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# Modulated hydrogen beam study of adsorption-induced desorption of deuterium from Si(100)-3×1:D surfaces

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We have studied the kinetic mechanism of the adsorption-induced-desorption (AID) reaction, H + D/Si(100)→$D_2$. Using a modulated atomic hydrogen beam, two different types of AID reaction are revealed: one is the fast AID reaction occurring only at the beam on-cycles and the other the slow AID reaction occurring even at the beam off-cycles. Both the fast and slow AID reactions show the different dependence on surface temperature $T_s$, suggesting that their kinetic mechanisms are different. The fast AID reaction overwhelms the slow one in the desorption yield for 300 K$\leqslant T_s \leqslant$650 K. It proceeds along a first-order kinetics with respect to the incident H flux. Based on the experimental results, both two AID reactions are suggested to occur only on the 3×1 dihydride phase accumulated during surface exposure to H atoms. Possible mechanisms for the AID reactions are discussed. © *2004 American Institute of Physics.* [DOI: 10.1063/1.1772758]

## I. INTRODUCTION

It is known that Si surfaces are inert against dissociative adsorption of hydrogen molecules but very active towards adsorption of hydrogen atoms. Preparation of hydrogen-terminated Si surfaces generally relies on such a method as surfaces are exposed to H atoms. During surface exposure to H atoms, already adsorbed H atoms can be abstracted by gas phase H atoms, generating a molecular desorption from surfaces. This hydrogen abstraction (ABS) by gas phase H atoms is of great technological relevance to electronic device processes such as plasma-enhanced chemical vapor deposition of thin Si films.[1] So far, the kinetic mechanism of the hydrogen abstraction reactions has been extensively studied by isotopic labeling of adatoms in the system H+D/Si from an uptake[2–9] as well as from a desorption[10–19] point of view. It has been well established that the abstraction reactions observed in the desorption experiments[13,14,18,19] can be categorized either into a direct abstraction (ABS) of adatoms by gas phase atoms to form HD molecules,

$$\text{ABS:}\quad \text{H}+\text{D/Si}\rightarrow\text{HD},$$

or into an indirect abstraction or adsorption-induced desorption (AID) of surface adatoms to form $D_2$ molecules,

$$\text{AID:}\quad \text{H}+\text{D/Si}\rightarrow\text{D}_2.$$

This paper is concerned with the AID reaction.

The Si(100) surfaces saturated with H(D) atoms have different phases depending on the hydrogen coverage $\theta_{\text{H(D)}}$ as well as surface temperature $T_s$. In Fig. 1 the basic hydrogen adsorption structures on the Si(100) surface are illustrated for the ease in understanding the AID models so far proposed. The H/Si(100) surface system takes a periodic structure with a 2×1, 3×1, or 1×1 phase for the H coverage $\theta_{\text{H}}$=1.0, 1.33, or 2.0 ML [1 ML (monolayer): one H atom per Si atom], respectively. For the 2×1 monohydride phase, every Si-Si dimer is doubly occupied by H atoms, taking symmetric structure of HSi-SiH. In the 3×1 phase a row of Si dihydride $SiH_2$ is added in between two rows of HSi-SiH. In the 1×1 phase HSi-SiH dimer bonds are broken with two H atoms and every Si atom is bonded by two H atoms. According to the experiments of the low-energy electron diffraction[20,21] and the scanning tunneling microscopy (STM),[22–25] the 3×1 phase is stable only at the narrow temperature region around 400 K. As $T_s$ is raised to, say 450 K, the 3×1 phase tends to be unstable, generating molecular desorption along the $\beta_2$ channel pathway. Hence the saturation coverage becomes smaller than 1.33 ML. For 1.0 ML $\leqslant\theta_{\text{H}}\leqslant$1.33 ML the surface contains both 3×1 and 2×1 phases characterized with an antiphase domain boundary with respect to Si dimer rows.[23,24] As $T_s$ is further raised above 600 K, all the dihydride species get extinguished and then the surface becomes fully monohydrided with the saturation coverage $\theta_{\text{H}}$=1.0 ML. For a low temperature region below 400 K, on the other hand, further H irradiation leads to the 1×1 dihydride phase.[23] Generally speaking, however, such a dihydrided surface is roughened due to etching of the surface Si atoms.[25,26]

Returning our interests to the AID reaction that occurs during surface exposure to H atoms, we know that the AID reaction includes complicated chemistry between H atoms and Si surfaces. It has been found that order of the AID reaction with respect to $\theta_{\text{D}}$ is unexpectedly high, ~4 or ~3 on Si(100) (Refs. 14–16 and 18) or Si(111) (Ref. 19), respectively, contrary to the reports by Dinger, Lutterloh, and Küppers[13,17] who had deduced the value of two for the reaction order on both surfaces. Khanom, Aoki, and Rahman[19] refitted the Dinger's H induced $D_2$ rate curve measured on Si(111) and found that it can be fitted with a reaction order much higher than two but close to three. Such an unexpectedly high reaction order is never reconciled with the so-called hot atom (HA) mechanism[27–31] because it claims a second-order kinetics with respect to $\theta_{\text{D}}$. Instead, the AID

