking of H₂ gas on a heated W filament [34].

Abstraction experiments were carried out in another H-surface reaction system. It consists of three differentially pumped plasma beam chambers and an UHV surface reaction chamber [14]. An atomic H or D beam with a flux of about 0.01 ML/s was generated by inductively coupled plasma discharge of H₂ or D₂ gases mixed with Ar (1:1 pressure ratio). The radio frequency (13.56 MHz) power injected to the plasma was generally 200 W. The H or D beam passes through three 3 mm diameter collimating apertures in the beam chambers. A beam chopper driven by a vacuum tight pulse motor was equipped in the second chamber of the beam system. It generates a modulated H-beam, having a 0.5 s pulse width characterized with a 0.1 s rise- and fall-time at 0.1 Hz rotation. The reaction chamber was equipped with an Ar⁺ ion gun, an Auger electron spectrometer, a quadrupole mass spectrometer, and a (*x, y, z*) precision sample manipulator. A commercially available Si(110) wafer (p-type, 10-15 Ω -cm) was cut into a 15×24×0.3 mm³ specimen and

attached to a sample holder on the manipulator. Surface temperatures (T_s) were determined from electrical resistance of the sample after calibrating with a pyrometer. The sample was cleaned by 1373 K flashing followed by annealing at 873 K for 10 minutes. Surface cleanliness was checked by AES. Both the C(KLL) and O(KLL) intensities were generally less than 1% of the Si(LVV) intensity. After annealing at 873 K, the surface was cooled to desired temperatures with 0.5 K/s cooling rate so as to ensure well ordered surface reconstruction. TD spectra were obtained under a condition of 3.4 K/s heating rate by means of a direct resistive heating.

For abstraction experiments, the clean Si(110) surface was first exposed to D atoms to prepare D-covered surface. Two different ways to prepare D-covered surfaces were employed by controlling exposure time and surface temperature: D-saturated surfaces were prepared by 5 min dosing at each temperature set for experiments of T_s dependence of abstraction. For abstraction experiments above 523 K, to minimize loss of D adatoms due to desorption before H exposure, we employed a quick heating of the sample within 1.5 seconds from the D dosing temperature of 523 K to 573 or 623 K. In this case H exposure was started coincidentally with the quick sample heating. Hence it is reminded that the D-saturated surfaces contain dideuterides before H exposure. On the other hand, 1 ML D-covered Si surface was prepared by 2 min D exposure at 523 K. Thus this surface does not contain dideuterides, and referred to as unsaturated surface, hereafter.

HD and D₂ molecules desorbed during surface exposure to the H beam were simultaneously detected with the QMS in the angle-integrated mode. Signal pulses from the QMS were fed into a multi-channel scalar (MCS, 1024 channels, dwell time of 9 ms) triggered with the rotating chopper.

To analyze HD and D₂ rate equations, rate versus t curves were converted to rate versus θ_D curves. To do this D coverages θ_D during H exposure were evaluated from

$$\theta_D = \int_t^{t_m} [R_{HD}(t) + 2R_{D_2}(t)]dt + \theta_D(t_m), \quad (1)$$

where t_m is the time when H irradiation was stopped, $R_{HD}(t)$ and $R_{D_2}(t)$ are the rate of HD and D₂ molecules at t , respectively. $\theta_D(t_m)$ was evaluated from HD and D₂ TD spectra when H irradiation was stopped [14].

III. RESULTS AND DISCUSSION

A. Surface entities

1. IR spectra

IR spectra of the H-terminated Si(110) surface were measured with an unpolarized light. The RHEED patterns showed a well ordered (16×2) structure on the clean

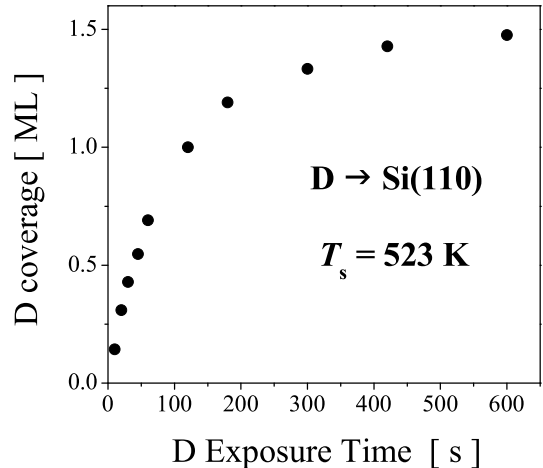


FIG. 4: D uptake curve measured at 523 K on the clean Si(110) surface.

