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Angular distributions of H-induced HD and D₂ desorptions from the Si(100) surfaces

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We measured angular distributions of HD and D₂ molecules desorbed via the reactions H + D/Si(100) → HD [abstraction (ABS)] and H + D/Si(100) → D₂ [adsorption-induced-desorption (AID)], respectively. It was found that the angular distribution of HD molecules desorbed along ABS is broader than that of D₂ molecules desorbed along AID, i.e., the former could be fit with $\cos^{2.0 \pm 0.2} \theta$, while the latter with $\cos^{5.0 \pm 0.5} \theta$. This difference of the angular distributions between the two reaction paths suggests that their dynamic mechanisms are different. The observed $\cos^2 \theta$ distribution for the ABS reaction was reproduced by the classical trajectory calculations over the London-Eyring-Polanyi-Sato potential-energy surfaces. The simulation suggests that the HD desorption along the ABS path takes place along the direction of Si–D bonds, but the apparent angular distribution is comprised of multiple components reflecting the different orientations of D-occupied Si dimers in the (2 × 1) and (1 × 2) double domain structures. © 2006 American Institute of Physics. [DOI: 10.1063/1.2163339]

I. INTRODUCTION

The reaction of atomic hydrogen with hydrogen-terminated Si surfaces is one of the simplest but the most important surface reactions relevant to Si device processes. H atoms stick to clean Si(100) surfaces taking various adsorption configurations,^{1,2} while they can abstract H adatoms on the Si surfaces. So far, kinetic mechanisms of the hydrogen abstraction by H have been extensively studied by isotopic labeling of surface adatoms with D atoms.^{3–17} The D abstraction by H on the D/Si surfaces can be categorized either as a direct abstraction (ABS) to form HD molecules, i.e., ABS: H + D/Si → HD, or as an indirect abstraction or adsorption-induced desorption (AID) to form D₂ molecules, i.e., AID: H + D/Si → D₂.

It has been so far revealed that the ABS reaction follows a second-order rate law in D coverage θ_D , and the AID reaction follows a fourth-order rate law in θ_D .^{8,9,11,12} The so-called hot atom (HA) mechanism cannot explain this unexpectedly high reaction orders since it claims a first- and second-order rate laws for ABS and AID, respectively,^{6,7} but the hot complex (HC) mechanism^{10,11,14} seems to reasonably explain the observed second-order ABS reaction. Here, by the HC mechanism it is meant that incident H atoms get into an excited state of the chemisorption potential at doubly occupied Si dimers DSi–SiD. H atoms at the bridge sites in between two Si atoms were found to be energetically metastable in Tersoff's potential calculation¹⁸ and density-functional calculations.¹⁹ Such excited H atoms in the chemisorption potential is denoted as a hot complex. During energy dissipation in the hot complex H atoms can either

abstract one of the two D atoms in the DSi–SiD units to generate HD desorption or break the Si–Si dimer bonds to form dihydrides HSiD, which may be precursors of the successive AID reaction.¹⁴ The series of kinetics experiments done by Namiki and co-workers on influences of experimental parameters such as surface temperatures T_s ,^{10,11} incident H flux,¹⁴ surface phases,¹⁴ and chopping of H beams^{13,14,16} on the reaction kinetics do not contradict the HC-mediated mechanisms. Rahman *et al.*¹⁴ suggested that the AID reaction occurs only on the (3 × 1) dihydride phase where DSi–SiD and DSiD units are alternately arranged. Breaking the DSi–SiD dimer bonds in such a (3 × 1) dihydride phase results in a formation of a local (1 × 1) dihydride domain, which is thermodynamically unstable above, e.g., 450 K, emitting a molecule to return to the original (3 × 1) phase.

Dynamics of D(H) abstraction by H(D) has been also studied experimentally^{4,5,17,22} as well as theoretically.^{18,20,21} Buntin^{3,4} measured the kinetic-energy distributions of abstracted HD molecules on D/Si(100) using a time-of-flight technique. He found that mean kinetic energies of the desorbed HD molecules are 1.2–1.3 eV, independent of incident energies in the range from 1.1 to 3.0 eV. This result suggests that the 1.2 eV exothermic energy in the abstraction reaction is disposed to the translational energy of desorbed molecules, while the incident energy is mainly dissipated to the surface phonons. Kratzer simulated the abstraction dynamics on London-Eyring-Polanyi-Sato (LEPS) potential-energy surfaces²⁰ (PES) as well as on *ab initio* PES,²¹ rather well reproducing Buntin's dynamics results. Takamine and Namiki²² measured the angular distribution of D-induced HD desorptions on the H/Si(100) surfaces, and found a desorption towards the direction of a Si–H bond with an angle of $\approx 23^\circ$ with respect to the surface normal. This directional