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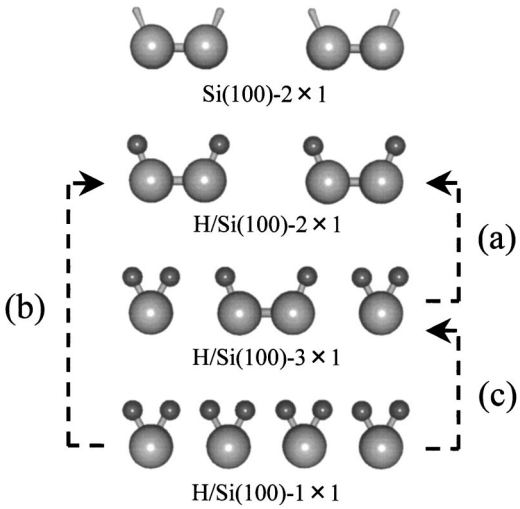


FIG. 1. Structure of the H/Si(100) surface and already proposed AID models. Various surface coverages are achieved during admission of H atoms onto the clean Si(100)-2×1 surface (top structure). (a) a H/Si(100)-3×1 dihydride phase is unstable with respect to molecular desorption to get to a H/Si(100)-2×1 monohydride phase. This is the so-called $\beta_2$ channel TPD reaction. (b) and (c) a pair of adjacent Si dihydrides are energetically unstable to emit a $H_2$ molecule, getting back either to the H/Si(100)-2×1 monohydride phase (b) or to the H/Si(100)-3×1 dihydride phase (c).

reaction may require a complicated hydrogen chemistry on the Si surfaces involving a formation of Si dihydrides which are formed during surface exposure to H atoms. Shimokawa *et al.*[14] considered that the observed high reaction order in AID is a manifestation of the Flowers' hydrogen uptake model that includes spontaneous thermal desorption of dideuterides transiently accumulated on the surface during surface exposure to H atoms.[8] Thus the AID mechanism seemed to be associated with the $\beta_2$ channel temperature-programmed desorption ($\beta_2$-TPD) from the 3×1 dihydride phase, denoted as process (a) in Fig. 1. It was indeed observed that the AID reaction is strongly dependent on $T_s$, and the AID yield plotted as a function of $T_s$ looks similar in line shape to the $\beta_2$-TPD spectrum.[16,19] Namely, the maximum of the AID yield appears around 600 K above which it rapidly decreases tending to zero at $T_s = 700-750$ K. Since the $\beta_2$-TPD reaction takes place along the second-order kinetics with respect to dihydride unit $SiH_2$,[8,32,33] a pair of neighboring dihydride units arranged via an isomerization reaction between $SiH_2$ and HSi-SiH are one of the possible structures in the $\beta_2$-TPD reaction.[8,22,34] As a possible $\beta_2$ TPD mechanism for such a pair of dihydride units, synergic (1,1)-elimination of two H atoms followed by (2,1) shift of a H atom[33] and (1,2) elimination of two H atoms[22] have been proposed.

Strictly speaking, however, the AID reaction takes place even around 400 K (Refs. 16 and 19) where the $\beta_2$-TPD rate is negligibly small. Furthermore, it is characterized with a small activation energy of 0.16 eV for the Si(111) surface[19] and 0.2 eV for the Si(100) surface,[18] which are much lower than the activation energy ~2.0 eV for $\beta_2$-TPD reaction.[33] In order to reconcile this discrepancy, Kubo, Ishii, and Kitajima[18] considered that the AID reaction occurs as thermally activated desorption from two adjacent dihydrides, leaving behind a 2×1 monohydride unit for $T_s \geqslant 480$ K and a 3×1 unit for $360\,\mathrm{K} \leqslant T_s \leqslant 410$ K, denoted as process (b) or (c) in Fig. 1, respectively. This was proposed because Boland[23] and Qin and Norton[24] had predicted that such an AID reaction occurs in the growth process of domains with a 3×1 phase on the H-terminated 2×1 Si(100) surface around 400 K. They considered that the steric stress exerted in the four repulsively interacting adjacent dihydride units formed at the domain boundaries gives rise to emission of a molecule, leaving behind a energetically stable 3×1 phase, i.e., process (c) in Fig. 1. It should be noted at this point that the so-formed HSi-SiH is shifted by a unit length of the 1×1 phase from its original position. The low activation energy observed in the AID reaction could be rationalized with such a steric stress exerted in the system of adjacent dideuteride units formed by the H atoms.[18] On the other hand, Khanom, Aoki, and Rahman[19] took a different way to explain such a low activation energy for the AID reaction: they considered that it stems from the adsorption process of the H atoms to form dihydride units which are precursors for the AID reaction, rather than from the nascent desorption process of molecules. This was suggested because the AID reactions were generally studied as a steady-state desorption with respect to uptake and loss of the H atoms during H irradiation. Thus the exothermic adsorption of H atoms onto the D-terminated Si surface could be an origin of such a small activation energy.