Si(110) surface, and diffuse (1×1) structure on the surface terminated with H atoms after 3000 L H₂ exposure. The IR spectrum measured on the H-terminated surface at room temperature was plotted in Fig. 2. There are four absorption peaks at 2070, 2084, 2099 and 2135 cm⁻¹. The intense 2070 and 2084 cm⁻¹ peaks are attributed to the out-of-phase and in-phase stretching vibration of monohydrides, respectively. The 2099 cm⁻¹ peak could be due to the Si-H stretching vibration originated from surface adatoms or hydrides at defect sites [31]. The peak at 2135 cm⁻¹ can be attributed to dihydrides [35]. According to Shinohara et.al. [31], dihydrides on the Si(110) surfaces are formed by breaking either the topmost -SiH-SiH- zigzag chain or the Si-Si bond between the first and second Si layers. As will be discussed in later subsections, the dihydrides may play a key role in the AID reaction.

2. TD spectra

The clean Si(110) surface was subjected to D atoms at 373 K to prepare D-precovered surfaces. D precoverages, θ_D^0 , were changed by controlling exposure time and determined from TD spectra. Figure 3 shows D₂ TD spectra measured on the D/Si(110) surfaces for various θ_D^0 . For $\theta_D^0 > 1$ ML, the β_2 peak around 600 K can be attributed to surface dideuterides [33]. On the other hand, for a very small value of θ_D^0 such as 0.12 ML, the peak depicted as β_1 has a maximum at around 800 K, being attributed to the surface monodeuterides. The β_1 peak shifted to a lower temperature region (~ 750 K) with increasing θ_D^0 as shown by the dashed curve in Fig. 3, suggesting that the TD rate law is of second-order [33]. The β_1 peaks in Fig. 3 look asymmetric in spectral line shape. Two different types of monohydrides could be involved there

[33].

One should note that no α -peak at around 960 K [24] is found in the TD spectrum of Fig. 3, suggesting no D atoms are taken into the subsurface layers. This was also reported in the literature [33]. D incorporation into the subsurface layers could be promoted by surface roughness created by Ar^+ sputtering or by H(D)-induced surface etching.

3. Uptake curves

Prior to abstraction experiments, we measured uptake curves of D atoms on the clean Si(110) surface as a function of exposure time t at 523 K. Yield of D adatoms was determined from TD spectra measured for various exposure times. The TD spectrum having the highest intensity but no β_2 peaks were assumed to define $\theta_D = 1.0$ ML. Figure 4 shows D uptake curve measured at 523 K as a function of t . One may find that the uptake curve is about linear at the early stages of D exposure. On the other hand, the rate of D uptake tends to be level off after sufficient exposure to D atoms. This feature would suggest that the sticking coefficient of D atoms might be small on the D-terminated surfaces. However, one should remind that such a decrease in the sticking coefficient is nominal since D abstraction by D followed by quick resupply of adatoms is involved there. In later subsections, this will be clearly seen as D abstraction by H.

B. Abstraction

1. HD and D_2 rate curves

During exposure of the D/Si(110) surfaces to H atoms, HD and D_2 molecules were found to desorb from the surface. HD and D_2 rate curves measured at various T_s were respectively plotted in Figs. 5 and 6 on the D-saturated ((a)) and unsaturated ((b)) surfaces. Immediately after the start of H exposure, both rate curves step up at $t = 0$. On the D-saturated surfaces, then they decay almost exponentially with t due to loss of D adatoms via abstraction reactions. On the unsaturated surface, on the other hand, the maximum of the peak apparently lags. With increasing T_s the peak maximum shifts to the shorter time region. The T_s dependent peak shift is caused not by ABS but rather by AID occurring among D adatoms and H adatoms, since H adatoms are gradually piled up during the H exposure.

Contrasted to the HD desorptions, the D_2 desorptions exhibit a strong T_s dependence on both the saturated and unsaturated surfaces. Almost no D_2 desorptions were observed at 373 K, but D_2 desorption becomes facile at the temperature region higher than 500 K where β_2 TD is activated. For $T_s > 573$ K where β_1 TD partially occurs as shown in Fig. 3, a sharp peak appears at