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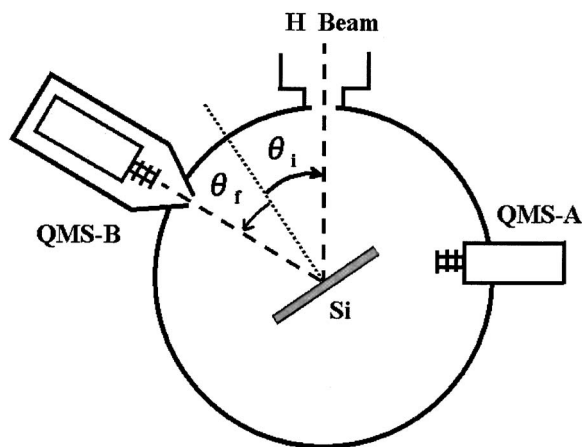


FIG. 1. Schematic illustration of the H-beam-surface reaction system. QMS-A in a reaction chamber measures angle-integrated desorption rates, and QMS-B measures angle-resolved desorption rates in a differential chamber. Incidence angle θ_i and desorption angle θ_f are defined with respect to the surface normal. The fixed arrangement of the beam and detector chambers gives a relation that $\theta_i + \theta_f = 60^\circ$.

desorption was theoretically supported since the minimum-energy path is along the Si–H bond direction.²³ On the other hand, Bisson *et al.*¹⁷ observed a quite broad angular distributions of H_2 molecules generated on the H/Si(100) surface under H irradiation. The results were considered to suggest that the desorbing molecules are accommodated with the surface.

In the above-mentioned experiments, however, ABS and AID reactions have not been consistently studied from a view point of related kinetics and dynamics. In this work we measure angular distributions of desorbed HD as well as D_2 molecules in the reaction system H+D/Si(100). The measured angular distributions of both HD and D_2 molecules show a peak at the surface normal. The width of the angular distribution of HD molecules is found to be apparently broader than that of D_2 molecules. The desorption angular distributions of HD molecules is explained by a classical dynamics simulation on the LEPS PES.²⁰

II. EXPERIMENT

The H or D atomic beam was generated in plasma of $H_2(D_2)/Ar$ mixed gas by injecting 200 W radio-frequency electrical power. Figure 1 shows a schematic illustration of a reaction chamber combined with a differentially pumped detection chamber. Quadrupole mass spectrometers (QMS-A and QMS-B) were installed in the reaction chamber and detection chamber, respectively. Base pressures of the reaction and detection chambers were both $\sim 1 \times 10^{-10}$ Torr. Signals from the two mass spectrometers were simultaneously counted to enable direct comparison of angle-resolved and angle-integrated desorption events. The angle between the H-beam axis and the detector axis is 60° . Hence, the polar angles of incidence θ_i and desorption θ_f fulfil that $\theta_i + \theta_f = 60^\circ$. Two 3-mm-diameter apertures were placed in front of QMS-B. The distance from the first aperture to the sample and to the second aperture is 6.4 and 2.0 cm, respectively. This geometry gives an angular resolution of $\Delta\theta_f \leq 2.5^\circ$ at $\theta_f = 0^\circ$ for a 3-mm-diameter H beam. Predepositions of D

atoms onto the clean Si(100) surface were done to prepare D-terminated Si(100) surfaces under the same irradiation geometry as for the successive H irradiation in the abstraction experiments, assuring the H beams can interact with D adatoms in the same surface area.

Angular distributions of H-induced HD and D_2 molecules as a function of θ_f were measured by means of sample rotation. This sample rotation rather than the detector QMS-B inevitably introduces a change in θ_i . The change in θ_i affected the abstraction reactions on two points. One is to enlarge the irradiated surface area with θ_i , effectively reducing the H flux. The other is to change reaction dynamics of ABS and AID reactions, which affects both ABS and AID yields. Since the ABS and AID reactions proceed along the first-order rate law in H flux,¹⁴ the former effect does not alter desorption angular distributions so long as the total, incident H atoms are unchanged. On the other hand, the latter dynamical effect was somewhat serious since as we will see later that HD and D_2 desorptions show an anticorrelation in their yield versus θ_i curves. Therefore, desorption angular distributions of ABS and AID reactions required correction. This was actually done by normalizing raw angle-resolved desorption rates with corresponding angle-integrated desorption rates.