To date, the kinetic mechanism of the AID reaction is still not completely understood. A question may be raised to the time domain behavior of the AID reaction; how quick is it? It is known that isothermal decay of the dihydride phase [Fig. 1(a)] proceeds with lifetimes from several seconds to several hours depending on $T_s$. It is interesting to compare the rates of decrease in the AID rates with those in the conventional $\beta_2$-TPD reaction. In this work, we study manner of occurrence of the AID reaction in time domain measurements using a modulated H beam.[35] We find the AID reaction proceeds along the fast [Fig. 1(c)] and slow [Fig. 1(a)] channels at around 600 K while only the fast channel [Fig. 1(c)] becomes dominant with $T_s$ decreasing below 550 K.

## II. EXPERIMENT

The experimental details have been reported elsewhere.[14] Therefore, the essential points are described here. The experimental setup consists of a beam chamber and an ultrahigh vacuum reaction chamber. The atomic hydrogen beam was generated in three differentially pumped chambers, which assure the high vacuum experiments in a pressure range of $10^{-10}$ Torr even when the H beam is applied. The beam was modulated in the second chamber with a rotating slit with a frequency of 0.25–0.35 Hz and a duty ratio of 50%. The 40 *l* reaction chamber was evacuated with a 500 l/sec turbo molecular pump which allows to pump out desorbed gases within ~0.1 sec. The reaction chamber was equipped with an $Ar^+$ ion gun, an Auger electron spectrometer, a quadrupole mass spectrometer (QMS), and a sample manipulator. A single crystalline Si(100) surface (*p*-type, B doped, ~10 Ω cm, 13×22×0.5 $mm^3$ was used. In order to obtain a clean surface, an $Ar^+$ ion-sputtered Si(100) surface

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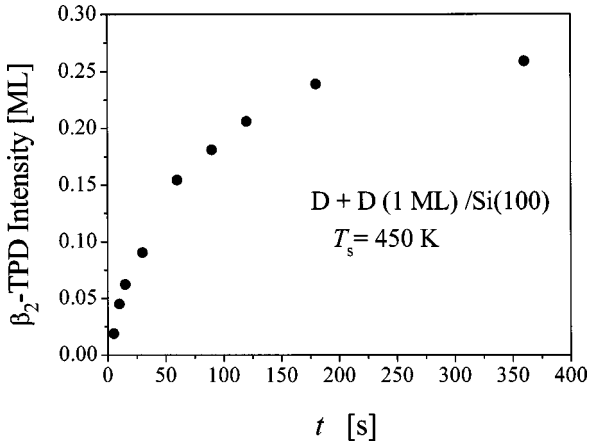


FIG. 2. Plots of the $\beta_2$-TPD intensity as a function of continuous D beam irradiation time $t$ on the D/Si(100) surface with $\theta_D^0 = 1.0$ ML at $T_s = 450$ K. The unit monolayer for the TPD intensity is calibrated from the saturated $\beta_2$-TPD intensity corresponding to 0.33 ML dideuterides for the 3×1 phase for the sample prepared at room temperature.

was flashed out at 1223 K for 30 sec and then annealed at 1083 K for 10 min. The sample was slowly cooled down to the desired temperatures with a cooling rate of 0.5 K/sec to ensure well-ordered surface reconstruction. The H or D beam was generated by a radio frequency (RF) plasma of $H_2$ or $D_2$ mixed with Ar (1:1 pressure ratio), respectively. The H or D flux was about $1\times10^{13}$ atoms/cm$^2$ sec which was determined from D and H uptake curves on the clean Si(100) surface after assuming unity sticking probability. The H flux was varied by controlling the RF power injected into the gas plasma. Unless otherwise stated, the clean Si(100) surface was first covered with D atoms at 585 K to get a 1 ML saturated surface, and then exposed to the modulated H beam for various $T_s$. Rates of H-induced $D_2$ and HD desorptions were measured simultaneously with the QMS in an angle-integrated mode.

## III. RESULTS AND DISCUSSION

### A. Uptake of dideuterides

Prior to the modulated beam experiments we first measured the uptake curve of dideuterides as a function of D irradiation time $t$ using a nonmodulated beam for $T_s = 450$ K on the D-saturated 2×1 surfaces, i.e., the initial D coverage $\theta_D^0 = 1.0$ ML. Figure 2 shows the plot of the $\beta_2$-TPD intensity as a function of $t$. The curve exhibits an initial quick rise followed by a saturation. From the initial slope of the uptake curve we evaluate the apparent D adsorption efficiency of about 0.5 with respect to the incident D flux. Taking the ABS reaction efficiency of about 0.4 (Refs. 15 and 36) into account, the value of 0.5 suggests that the net efficiency of D adsorption onto the 1 ML D-saturated surface is comparable to the sticking probability of D atoms onto the clean, D-free surface. This fact suggests that bond breakage of the surface Si dimers by D(H) atoms, followed by formation of dideuterides, is quite facile.