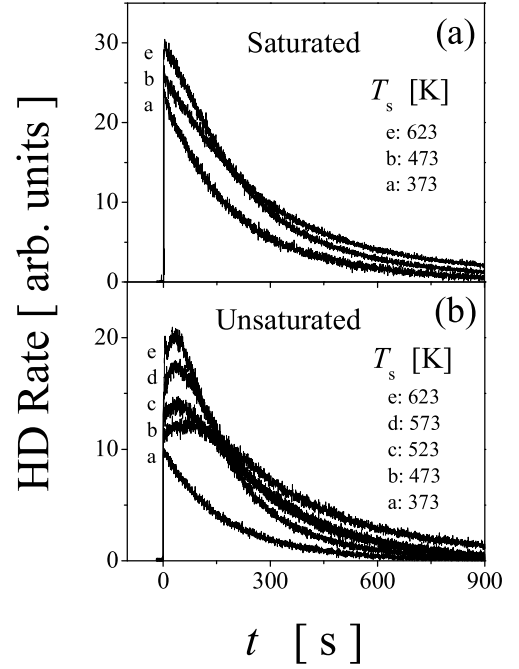


FIG. 5: Plots of HD rate curves as a function of H exposure time, t . (a): on the saturated surface, and (b): on the unsaturated surface.

around $t = 0$. This sharp peak is not due to H-induced desorption but due to nonequilibrium TD induced by the quick temperature jump. Nascent D_2 desorption induced by H can be analyzed in the time region after this sharp peak. The rates of AID were much higher than that of equilibrium TD for the temperature region studied in this work.

An induction time can be recognized for the D_2 desorption at 473 and 523 K on the unsaturated surface as shown in Fig. 6 (b). If this induction time is added by 2 min for the preparation of 1 ML precoverage, considerable dihydrides must be excessively formed on the surface after the induction time. Hence the induction time may be correlated to the H exposure time needed for the surface saturation.

2. Rate Equation Analysis

As described above, the observed feature of the H-induced D_2 and HD desorptions from the D/Si(110) surfaces looks similar to that on the Si(100) [15, 17, 18] or Si(111) [7] surfaces, where a second- and nearly fourth- or third-order kinetics have been recognized for ABS and AID, respectively. In order to estimate the AID and ABS reaction orders on the Si(110) surface, the measured D_2 and HD rate curves were first fitted to a single term rate

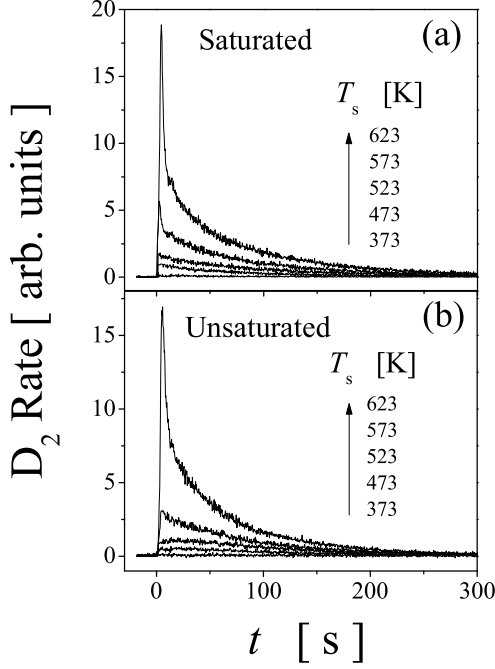


FIG. 6: Plots of D_2 rate curves as a function of t . (a): on the saturated surface, and (b): on the unsaturated surface.

equation $R_{D_2} = k\theta_D^m$ and $R_{HD} = c\theta_D^m$, where R_{D_2} and R_{HD} are the D_2 and HD desorption rate, respectively. As a result, it turned out that the fourth- and second-order rate laws are operative for AID and ABS, respectively. On the basis of the evaluated values for the reaction orders, the D_2 and HD rate equations proposed for the Si(100) surface [15] are employed for more detailed analysis of the measured rate curves. First, we construct a D_2 rate equation which consists of only AID terms. As mentioned above the AID reaction obeys a fourth-order rate law in θ_D and θ_H , which implicates four adatoms are necessary as a target of an H atom for AID. For such a mixed phase of H and D adatoms, three possible configurations for four adatoms are now referred to as 4D, 3D1H, and 2D2H configuration. Here the 4D, 3D1H, and 2D2H configurations contain four D adatoms, three D and one H adatom, and two D and two H adatoms, respectively. From the analogy to the AID mechanism proposed on the Si(100) surface [19], we tacitly assume that two adatoms among the four adatoms are on a same Si dideuteride and the other two adatoms are on two monodeuterides both adjacent to the dihydride on a zigzag Si chain (see also the discussion given in the last subsection and Fig. 12). The rate equation for the D_2 desorption is thereby written as follows,

$$R_{D_2} = \eta(t)[k_1\theta_D^4 + k_2\theta_D^3\theta_H + k_3\theta_D^2\theta_H^2], \quad (2)$$