The HD and D_2 molecules desorbed by H were spread over the reaction chamber, and leaked into the differentially pumped detection chamber through the 3-mm-diameter aperture. This resulted in unwanted increases in the desorption rates. The increases of HD or D_2 desorption rates due to such effusive gases from the reaction chamber were corrected by subtracting constant desorption yield detected for $\theta_f > 90^\circ$.

A commercially available single-crystalline Si(100) wafer (*p* type, *B* doped, $\sim 10 \Omega \text{ cm}$, miscut angle $\leq 0.3^\circ$) was cut along the orientation flat into $13 \times 22 \times 0.5 \text{ mm}^3$ specimens. The sample was attached onto a sample holder so that the azimuthal angle φ with respect to the axis of Si–Si dimers in one (2×1) domain was zero. The clean Si(100) surface was first subjected to the D beam to prepare the D-saturated surface at the desired surface temperature T_s , thus containing (3×1) dideuteride domains depending on T_s . Three representative temperatures of 300, 473, and 573 K were tested. The H or D beam flux was $1.0 \pm 0.5 \times 10^{13} \text{ cm}^{-2} \text{ s}^{-1}$. Other experimental details have been reported previously.⁸

III. RESULTS

A. Angle-integrated HD and D_2 yields

Angle-integrated and angle-resolved HD and D_2 rate curves were measured simultaneously as a function of H dosing time t at 300, 473, and 573 K. Figure 2 shows the plots of HD (left panel) and D_2 (right panel) rate curves measured in an angle-integrated mode at 473 K. Both curves show a quick rate jump immediately after turning on the H irradiation, which is followed by an almost exponential decrease with t . One can notice that the HD rate curve at $\theta_i = 60^\circ$ shows a slower decay than the others. This is due to the reduced H flux at $\theta_i = 60^\circ$. Considering the complicated contribution of the HD AID channel in the late H dosing time^{9–12}

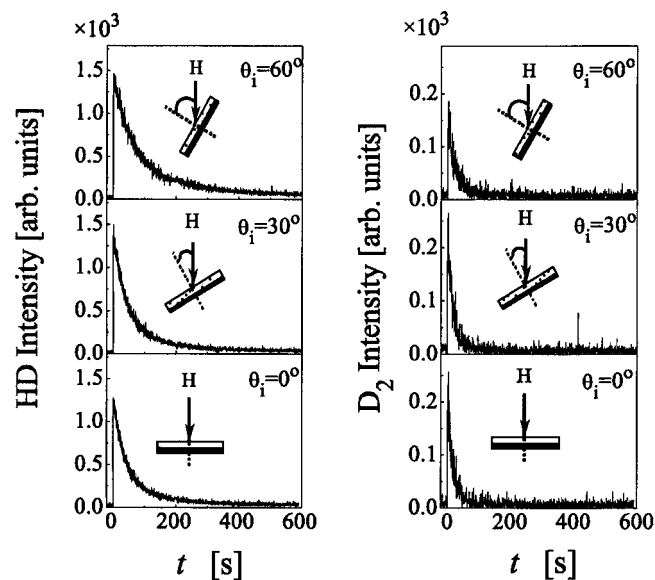


FIG. 2. Angle-integrated desorption rates of HD (left panel) and D₂ (right panel) molecules on the D/Si(100) surface at 473 K.

into consideration, peak intensities at the early dosing time rather than time-integrated total yields are plotted for the HD and D₂ rate curves as a function of θ_i in Fig. 3. One may notice that there is a weak anticorrelation between the two curves, since the HD rate curve becomes minimum but the D₂ rate curve becomes maximum at $\theta_i=0^\circ$. This anticorrelation could justify the HC mechanism by which the ABS reaction competes with the formation of dihydrides, acting as precursors for the successive AID reaction. Because of a possible steric effect such normal incidence could enhance dissociation of Si-Si dimer bonds rather than grazing incidence.