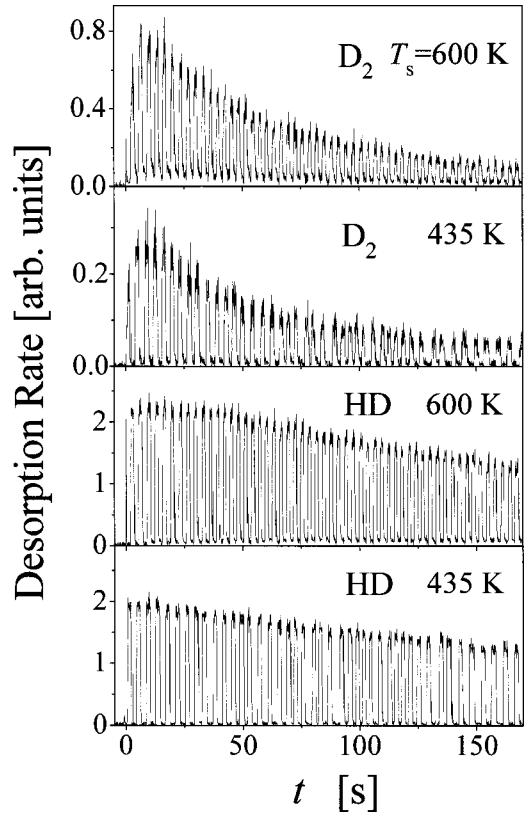


FIG. 3. Plots of $D_2$ (two upper panels) and HD rates (two lower panels) as a function of the modulated H-beam irradiation time $t$ on the D/Si(100) surface with $\theta_D^0 = 1.0$ ML for $T_s = 600$ and 435 K.

### B. Response to the modulated H beam

The D(1 ML)/Si(100) surface was exposed to the modulated H beam at various $T_s$. Desorption rates of HD as well as $D_2$ molecules were measured during surface exposure to the H beam for 900 sec. Figure 3 shows results for the $D_2$ (two upper panels) and HD (two lower panels) rate curves. The overall trends of both two rate curves are found to be quite similar to those observed in the exposure to the continuous H beam.[14,16,19] Namely, the apparent maximum of the $D_2$ rate curve is delayed with an induction time, and the value of the maximum rate decreases with decreasing $T_s$. On the other hand, the HD rate curves are characterized with a rapid increase in the rate at the very first cycle of the modulated beam, thus without any induction time, and a somewhat $T_s$ insensitive feature can be seen. This reveals that the HD desorption is mainly due to the direct abstration of D adatoms by the H atoms.[14,19] In this way, we confirm that the introduction of periodic ~1.5 sec off-cycles in the H beam do not seriously affect the kinetics for the ABS as well as AID reactions.

It is found that both the rates for $D_2$ and HD desorptions quickly rise up at the onset of each beam on-cycle and rapidly decrease at off-cycles. However, one should notice that for $T_s = 600$ K the rates of $D_2$ AID reaction at off-cycles do not become zero but still exhibit a slowly decaying component. This is more clearly demonstrated in Fig. 4 where the rate of $D_2$ desorption during one full cycle is retraced. Thus the curve in Fig. 4 can be decomposed into fast and slow

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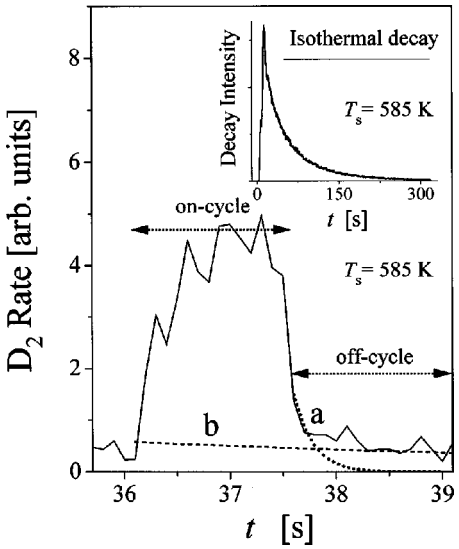


FIG. 4. $D_2$ rate curve recorded during one full cycle of the modulated hydrogen beam at $T_s = 585$ K. The inset shows the isothermal decay curve of the 3×1 dideuteride phase at $T_s = 585$ K.

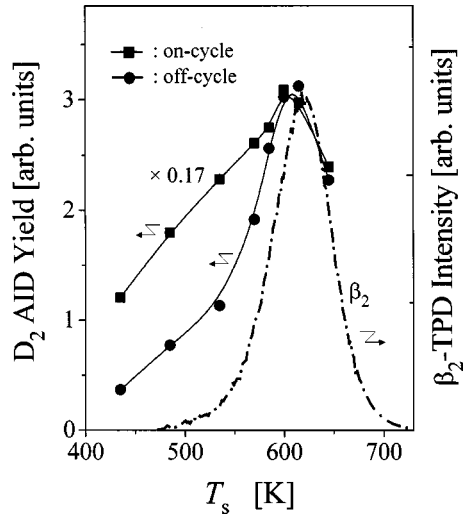


FIG. 5. Plots of the $D_2$ yield integrated for the beam on- and off-cycles as a function of $T_s$. The $\beta_2$-TPD spectrum is also plotted for comparison.

