Time-of-flight distributions of HD molecules abstracted at a Si(100) surface

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We study the dynamics of D abstraction by ~ 0.05 eV H atoms on a Si(100) surface. Time-of-flight (TOF) distributions of the abstracted HD molecules are measured using a quasi-random chopper/cross-correlation method. The measured TOF distribution is found to be broad and fast. The distribution is decomposed into two components being related to direct abstraction (ABS) and adsorption-induced-desorption (AID), which were revealed in the kinetics studies. The best curve fits yield mean kinetic energies of 1.15±0.20 eV and 0.33±0.05 eV for the ABS and AID components, respectively. Dynamics and kinetics of hydrogen abstraction at Si(100) surfaces are consistently understood.

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I. INTRODUCTION

Gaseous hydrogen atoms can abstract hydrogen (deuterium) adatoms on Si surfaces, causing molecular desorption. The kinetics of the reaction, H(g) + D(ad)/Si → HD(g) + ·Si, have been extensively studied on Si(100) [1–19], Si(111) [20, 21], and Si(110) [22]. In contrast, the dynamics on Si surfaces have been less well-studied [23, 24]. To generate H atoms which can abstract D adatoms on a Si(100) surface, Buntin used pulsed excimer laser photolysis of HI molecules, thereby controlling the incident mean kinetic energies of the H atoms < E_H > in the range from 1.1 to 3.2 eV. He measured time-of-flight (TOF) distributions of the abstracted HD molecules with a multi-channel scaler (MCS) triggered by the laser pulse. Desorbed HD molecules traversed an 8.9 cm flight with TOF distributions within a few tens of μs. The energy distributions deduced from the measured TOF data were asymmetric around 1.0 eV, with a low-energy tail extending to zero and a high-energy tail extending to 2-3 eV, depending on < E_H >. The energy distribution curve became broader with increasing < E_H >, but the mean translational energy < E_trans > remained nearly constant at around 1.2 eV. Since the HD molecules would carry away a majority of the available energy, D abstraction by H at the Si(100) surface was believed to proceed by an Eley-Rideal (ER) mechanism.

Molecular dynamics simulations of D abstraction by H atoms at a Si(100) surface were performed by Kratzer [25, 26] using the potential energy surfaces given by a London-Eyling-Polany-Sato (LEPS) theory or by density functional theory. Employing a cube model for the substrate, which therefore did not allow H atoms to stick to the Si substrate, he obtained < E_trans >=0.82 eV with mean internal energies of 0.62 eV for vibration and 0.31 eV for rotation at < E_H >=0.1 eV and T_s=700 K. He also simulated abstraction dynamics mimicking Buntin’s experiments, but the characteristic feature of < E_trans > being independent of < E_H > was not reproduced. Moreover, the simulation yielded a predominance of hot-atom (HA)-mediated abstraction, rather than direct ER abstraction. On the other hand, Hansen and Vogl [27] employed a Tersoff’s potential which allowed H atoms to stick to the Si surface, which was thus more realistic than a cube model. They found that the probability of D abstraction by H via the ER pathway is ~40% at < E_H >=0.1-0.2 eV, while the other ~60% is due to adsorption to the surface near a doubly-occupied Si dimer DSi-SiD. They observed that the probability of H abstraction by D atoms decreased remarkably, from 42% to 15% with increasing D kinetic energy from 0.1 eV to 1.5 eV. However, < E_trans > increased with increasing incident kinetic energy, in contradiction to Buntin’s result. Trapping of H atoms by DSi-SiD was reported by Tok et al. [28] who showed using ab initio calculations that H atoms can bridge the two Si atoms of a Si dimer. Because their diffusion barrier along the dimer row is low, the bridging H atoms were expected to abstract D atoms during diffusion.

The detailed kinetics experiments carried out after the above mentioned dynamics studies revealed complex features of the abstraction reaction on Si surfaces. Not only was the direct abstraction reaction as found by Buntin [23, 24] observed, but efficient indirect abstraction, through which impinging H atoms were not involved in the desorbed molecules, took place, depending on the surface temperature T_s and the surface coverage θ(D/H). In situ mass spectrometric experiments revealed that as the D-terminated Si surfaces were exposed to H atoms, both HD and D_2 molecules desorbed from the surface [6–13, 19–22]. This D_2 desorption suggested that recombinative desorption of surface adatoms was induced by the adsorption of H atoms. The direct and indirect abstrac-
tions have been respectively referred to as ABS (abstraction) and AID (adsorption-induced-desorption) [9, 21]. The angular distributions of the abstracted molecules, \( Y(\theta_f) \), were measured as a function of desorption angle \( \theta_f \) with respect to the surface normal [29]. As a result, \( Y(\theta_f) \propto \theta_f^2 \) and \( \theta_f^2 \) were obtained for HD molecules along the ABS pathway and D\(_2\) molecules along the AID pathway, respectively. As the surface D adatoms were gradually replaced by H atoms during H exposure, HD desorption occurred via the same AID pathway for D and H adatoms [8–12, 17]. The kinetics experiments [8–10] revealed that the ABS and AID reactions were respectively governed by a second- and a fourth-order rate law in \( \theta_D \) and \( \theta_H \) on Si(100) surfaces. The rates of HD ABS and AID reactions were proportional to \( \theta_D^2 \) and \( \theta_D^2 \theta_H \), respectively. Because of their unexpectedly high reaction orders, both ER and HA mechanisms were ruled out. The high reaction order suggested instead that the hydrogen abstraction reaction proceeds via many-body interactions between H atoms and surface D(H) adatoms at the unit cell of impact.