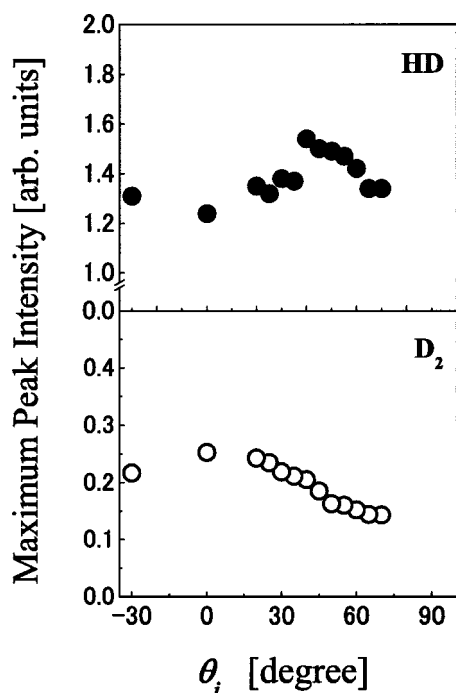


FIG. 3. Angle-integrated peak maximum of HD (upper panel) and D₂ (lower panel) rates as a function of incident angle θ_i at 473 K.

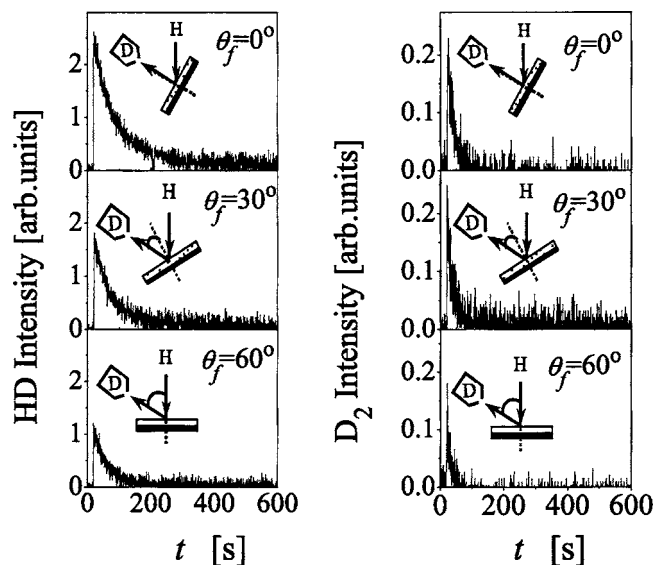


FIG. 4. Angle-resolved desorption rates of HD (left panel) and D₂ (right panel) molecules on the D/Si(100) surface at 473 K.

B. Angle-resolved HD and D₂ rate curves

Figure 4 shows the angle-resolved HD (left panel) and D₂ (right panel) rate curves measured at 473 K as a function of t . They were measured simultaneously with the angle-integrated desorption rate curves plotted in Fig. 2. We found that angular distributions of HD and D₂ desorption rates show an apparent maximum at $\theta_f=0^\circ$ and $13\sim 14^\circ$ for the HD and D₂ desorptions, respectively (not shown). Since as described in the previous section the data in Fig. 4 include some artifacts arising from the sample rotation, the apparent angular distributions of both HD and D₂ desorptions were corrected along the method described in the previous section. In Fig. 5, we plot the corrected peak maxima as a function of θ_f for the HD (upper panel) and D₂ (lower panel) rates at 473 K. Both of the HD and D₂ angular distributions exhibit forward desorption peaking at the surface normal.

In a similar way, corrected angular distributions of HD and D₂ molecules were also obtained for $T_s=300$ and 573 K (not shown). Consequently, we recognized that the D₂ desorption intensities at 300 K are quite small, while the HD angular distribution measured at 300 K has a somewhat smaller peak intensity by about 15% than that at 473 K. For $T_s=573$ K the angular distribution curves for HD and D₂ molecules are more or less the same in their line shape to those measured at 473 K as plotted in Fig. 5. The T_s dependence of the ABS and AID yields is consistent with the previous reports done by the angle-integrated mode.^{10-12,14}

The angular distributions of HD molecules are broader than that of the D₂ molecules. The measured angular distribution curves were tried to fit with a function $\cos^n \theta$. As shown in Fig. 5, the HD and D₂ angular distributions were best fit with $n=2.0\pm 0.2$ and with $n=5.0\pm 0.5$, respectively. The deviation recognized for HD molecules at around $\theta_f=0^\circ$ could be due to a possible contribution by the AID reaction between H and D adatoms.⁹