AID reactions; the former reaction is efficient only at on-cycles, while the latter has a long tail even at off-cycles. In order to compare the rate of decrease of the slow AID reaction with that of $\beta_2$-TPD reaction, we measured isothermal desorption rate of the dideuteride phase at $T_s = 585$ K. Result is plotted in the inset of Fig. 4. Note that the rate of decrease in $\beta_2$-TPD reaction is very slow with a lifetime ~100 sec comparable to that of the slow AID reaction. Therefore, the slow AID reaction may be attributed to thermal desorption of dideuterides accumulated during the surface exposure to the H beam. At $T_s = 435$ K, on the other hand, the rates of AID reaction at off-cycles are nearly zero as demonstrated in Fig. 3. This fact indicates that the two AID reactions have different kinetic origins.

As can be seen in Fig. 3, the HD rate curve measured for $T_s = 600$ K also includes such a slow component. This implies that the HD desorption is generated not only along the ABS pathway but also the AID pathway.[15,19] The HD desorption along the latter pathway is possible since the D adatoms are substituted with H adatoms with *t*. The rates of HD desorption at off-cycles tend to increase with *t*, being contrasted to the case of the $D_2$ AID reaction. This gives rise to the induction time during which the substitution of D adatoms by H atoms is taking place.

In order to know how the change of $T_s$ influences both the slow and fast AID reactions, the rates of the AID reaction at both on- and off-cycles are integrated with *t* to evaluate their yields for various $T_s$. Results are plotted in Fig. 5, where the $\beta_2$-TPD spectrum is also plotted for comparison. It is quite clear that the yield spectrum obtained at off-cycles looks similar in line shape to that of the $\beta_2$-TPD spectrum particularly at the temperature region around 600 K, supporting the assignment given above, i.e., the slow AID reaction is associated with the isothermal desorption of transiently accumulated dideuteride phase. Strictly speaking, however, the spectrum is a bit broader than the $\beta_2$-TPD spectrum, and the spectral deviation from it becomes larger at the temperature region for $T_s < 550$ K. This deviation could be attributed to tailing of the fast AID reaction into the time region at off-cycles.

In contrast to the case of the slow AID reaction, the yield spectrum of the fast AID reaction at on-cycles is much broader than that of the $\beta_2$-TPD spectrum, suggesting that the mechanism of the fast AID reaction is different from that of the slow one. At around 600 K where the rate of the AID reaction becomes maximum, approximately 20% of the total AID yield are for the slow AID reaction and the rest 80% are for the fast one. Thus we know that the fast AID pathway is the major desorption channel among the two AID reactions.

### C. AID on the 3×1 phase

Taking the surface structures of the H-terminated Si(100) surfaces[23,24,26] into consideration, the $T_s$ dependence of $D_2$ yields shown in Fig. 5 or Fig. 3 of Ref. 16 suggest that both of the fast and slow AID reactions take place only on domains with the 3×1 phase. In order to further affirm this fact, we measured AID rate curves at $T_s = 423$ K on the two different D-covered surfaces with the 3×1 or 2×1 phase. The surface with the 3×1 phase was specially prepared at $T_s = 423$ K by saturating the surface with sufficient D dose. Results are plotted in Fig. 6, where curve (a) was measured on the former surface, while curve (b) on the latter surface. The inset shows the two rate curves at the early stages of H irradiation. The initial rate step at the very beginning of H irradiation is much higher on the 3×1 phase than on the 2×1 phase, indicating that the fast AID reaction occurs on the 3×1 phase but not on the 2×1 phase. The observed gradual increase in the $D_2$ rate for curve (b) indicates the presence of an induction time for accumulation of dihydrides to complete the saturation of the 3×1 phase. Since the two curves overlap with each other after the maximum of curve (b), the surface initially prepared as a monodeuteride surface gets nearly saturated with 3×1 phase after dosing approximately 0.5 ML H atoms.

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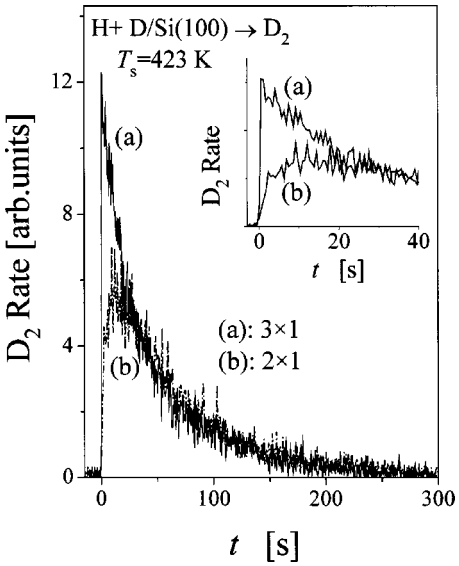


FIG. 6. $D_2$ rate curves as a function of continuous H beam irradiation time $t$ at $T_s = 423$ K on the D/Si(100) surfaces. (a) 3×1 dideuteride phase, (b) 2×1 monodeuteride phase. Note that the $D_2$ AID reaction occurs more efficiently on the surface already saturated with the 3×1 dideuteride phase than on the surface without any 3×1 dideuteride phases before exposure to the H beam.