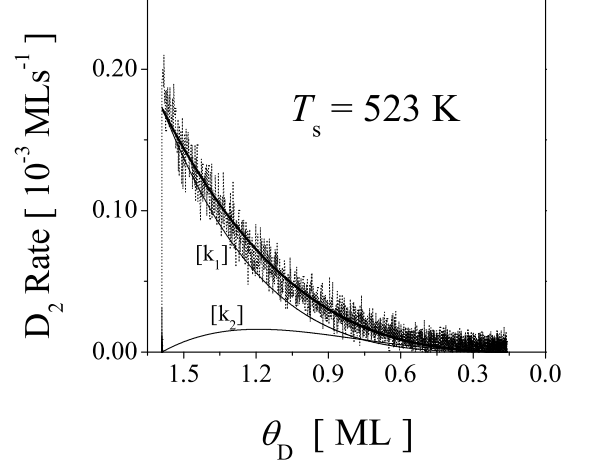


FIG. 7: Decomposition of the D_2 rate curve measured on the saturated surface at 523 K by best curve fitting to the D_2 rate equation, Eq. (2) in the text. Thin solid lines represent the decomposed AID terms in Eq. 2; $[k_1]$: $k_1\theta_D^4$, $[k_2]$: $k_2\theta_D^3\theta_H$, and thick solid line is the sum of $[k_1]$ and $[k_2]$. Here $k_1 = 2.7 \times 10^{-5} \text{ML}^{-3} \text{s}^{-1}$ and $k_2 = 2.3 \times 10^{-5} \text{ML}^{-3} \text{s}^{-1}$.

for

$$\eta(t) = \frac{1}{2}[1 + \text{erf}(\frac{\theta_{D+H}(t) - \vartheta_D^0}{w(\theta_D^0)})]. \quad (3)$$

Here, $k'_i (i = 1, 2, 3)$ are the intensity of the each term involving both the rate constant and H flux. The function $\eta(t)$ gives time evolution of surface area at which AID can take place, being related to the observed induction time for AID [7]. It shows an s-shaped curve characterized with the threshold coverage ϑ_D^0 , and the width $w(\theta_D^0)$. In case of the Si(100) surface, (3×1) dihydride/monohydride domains were considered for such a surface area [19]. We think of that even on the Si(110) surface the situation must be similar. This is because as shown in Fig. 6 (a) no induction times were present for the surfaces already saturated with dideuterides before H exposure. Hence, for the saturated surfaces we can set $\eta(t)=1.0$. On the other hand, on the unsaturated surface, the peak maximum obviously timely lags at 523 K as shown in Fig. 6 (b) or will be more clearly seen in Fig. 10. This time lag in the peak of the D_2 rate curve is caused by the delay in the surface saturation during H exposure.

Now we construct a HD rate equation. The AID channels must be involved even in the HD desorption as H adatoms are piled up during H exposure. Taking this contribution of AID into account, the HD rate equation can be written as follows,

$$R_{HD} = c_1\theta_D^2 + \eta(t)[c_2\theta_D^3\theta_H + c_3\theta_D^2\theta_H^2 + c_4\theta_D\theta_H^3]. \quad (4)$$

Here, c_i ($i=1, 2, 3, 4$) stands for the intensity which includes the H flux as well as the rate constant for each desorption pathway. The function $\eta(t)$ is again used for the AID term but not for the ABS term [7]. The 1D3H situation which contains one D and three H adatoms is newly added in Eq. (4).

In analyzing the experimental rate curves with Eqs. (2) and (4), we begin with the saturated surface where $\eta(t) = 1$. All the D_2 rate data obtained at different T_s are decomposed into three components arising from the 4D, 3D1H, and 2D2H configurations by fitting to Eq. (2). Figure 7 shows fit results of the D_2 rate curve measured at 523 K. For all the D_2 rate curves obtained on the saturated surfaces we found that the 4D configuration mainly contributes to D_2 AID. The D_2 desorption tends to decrease with decreasing number of D atoms in the configurations. The 2D2H configuration indeed hardly contributes to D_2 AID. As will be discussed later, HD AID competes with the D_2 AID for the same 3D1H or 2D2H configuration.

The HD rate curves measured on the saturated surfaces were fit to Eq. (4) under the condition $\eta(t) = 1$. Figure 8 shows results of decomposition of the HD rate curves measured at 373 K ((a)) and 623 K ((b)). At 373 K, the lowest temperature in this study, the HD desorption arises solely along the ABS path but not along any AID paths. This result is consistent with the fact that no D_2 desorptions take place at this temperature as shown in Fig. 6. On the other hand, at temperatures higher than 473 K the HD rate curves are contributed by AID. Although the HD desorptions predominantly proceed via ABS channel, the total yield along the three AID channels is approximately equal to that along the ABS channel.