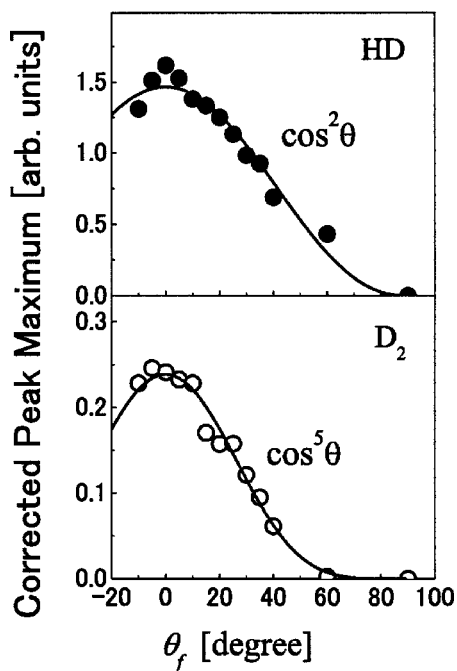


FIG. 5. Plots of corrected angular distributions of HD (upper panel) and D_2 (lower panel) peak intensities on the D/Si(100) surface at 473 K. The solid lines in the upper and lower panels are the best fit curves of \cos^n for $n=2, 0$ and 5,0, respectively.

IV. DISCUSSION

Kim and Lee^{24,25} measured the angular distributions of desorbed HD and D_2 molecules on the Pt(111) surface under the similar reaction conditions as for the present experiments. However, the results were quite different from the above-mentioned results, since the angular distributions of HD molecules desorbed from the Pt(111) surface were found to exhibit a presence of two distinct ABS paths. One was the ABS path that was characterized with a forward desorption, explicable with a direct Eley-Rideal mechanism. The other was the path that was characterized with an off-normal desorption peaking around 40° . This off-normal desorption could be explained in terms of the parallel momentum conservation in the ABS reaction along the HA mechanism. The D_2 desorptions induced by H were also characterized with similar off-normal angular distributions, and well interpreted in terms of the HA mechanism including secondary hot D atoms generated by primary H atoms. On the contrary, as shown in Fig. 5, both the angular distributions of HD and D_2 molecules on the Si(100) surface have the single peak along the surface normal without any such off-normal components. Therefore, the ABS and AID reactions on the Si(100) surface cannot be explained in terms of such a HA scenario at all.

The HC mechanism proposed for the ABS reaction¹¹ claims that H atoms first get absorbed in the excited states of chemisorption at doubly occupied Si dimers DSi-SiD. Such an excited state of H chemisorption was called a hot complex and denoted as $(H+DSi-SiD)^*$. Hot complexes may not be able to move freely across the surface but may tend to localize at the same DSi-SiD unit. During the energy dissipation, H atoms in the hot complex may abstract one of the two D adatoms in the DSi-SiD unit to generate ABS reaction. Thus,

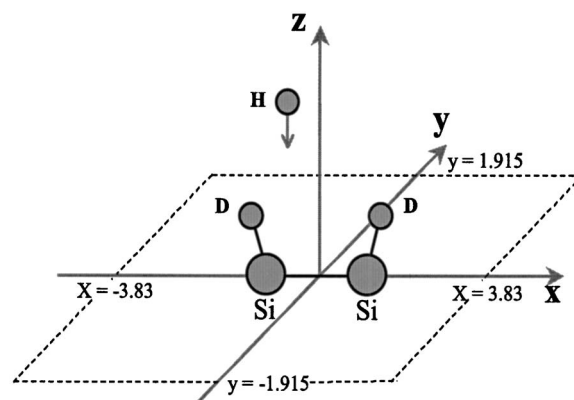


FIG. 6. Unit cell geometry for the classical trajectory calculations. A DSi-SiD unit is placed at the center of the Si(100)- (2×1) unit cell. H atoms are introduced on the surface spatially randomly. In the LEPS PES, the Si-Si dimer is actually assumed to be a hard cube. This means no breaking of the Si-Si dimer bond and thus no formation of a dihydride at the collision of H atoms with the surface.