In order to know the value of the AID reaction order with respect to incident H atoms, we plot the $D_2$ AID intensity at $T_s = 585$ K versus H flux in Fig. 7. A quite good linear relationship is recognized, suggesting the first-order kinetics with respect to the H flux is held. This may imply that the molecular desorption along the fast AID pathway is promoted in a single atomic process. In this case one should recall that it is nearly a fourth-order reaction with respect to $\theta_D$ (Refs. 14 and 18), i.e., possible targets of the H atoms for the fast AID reaction must contain four D adatoms. A unit cell of a 3×1 phase can fulfill this criterion since it contains a pair of $SiD_2$ and DSi-SiD (Refs. 20 and 22–26). It is thus plausible that the fast AID reaction proceeds through a single atomic collision with a unit cell of the 3×1 phase.

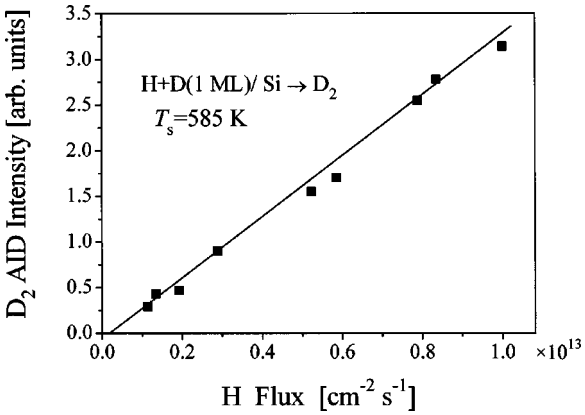


FIG. 7. Plots of the $D_2$ AID intensity at $T_s = 585$ K as a function of H flux. The $D_2$ AID intensity linearly increases with the H flux, suggesting the AID reaction order with respect to the incident H atoms is one.

### D. A possible AID model

As was observed in the preceding section, the AID reaction seems to be related to the 3×1 phase formed during H irradiation. Our surfaces subject to the H beam may have domain structures different from those observed in the static STM images which were generally obtained after turning off H irradiation.[22–25] During the H-beam irradiation the saturation coverage of hydrogen must shift upward due to the supply of H atoms. For $T_s = 600$ K, for instance, the H-saturated surface subject to the H beam must allow more than 1.0 ML hydrogen coverage, consisting of mixed 2×1 and 3×1 phases rather than random distribution of Si dihydrides in 2×1 monohydride phases.[37] The surface saturation coverage and thus the fraction of area with such dihydride phase during H irradiation may be determined by $T_s$ as well as by H flux. The saturation coverage achieved under a steady-state condition during H irradiation may be practically determined by balance of two rates of adsorption and desorption of hydrogen. Here desorption of hydrogen includes the ABS and AID reactions as well as both $\beta_1$ and $\beta_2$ channel thermal desorptions. Since all the rates relevant to desorption are $T_s$ dependent, the saturation coverage is also $T_s$ dependent. Taking these facts into account, for the fraction of area of each phase ($\xi$) a domain diagram of $T_s$ versus $\xi$ curves is drawn in Fig. 8 for four phases, H(D)-free, monohydrided, partially dihydrided, and fully dihydrided domains, characterized with a 2×1, 2×1, 3×1, and 1×1 phases, respectively. One should note that $\xi$ is defined as a steady-state value during H-beam irradiation. Three lines (a), (b), and (c) in Fig. 8 separate the surface area into such domains each of which is characterized with one of the four phases. In the right panel of Fig. 8, some representative events of the AID and TPD reactions are denoted to scale $T_s$ for the diagram. Presently, however, because of the lack of knowledge on the exact phase diagram described as a function of $\theta_H$ for the H/Si(100) system, the lines are drawn somewhat arbitrarily and thus the $\xi$ axis is not explicitly scaled.