In order to evaluate activation energies E_a for ABS and AID, we make Arrhenius plots of c_1 and k_1 in Fig. 9. The slopes of the curves yield $E_a = 0.06 \pm 0.01$ eV for HD ABS, and $E_a = 0.43 \pm 0.06$ eV for D_2 AID. The activation energy of 0.06 eV for ABS is just equal to that on Si(100) [18]. Such a low activation energy suggests that the desorption along ABS is really direct in nature. The physical origin of such a small activation energy in ABS may be related to vibrational excitation of the Si-D bond to be abstracted by H, since Koleske et al. [10] calculated that ABS probability becomes higher with vibrational excitation of the Si-D bonds. On the other hand, the activation energy of 0.43 eV evaluated for AID is somewhat larger than that for ABS. This value is close to the values reported for AID on the Si(100) surface (0.2 eV [18]), with a certain deviation towards a larger value, however. This will be discussed in the last subsection.

From the comparison between c_2 ($3.9 \times 10^{-4} \text{ ML}^{-3} \text{ s}^{-1}$) and k_2 ($0.23 \times 10^{-4} \text{ ML}^{-3} \text{ s}^{-1}$ at 523 K), we can extract a possible isotope effect on the HD and D_2 AID generated in the same 3D1H configuration. Since $c_2 > k_2$, HD AID takes place more efficiently than D_2 AID. Isotope effect may lead to

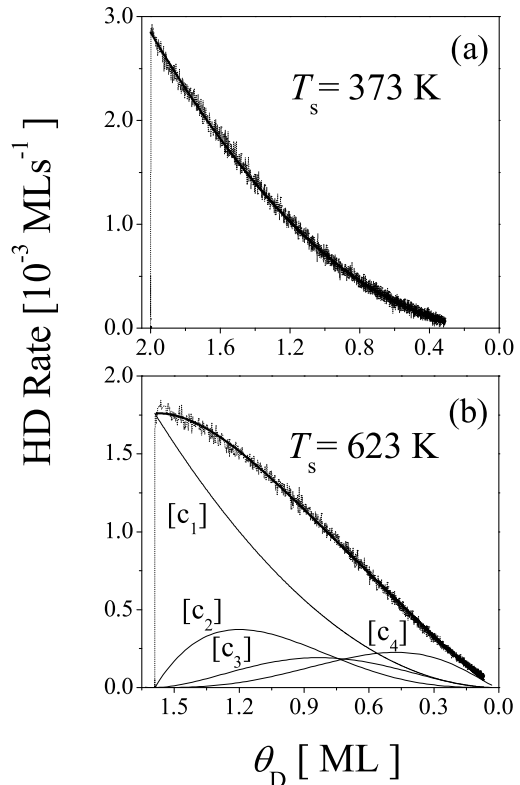


FIG. 8: Decomposition of the HD rate curves measured on the saturated surface at 373 K ((a)) and 623 K ((b)) by best curve fitting to the HD rate equation, Eq. (4) in the text. Thin solid lines are the decomposed curves by Eq. 4; $[c_1]$: $c_1 \theta_D^3$, $[c_2]$: $c_2 \theta_D^3 \theta_H$, $[c_3]$: $c_3 \theta_D^2 \theta_H^2$, $[c_4]$: $c_4 \theta_D \theta_H^3$. Here $c_1 = 5.1 \times 10^{-4} \text{ ML}^{-1} \text{ s}^{-1}$, $c_2 = 0$, $c_3 = 0$, and $c_4 = 0$ for $T_s = 373$ K, and $c_1 = 6.8 \times 10^{-4} \text{ ML}^{-1} \text{ s}^{-1}$, $c_2 = 6.3 \times 10^{-4} \text{ ML}^{-3} \text{ s}^{-1}$, $c_3 = 6.4 \times 10^{-4} \text{ ML}^{-3} \text{ s}^{-1}$, and $c_4 = 6.1 \times 10^{-4} \text{ ML}^{-3} \text{ s}^{-1}$ for $T_s = 623$ K. Thick solid line is the sum of the four decomposed curves $[c_1]$, $[c_2]$, $[c_3]$, and $[c_4]$.

a preferred association between lighter adatoms than heavier one due to quantum effects on, e.g. potential energy barriers which could be lowered by an amount of zero-point vibrational energy, tunneling probabilities through reaction barriers, or attempting frequency factors for access to transition states. Such a quantum effect on nuclear displacement predict that the lighter atom can be superior to the heavier one for such a transition from atomic to molecular state.