the ABS reaction process is energetic and prompt, disposing the large part of the ~ 1.2 eV reaction energy into the translational motion of product molecules.^{3,4} The molecules generated just after the abstraction reaction may be directed along the Si-D(H) bond axis as seen in the H abstraction by D (D on H).²² However, in the present experiment of D abstraction by H (H on D) does not show such preferential desorptions along the Si-D bond but show a somewhat broad angular distribution peaking around the surface normal. Some isotope effects could be responsible for this difference in the angular distributions among the isotopic combinations of H on D or D on H. The Si(100) surface used in the present experiment contains double domains with different Si dimer orientations. The Si-Si dimer bonds in one domain are rotated by an angle of 90° with respect to the dimer bond axis in the other domain. Thus the HD angular distributions must be comprised of a superposition of two components arising from the different domains.

In order to understand this feature, we calculate the classical trajectories for desorbing HD molecules over the LEPS PES given by Kratzer.²⁰ We assume that motion of the H atom in the hot complex can be described by a classical mechanics in the chemisorption potential of the hot complex. We basically follow Kratzer's method²⁰ to evaluate angular distributions of desorbing HD molecules in the ABS reactions. Therefore, we here refrain to describe equations necessary to trajectory calculations, but illustrate schematically only the reaction system in Fig. 6 and describe the initial conditions for the trajectory calculation as follows. Figure 6 shows a unit cell of the Si(100)- (2×1) monodeuteride phase on which D abstraction by H is simulated. At the center of the unit cell a doubly occupied Si dimer DSi-SiD is placed. The x and y axes with their origin at the center of DSi-SiD are taken so that they are parallel and perpendicular to the Si-Si dimer bond axis, respectively, while the z axis is taken along the surface normal. Hence, the unit cell covers the area $-3.83 \text{ \AA} \leq x \leq 3.83 \text{ \AA}$ and $-1.915 \text{ \AA} \leq y \leq 1.915 \text{ \AA}$. A periodic boundary condition was employed for the atoms and molecules which enter into the neighboring unit cells.

H atoms were released normally to the surface from $z = 10 \text{ \AA}$ with initial kinetic energy of 0.1 eV. Their initial positions in the (x, y) plane were randomly chosen using a random function. It was assumed that two D adatoms were initially vibrating along a stretching mode as well as along two tilting modes with Boltzmann energy distributions, which allow us to simulate the temperature dependence of ABS. For the surface adatoms, their initial phases and momenta were also randomly chosen. The substrate Si atoms were treated as a hard cube with an effective mass of two Si atoms. Since the employed LEPS potentials do not allow formation of dihydrides followed by AID of D₂, we neglected the D abstraction by secondary hot D atoms to generate D₂ desorptions of which process shares at most 5% of the total events.²⁰

Generally, 1.5×10^5 trajectories were calculated with a time step of 1.21×10^{-16} s to achieve good statistics. Abstracted HD molecules with momentum \mathbf{p} are detected at $z = 10 \text{ \AA}$ in the (x, z) plane and (y, z) plane to determine angular distributions $Y_i(\theta_f)$ for $i=(x, z)$ and (y, z) . For HD angular distributions, we set two angles, $\theta_{(x,z)}$ and $\theta_{(y,z)}$, that are the angles between the z axis and the momenta $\mathbf{p}_{(x,z)}$ and $\mathbf{p}_{(y,z)}$ projected into the (x, z) plane and the (y, z) plane, respectively. In actual practice of calculation of $Y_{(x,z)}(\theta_f)$, we counted up molecules that got entered into the angle windows $\theta_f - 5^\circ \leq \theta_{(x,z)} \leq \theta_f + 5^\circ$ for $-5^\circ \leq \theta_{(y,z)} \leq +5^\circ$. For $Y_{(y,z)}(\theta_f)$, on the other hand, those counted were the molecules that got entered into the angle windows $\theta_f - 5^\circ \leq \theta_{(y,z)} \leq \theta_f + 5^\circ$ for $-5^\circ \leq \theta_{(x,z)} \leq +5^\circ$. Taking into consideration the two types of Si dimer orientations in domains A and B as illustrated in the upper inset of Fig. 7, angular distributions calculated as a sum of $Y_{(x,z)}(\theta_f)$ and $Y_{(y,z)}(\theta_f)$ relevant to domains A and B, respectively, are compared in Fig. 7 with the experimental angular distributions measured at 473 K. Apart from the deviation at $\theta_f = 0^\circ$, the trend of the calculated angular distribution (open circles) agrees with the experimental data (solid stars). The calculated curve can be fit with a $\cos^n \theta_f$ function with $n=2.0$.