We propose that while the ABS reactions take place on any phases except for the H-clean 2×1 phase the AID reaction takes place only on the 3×1 phase. The $D_2$ desorption, as observed in the present experiments; proceed along either the slow or the fast AID pathway. We discuss here a possible mechanism for the fast AID reaction rather than for the slow one, since the latter is well attributed to the $\beta_2$-TPD reaction. We intend to propose a kinetic but not dynamic mechanism, invoking a local phase transition between the 1×1 and 3×1 phases as shown in Fig. 1(c), which however illustrates only a half reaction of desorption. Our kinetic model that includes a full reaction from adsorption to desorption is illustrated in Fig. 9 for the fast AID reaction. The fast AID reaction proceeds along the path **A**→**B**→**C**. At stage **A**, one H atom approaches the HSi-SiH unit in between two dihydride units on the 3×1 phase, for which $\xi$ at given $T_s$ can be known from Fig. 8. At stage **B**, the doubly occupied HSi-SiH dimer is attacked by the H atom to break the dimer bond, forming a 1×1 unit in the 3×1 phase. Since the 1×1 unit in the 3×1 phase is thermodynamically unstable for such a temperature region where the AID reaction can occur, it promptly emits a molecule at stage **C**, thereby returning to the 3×1 phase that

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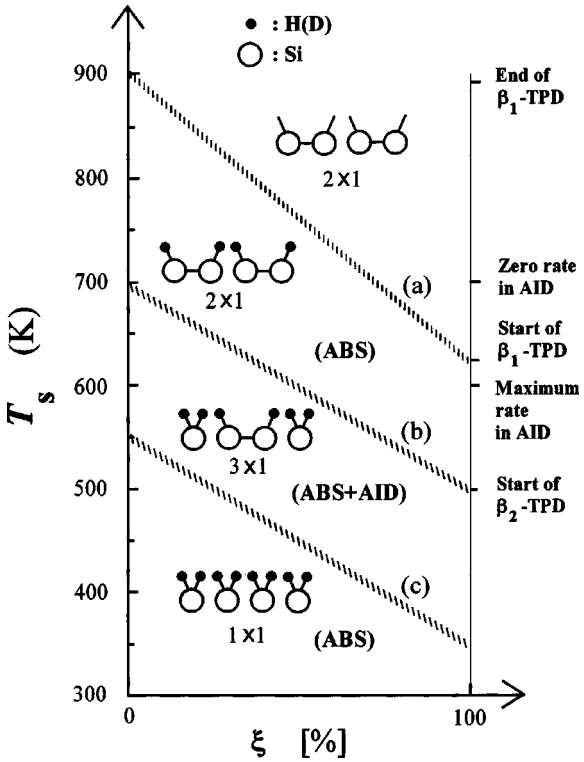


FIG. 8. Domain diagram of $T_s$ vs $\xi$ defined as fraction of domain area with different phases on the Si(100) surface under exposure to the H beam. The $\xi$ axis is not explicitly scaled because of the lack of knowledge on the exact phase diagram under H irradiation. Line (a) separates out the monodeuteride 2×1 phase from the clean 2×1 phase. The surface must be mostly clean around $T_s = 900$ K since the thermal desorption rate of the 2×1 monodeuteride phase ($\beta_1$-TPD) becomes extremely large so that the adatoms immediately desorb from the surface. Line (b) separates out the 3×1 phase from the 2×1 phase. The 2×1 domains begin to be present at around 500 K since the $\beta_2$-TPD reaction starts to occur at this temperature. Line (c) separates out the 1×1 phase from the 3×1 phase. The AID reaction can take place only on the 3×1 phase, while the ABS reactions can take place on any phases.

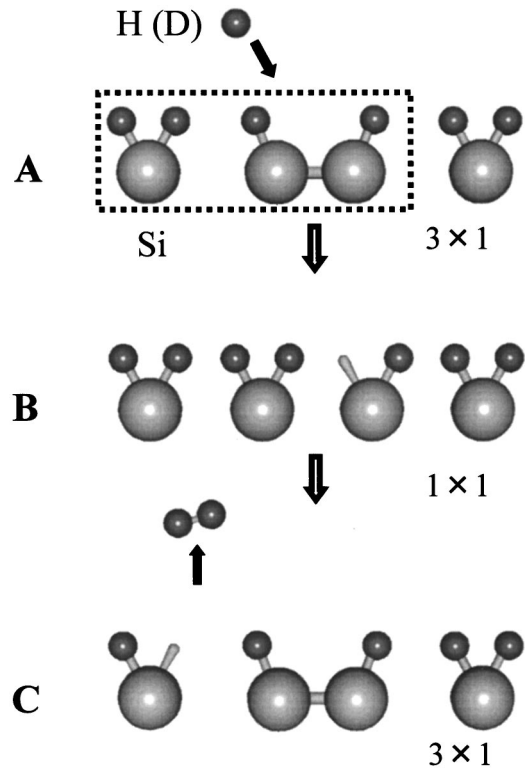


FIG. 9. A possible kinetic model for the fast AID reaction on the 3×1 phase. H adsorption to a monohydride unit on the 3×1 phase (**A**) breaks Si-Si dimer bond to excessively form Si dihydrides, transiently forming a 1×1 unit (**B**). Since the 1×1 unit is thermodynamically unstable in the 3×1 phase, the 1×1 unit emits a molecule, returning to the original 3×1 structure (**C**). See the text for the transition from **B** to **C**.