In contrast to the saturated surfaces, D_2 suggesting that the TD rate law is of second-order [33]. and HD rate curves obtained on the unsaturated surfaces are characterized with induction times. They are again analyzed with Eqs. (2) and (4), taking the contribution from $\eta(t)$ into account. Considering the slow D uptake after the 1 ML D coverage as plotted in Fig. 4, the total

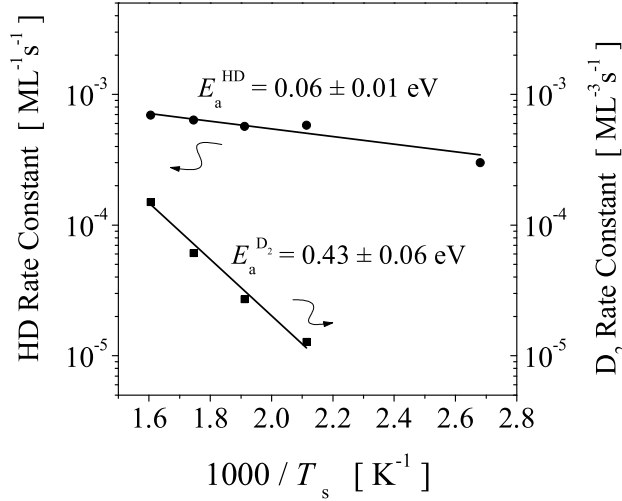


FIG. 9: Arrhenius plot of HD and D₂ desorption rate constants, c_1 for ABS and k_1 for AID determined by the best curve fitting method for the rate curves obtained on the D saturated Si(110) surface. The evaluated activation energies are written in the figure.

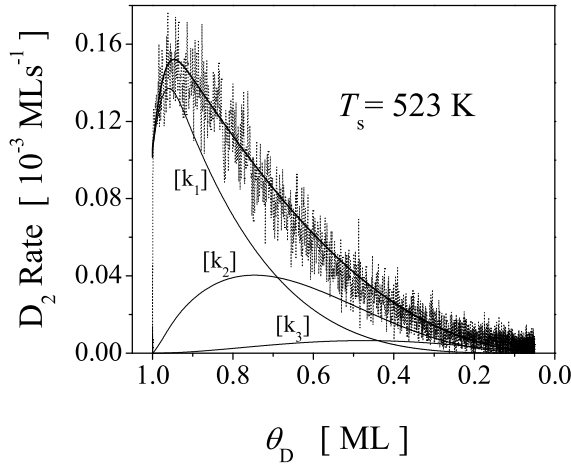


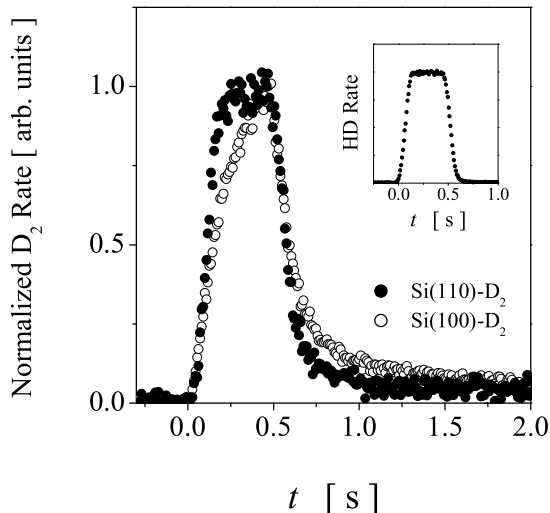
FIG. 10: Decomposition of the D₂ rate curve measured on the unsaturated surface at 523 K by best curve fitting to the D₂ rate equation, Eq. (2) in the text. Thin solid lines represent the decomposed AID terms in Eq.(2); $[k_1]$: $k_1\eta\theta_D^4$, $[k_2]$: $k_2\eta\theta_D^3\theta_H$, $[k_3]$: $k_3\eta\theta_D^2\theta_H^2$, and thick solid line is the sum of the three curves $[k_1]$, $[k_2]$ and $[k_3]$. Here $k_1 = 1.7 \times 10^{-4} \text{ML}^{-3} \text{s}^{-1}$, $k_2 = 3.0 \times 10^{-4} \text{ML}^{-3} \text{s}^{-1}$, and $k_3 = 0.6 \times 10^{-4} \text{ML}^{-3} \text{s}^{-1}$. The values of parameters of $\eta(t)$ are 0.013 ML for $\omega(\theta_D^0)$ and 0.998 ML for ϑ_D^0 .