To understand why the HD angular distribution by the ABS pathway is broad, we decompose the calculated angular distribution curve into three components as shown in the lower inset of Fig. 7. Components A1 and A2 are attributed to the two ABS paths arising from abstractions of the right and left D atoms in one DSi-SiD unit present in domain A. Component B is attributed to ABS on domain B. The solid (A1) and open (A2) triangles show the calculated angular distributions arising from abstraction of D atoms on the right Si atom and the left Si atom as denoted in Fig. 6, respectively. Note that both curves appear asymmetric in θ_f around the peak maximum at $\pm 23^\circ$, which is the angle between the z axis and the Si-D bond. Thus, it is suggested that the Si-D stretching vibration plays a crucial role in causing such a directional desorption in ABS.

The solid lines A1 and A2 are the best fit curves by the functions $\cos^4(\theta_f \mp 23^\circ)$ for $\theta_f > \pm 23^\circ$ and $\cos^2(\theta_f \mp 23^\circ)$ for $\theta_f \leq \pm 23^\circ$. Sum of A1 and A2 makes a function of $\cos^2 \theta$. We

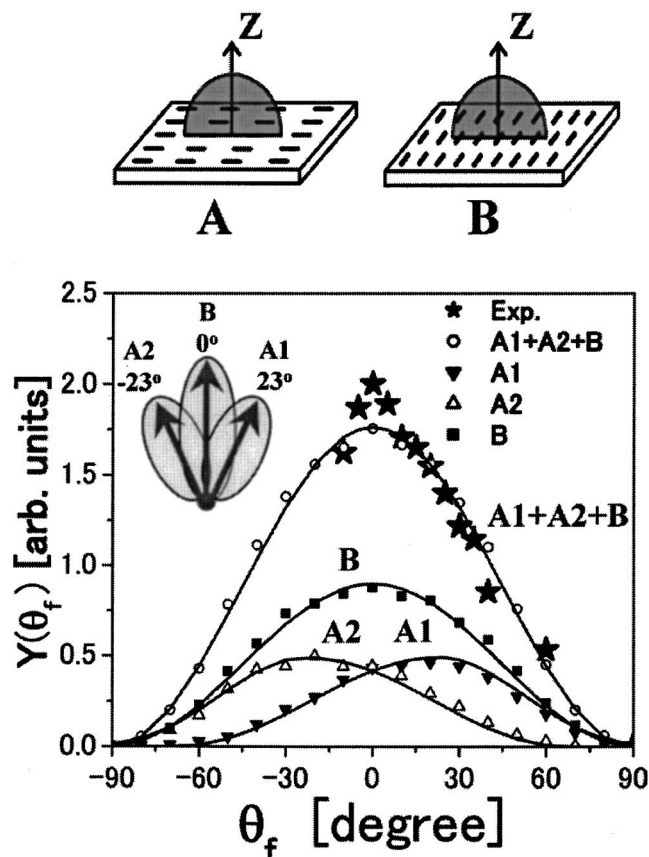


FIG. 7. Plots of calculated angular distributions $Y(\theta_f)$ for HD ABS molecules desorbed from the two domain Si(100)-(2 × 1) surfaces at 473 K. The calculated $Y(\theta_f)$ for HD ABS (open circles) is compared with the experimental data (solid stars). The calculated $Y(\theta_f)$ can be fit with $\cos^2 \theta$, and decomposed into A1, A2, and B components as illustrated in the inset. A1 and A2 components are attributed to D abstraction by H on the right and left Si atoms of DSi-SiD in domain A, respectively, and B component is attributed to D abstraction on domain B. The line shape of A1 and A2 components is asymmetric in θ_f around the peak maximum, while that of B component is symmetric around the surface normal. See the text about solid lines which can fit the calculated angular distribution curves.

also plot the calculated angular distribution contributed by ABS in domain B (solid rectangles, B), i.e., $Y_{(y,z)}(\theta_f)$, which can be fit also with $\cos^2 \theta_f$.