is allowed under the steady-state condition for the given $T_s$ and H flux. The dangling bond created at stage **B** would not be terminated before desorption reaction for stage **C** since the fast AID reaction follows the first-order kinetics with respect to H flux as demonstrated in Fig. 7. The hydrogen molecular desorption in stage **C** could proceed in such a way that the dangling bond in stage **B** interacts with the adjacent $SiH_2$ unit to form a Si dimer bond. To achieve this reaction an excess H atom of the $SiH_2$ unit would react with the nearest neighboring H atom on the left-most Si atom to induce molecular desorption, leaving behind one dangling bond on the left-most Si atom. Such molecular desorption may proceed either along the so-called (1,1) or (1,2) elimination of two H atoms. This AID picture seems to be consistent with the experimental fact that the fast AID reaction prefers $D_2$ desorption rather than HD desorption in the reaction system H+D/Si(100) as observed in Fig. 3. Furthermore, the observed fourth-order AID reaction could be reconciled with this AID mechanism: The apparent reaction order is determined by the number of H(D) adatoms relevant to the reaction site at stage **A**. The unit cell of the 3×1 phase possesses four H(D) surface adatoms; two are on the left-most Si atom and the other two atoms are on the Si dimer. Thus the reaction order can be understood to be four. Full termination of the target Si atoms is a necessary condition for the AID reaction since otherwise termination of dangling bond by a H atom precedes AID reaction.

According to this scenario, it is anticipated that AID yield is proportional to the total area of the 3×1 phase achieved under the steady-state condition during the surface exposure to H atoms. This allows us to understand the physical meaning of the $T_s$ dependence of the fast AID yield plotted in Fig. 5. For $500\,\mathrm{K} \leqslant T_s \leqslant 650\,\mathrm{K}$, the area of the 3×1 dihydride phase is large and therefore the AID yield becomes large. As $T_s$ is lowered below 500 K the saturation coverage can exceed $\theta_H = 1.33$ ML. For $\theta_H > 1.33$ ML, 3×1 and 1×1 phases are both present on the surface.[37] With decreasing $T_s$ the saturation coverage increases further and thereby the fraction of the 1×1 phase increases. This accompanies the concomitant reduction of the 3×1 phase and in turn the reduction of the AID yield. We expect that the H adsorption probability on the 1×1 phase is also high to form higher hydrides, but it may not generate molecular desorption. Instead, the system finally undergoes $SiH_4$ desorption or etching of surface Si atoms, causing such rough surfaces.[23,26] Thus the rough surface observed in the STM images would not necessarily mean that the 1×1 phase is unstable to generate Si desorption, but the Si etching reaction is inevitable due to efficient adsorption of H atoms breaking the Si-Si back bonds. On the other hand, as $T_s$ is raised above 650 K,

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spontaneous thermal desorption along the $\beta_2$ channel pathway gives rise to reduction of area of the $3\times1$ phase, thereby causing the decrease of the AID yield. Above 650 K, spontaneous thermal desorption along the $\beta_1$ channel pathway from the monohydride $2\times1$ phase further accelerates the reduction of the $3\times1$ phase. Then no domains of $3\times1$ phase remain on the surface at $T_s = 700-750$ K any longer, resulting in no occurrence of the AID reaction at all.

Finally we discuss why the fast AID reaction is not possible on $2\times1$ monohydride phases, where such a bond breaking of Si dimers by H atoms may also occur to locally form a pair of dihydride units. Since the interaction between the two dihydrides is repulsive,[37] they may spontaneously split at higher temperatures, diffusing over the surface. During the diffusion process the dihydrides may be consumed to terminate dangling bonds created either by ABS reaction or by $\beta_1$ channel desorption. Alternatively, it may be also conceivable that they may reach domain boundaries, compensating the decrease in the area of $3\times1$ dihydride phases due to the slow AID reaction. On the other hand, if the surface temperature is not high enough to allow such a rapid diffusion, the surfaces first prepared as a monohydride phase may tend to possess dihydrides rather than to induce AID reaction, forming a $3\times1$ dihydride phase during surface exposure to H atoms as was found in Fig. 6 [curve (b)].

## IV. SUMMARY

We studied the kinetic mechanism of the AID reaction, $H+D(1\ ML)/Si(100)\rightarrow D_2$, using a H beam modulated at about 0.3 Hz. The $D_2$ AID reaction took place not only at beam on-cycles but also at beam off-cycles. The AID reactions were categorized into the fast and slow AID reaction that efficiently occurs only at beam on- and even at beam off-cycles, respectively. The rate spectrum of the slow AID reaction was found to be similar to that of $\beta_2$-TPD spectrum, suggesting that the slow AID reaction is attributed to the thermal desorption from the $3\times1$ phase. The fast AID reaction took place even at around 400 K where the $\beta_2$-TPD rate is small. The $D_2$ yield along the fast AID reaction was always larger than that of the slow one for any $T_s$ studied. The fast AID reaction was found to occur efficiently even at the very beginning of H irradiation on the $3\times1$ phase, but it was inefficient on the $2\times1$ monohydride phase. The fast AID reaction was explained in terms of the thermodynamical instability of the system consisting of four adjacent dihydride units ($1\times1$ unit) which are formed on the $3\times1$ phase by sticking of a H atom to a doubly occupied Si dimer.

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