H and D coverage under H exposure was assumed to increase linearly with t on the unsaturated surfaces, i.e., $\theta_{H+D} = at + 1.0$, where a is the proportional constant and evaluated from θ_{H+D} at 900 s by measuring H₂, HD and D₂ TD spectra. Figure 10 for D₂ molecules shows results of the best curve fit to Eq. (2). The delayed peak of the D₂ rate curve measured at 523 K can be reproduced with $\eta(t)$ for the values of 0.013 ML for $\omega(\theta_D^0)$ and 0.998 ML for ϑ_D^0 . The induction time for AID is discernible for the 4D configuration or the curve $[k_1]$ in Fig. 10. At the beginning of H exposure the surface does not contain any dihydrides. As was discussed above, AID requires presence of dideuterides or dihydrides such as -DSiD- or -DSiH-. For $\theta_D^0 = 1.0$ ML, building up such dihydrides on the surface is done at the initial stages of H exposure, giving rise to the induction time. This is also the case for HD AID since as shown in Fig. 5 (b) a clear peaking at $t > 0$ can be seen in the measured rate curves.

3. Time Response

In order to know dynamical behavior of the ABS and AID reactions, we measured time response of HD and D₂ molecules to the modulated H beam. The D-saturated Si(110) surface was exposed to the modulated H beam with 0.5 s on- and 9.5 s off-time at 573 K. Figure 11 shows the measured transient desorption of D₂ and HD (inset) molecules. Desorption of D₂ is noted to be fast since its line shape is more or less similar to the incident H impulse (not shown). However, the time profile shows a somewhat slow rise and a tailing. This is obvious in comparison with the time profile of HD molecules which is quite prompt as shown in the inset to Fig. 11. The fast desorption of HD molecules implicates that the main HD desorption occurs along the ABS path, consistent with its direct nature as confirmed in the extremely low activation energy of 0.06 eV as determined in Fig. 9. Therefore, it is concluded that while the ABS process is fast, the AID process comprises from both a fast and a slow channel.

Taking into account the second-order kinetics in θ_D and the prompt desorption of HD molecules, likely to the case on the Si(100) or Si(111) surfaces, the HC mechanism may be invoked to play a role in the ABS reaction. Figure 12 shows a model of the HC on the Si(110) surface to illustrate the ABS. To explain not only the ABS but also the AID process, we take a surface mixed with di- and monodeuterides. Since structure of dideuterides(dihydrides) on the Si(110) surface has not been established, we here tacitly assume that dihydrides are formed in the backbonds of zigzag Si chains. The local structure of -DSi-SiD- is similar to a doubly occupied Si dimer DSi-SiD on Si(100) surfaces. An incident H atom is first trapped in an excited state of vibration in the chemisorption potential at a cell of -DSi-SiD-. During



suggesting that the TD rate law is of second-order [33].

FIG. 11: Plots of transient D_2 desorption induced by the pulsed H beam at 573 K. The transient desorption of D_2 molecules on the Si(100) surface [21] is also replotted for comparison. The rising and tailing parts of the two curves are different. The inset shows the HD desorption rate on the Si(110) surface. The ABS reaction is quite prompt in nature.

energy relaxation process, the H atom in the HC abstract one of the two D adatoms to generate HD ABS. If one of the two adatoms is H, the H atom of the HC may preferentially abstract the H adatom rather than the other D adatom because of an isotope effect. Therefore, to generate HD ABS the target must be bonded with two D adatoms, which causes the second-order kinetics with respect to θ_D . The lifetime of the vibrationally excited state determine reaction time for ABS, being expected shorter than a few ns [36]. If ABS is skipped in the energy relaxation, the Si-Si bond or a Si backbond may be broken to make a dihydride, which would play a role in AID as will be discussed below.

Generation of AID along the fast and slow paths has been also found on the Si(100) surface [19, 21, 22]. The transient desorption of D_2 molecules measured on the Si(100) surface [21] is replotted in Fig. 11 for comparison. One may notice that on the Si(110) surface, the contribution from the slow component is relatively smaller than that on the Si(100) surface. As was reviewed in the Introduction, AID on the Si(100) surface exclusively occurs on the (3×1) dihydride/monohydride domains which can be built up by H adsorption even in the temperature range for β_2 TD [19, 21, 22]. The fast AID on Si(100) was related to a local phase transition from a (1×1) dihydride phase to a (3×1) dihydride/monohydride phase on the (2×1) monohydride surface. On the other hand, the slow AID was related to a phase transition from a (3×1)