In this way, the experimental HD angular distributions can be well reproduced by the classical trajectory calculations on the LEPS PES. In the trajectory calculations, some H atoms are found to be scattered from either of two D atoms in one DSi-SiD unit and then abstract the counter D atom in the same DSi-SiD, generating HD desorptions. Kratzer considers this is the HA-mediated ABS.²⁰ However, we consider this is the HC-mediated ABS since H atoms tend to spend at the same DSi-SiD, with multiple bouncing prior to ABS. Thus, such a broad angular distribution lobe could be caused partly by the effect of parallel momentum of H in the HC potential. The two tilting modes could also partly contribute to the observed broadening as well.

Because of the quite large difference observed in the angular distribution widths, dynamic mechanisms of the ABS and AID reactions are suggested to be different. This seems not to be at variance with the so far proposed kinetic mechanisms for ABS and AID.^{10,11,14} The AID reaction is

basically thermal in nature. Rahman *et al.*¹⁴ observed that there are two types of the AID reactions; one AID path occurs promptly as H atoms impinge the surface and the other AID path occurs slowly even after turning off the H beam. The prompt AID path is understood to include a thermodynamical instability of (1×1) dihydrides excessively formed during H irradiation on the (3×1) dihydride phase, emitting a molecule to get back to the (3×1) dihydride phase.¹⁴ On the other hand, the slow AID path is attributed to the conventional β_2 -temperature-programmed-desorption (TPD) channel. It occurs as the (3×1) dihydride phase excessively formed beyond the equilibrium under the H irradiation is transformed into a (2×1) monohydride phase. Recently, the dynamics of D_2 molecules desorbed in the β_2 -TPD channel has been measured: the desorbed molecules exhibit a forward desorption with a $\cos^{2.3} \theta_f$ angular distribution, and a translational heating with a mean kinetic energy of ~ 0.24 eV.²⁶ The angular distributions, sharper than that of the β_2 -TPD, can be categorized to the prompt AID process as described above. The sharper angular distributions may imply that the D_2 desorptions along the prompt AID channel must be more energetic than those along the β_2 -TPD channel.²⁷ If the emission of molecules proceeds via a synergic (1, 1) or (1, 2) elimination of two D atoms in the four neighboring deuteride units,¹⁴ the molecular emission could be directed into a narrow solid angle toward the surface normal.

Quite recently, Bisson *et al.*¹⁷ reported the angular distribution of H_2 molecules desorbed during pulsed-H irradiation onto the H-terminated Si(100) surface. They rotated a mass detector around the sample to measure angular distributions of desorbed molecules. Signals from the detector were processed with a lock-in amplifier. The rotation of the detector allows one to measure the angular distributions free from such artifacts involved in a sample rotation. They noticed that the angular distribution of H_2 molecules desorbed at 650 K was fit with $\cos^n \theta_f$ with $n=0.3$, thus extraordinarily broader than the present results. Such angular distributions broader than $\cos \theta$ could be considered to suggest that the ABS desorptions are thermally equilibrated with the surface,¹⁷ which seems to, however, apparently contradict the energetic ABS desorptions with as high as 1 eV kinetic energy as observed by Buntin.^{4,5} Bisson *et al.* did not use the isotopic labeling method because the H flux used was so high that surface D atoms were quickly lost before enough data collection. The data obtained for the H-on-H system did not separate out the desorptions via ABS from those via AID. Yet, right now, we do not have any reasonable explanations to reconcile this large gap observed between the present experiments and the experiments of Bisson *et al.*

V. SUMMARY

Angular distributions of HD and D_2 molecules desorbed in the reaction system H+D/Si(100) were measured by means of sample rotation. It was found that the angular dis-

tribution of HD molecules desorbed along a direct abstraction (ABS) path could be fit with $\cos^{2.0 \pm 0.2} \theta_f$, while the angular distribution of D_2 molecules desorbed along an adsorption-induced-desorption (AID) path could be fit with $\cos^{5.0 \pm 0.5} \theta_f$. This difference of the angular distributions between the two reaction paths suggests that their dynamic mechanisms are different. The measured $\cos^2 \theta_f$ distribution for the ABS reaction was reproduced by the classical trajectory calculations over the LEPS potential-energy surfaces given by Kratzer.²⁰ The simulation suggests that the HD desorption via the ABS path takes place along the direction of Si-D bonds, but the actual angular distributions are comprised of three components attributed to the ABS desorptions occurring along the two off-normal Si-D bonds in the (2×1) terraces and a desorption component detected along the surface normal for the (1×2) terraces on the double domain surface.

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