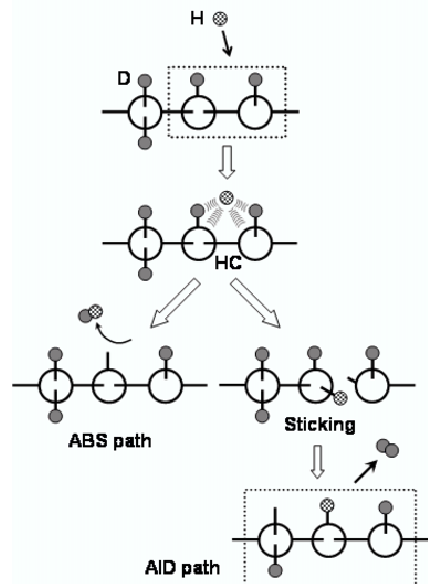


FIG. 12: Schematic illustration of the hot complex (HC) mediated ABS and AID mechanisms. The D/Si configuration is schematically drawn (side view) for the mixed phase with di- and mono-deuterides. An incident H atom is bounded in a chemisorption potential to form HC. The cell of the HC consists of a pair of adjacent -DSi- units in a zigzag Si chain. The H atom of the HC interacts with neighboring D adatoms as well as Si atoms. During energy relaxation the H atom abstracts a nearby D adatom to generate HD ABS. Breaking the Si-Si bond in the zigzag chain or the backbonds is an alternative energy relaxation path for the HC. It results in locally high density of dideuterides, from which a D_2 molecule is emitted, generating the fast AID.

dihydride/monohydride phase to a (2×1) monohydride phase [22]. We invoke the same mechanism, i.e., the AID on the Si(110) surface also occurs at such a site where β_2 TD can occur. A possible kinetic mechanism to reconcile the fourth-order rate law is such that an incident H atom break a Si-Si bond of -DSi-SiD- unit in a zigzag Si chain, of which adjacent sites are occupied with a dideuteride (see Fig. 12), i.e.,



Sticking of an H atom to the monodeuteride results in a locally high density of dihydrides (dideuterides). If such a local system with excessively high density dihydrides is thermodynamically unstable, it returns to the original phase by emitting a molecule. This process could give rise to the fast AID. If the temperature is in contrast low enough that such high density dihydride phase is thermodynamically stable, the fast AID cannot result. This is indeed recognized in the no occurrence of AID at 373 K as described in the previous subsection.

The activation energy for the fast AID does not necessarily mean that it stems from the D_2 desorption process but rather means that it comes from the H sticking process to monodeuterides [7]. In this context, the some-

what larger activation energy of 0.43 eV evaluated in the previous subsection may suggest that sticking to Si monodeuterides on the zigzag Si chains is more difficult in comparison to the Si(100) surfaces. This could be caused by the less strained zigzag Si chains compared with the highly stressed Si dimer bonds on the Si(100) surfaces.

The slow AID may be related to β_2 TD [21, 22]. The β_2 peak appeared in Fig. 3 is a bit smaller in its intensity in comparison to the Si(100) surface. On the Si(110) surface, if it is related to such a conventional β_2 TD, the slow AID may be less efficient in comparison to the Si(100) surface. The observed second-order rate law suggests that β_2 TD requires diffusion of dihydrides along or across the zigzag Si chains to make an adjacent pair of dihydrides. To date, however, detailed mechanism of β_2 TD has not been given, yet. Particularly, local configuration of dihydrides that is responsible for β_2 TD is unclear. In order to completely understand the mechanism of slow AID we have to wait for more detailed knowledge on the β_2 TD on the Si(110) surface.

IV. SUMMARY

We studied the reactions of H(D) atoms with the Si(110) surface. IR and TD spectra showed presence of dideuterides as well as monodeuterides. We measured

D abstraction by H atoms on the D-saturated and unsaturated Si(110) surfaces for various temperatures. HD and D₂ molecules were recognized as abstracted products. The HD molecules were produced either by a direct abstraction (ABS) or by an adsorption-induced desorption (AID), while D₂ molecules were produced exclusively through the AID path. The ABS was governed by a second-order rate law in θ_D . On the other hand, the AID followed a fourth-order rate law in θ_D . Even in the HD desorption, AID channels were involved because of coadsorption of D and H adatoms during exposure. We find that AID is promoted by dideuterides, suggesting that dideuterides (dihydrides) play an essential role in AID. Hence, the kinetics of the abstraction reactions on the Si(110) surfaces looked similar to those on the Si(100) surface. The measured HD and D₂ rate curves were analyzed with rate equations that include a second-order ABS and three fourth-order AID terms. We measured a time response of the HD and D₂ desorptions under the surface exposure to a pulsed H beam. We found that the HD ABS is prompt, but the D₂ AID consists of a slow process as well as a prompt one. Possible kinetic mechanisms for ABS and AID on the Si(110) surface were comparatively discussed with those on the Si(100) surface.

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