To reconcile the observed second-order kinetics with the direct nature of the ABS reaction, Hayakawa et al. [9] proposed a hot complex (HC) mechanism. By HC they meant a still-hot H atom bound in a chemisorption well around a DSi-SiD, and denoted as \((\text{H}+\text{DSi-SiD})^\circ\). Such a hot complex would be related to the theoretically predicted bound H atoms around DSi-SiD [27] or to bridging H atoms between two Si atoms [28]. During energy relaxation of the HC, the H atom was expected to recombine with one of the two D adatoms of the DSi-SiD, causing HD desorption. If one of the two D adatoms was replaced with an H atom during H exposure, the HC would have the structure of \((\text{H}+\text{HSi-SiD})^\circ\). In this configuration H abstraction by H was preferred to D abstraction by H because of an isotope effect [8, 16, 21]. The observed second-order kinetics in the ABS reaction were thus explained using the hot complex scenario.

Modulated H beam experiments [12, 13, 19] revealed that the AID reaction is of a Langmuir-Hinshelwood (LH) type, or thermal in nature. This is because the desorption of D\(_2\) molecules was discernible even after the H exposure was turned off. Furthermore, the desorption was strongly dependent on \( T_s \), active only in the somewhat lower temperature window from 400 to 700 K. A mechanism for the AID channel reactions [12, 13, 19] was proposed relating to the thermodynamic instability of the \((1 \times 1)\) dihydride phase, locally formed by the adsorption of H atoms in a \((3 \times 1)\) monohydride/dihydride domain on the \((2 \times 1)\) monohydride surface [30]. In other words, the collapse of the transiently-formed \((1 \times 1)\) phase to the original \((3 \times 1)\) phase accompanies the emission of a molecule.

From the above kinetics studies, one may expect that abstracted HD molecules would manifest characteristic dynamical features in their energy distributions, with high and low kinetic energy components relevant to the ABS and AID channel reactions. In this context, Buntin’s observation that \( < E_{\text{trans}} > \) was independent of \( < E_H > \) seems consistent with the HC scenario. However, the mean energies \( < E_H > \approx 1.1-3.2 \text{ eV} \) used in his TOF experiments were too high to extract the net desorption dynamics of abstracted HD molecules, since they are comparable to or even larger than the reaction exoenergetics \( \Delta E_{\text{rxn}} \approx 1.5 \text{ eV} \). In this paper, we revisit the dynamics of the reaction H(g) + D(ad)→HD(g) on a Si(100) surface. We used as low as 0.05 eV H atoms generated in a radio-frequency (13.56 MHz) plasma [31]. Hence, the reaction conditions were nearly identical to those employed in previous kinetics studies [7–13, 19]. This allowed us to analyze TOF data relating to the already-known kinetics of D abstraction by H on Si(100) surfaces.

II. EXPERIMENT

TOF distributions of HD molecules desorbed as a result of D abstraction by H on a Si(100) surface were measured with an experimental setup combining three systems: an H(D) beam generation system, a gas-surface reaction system, and a TOF measurement system, as illustrated in Fig. 1. D and H atoms were generated by a radio-frequency (13.56 MHz) plasma of D\(_2\) and H\(_2\) gas. In order to enhance H flux, H\(_2\) gas was mixed with O\(_2\) gas (about 5 %), thereby enabling a count of abstracted HD molecules separate from the background noise. The gas-

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**FIG. 1:** Illustration of the experimental apparatus used. QMS: quadrupole mass spectrometer; AES: Auger electron spectrometer; TMP: turbo molecular pump; TSP: titanium sublimation pump; DP: oil diffusion pump; GV: gate valve; MCS: multi-channel scaler.

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surface reaction chamber was equipped with an Auger electron spectrometer (AES), an Ar\textsuperscript{+} ion gun for sputter-cleaning the sample surface, and a quadrupole mass spectrometer (QMS). The TOF measurement system consisted of a quasi-random chopper with two identical sequences of 255 open and blank slots made along the periphery of an approximately 10 cm diameter Cu-Be disk. After passing the second buffer chamber, which can reduce the effusive gases from the reaction chamber, desorbed HD molecules were detected using a highly sensitive quadrupole mass spectrometer. Output pulses from the QMS were sent to an MCS, triggered by the quasi random chopper. The cross-correlation spectrum between the quasi-random chopper and accumulated MCS data was a TOF spectrum, the same as if it had been obtained with a single open slot. In this study, the net flight distance from the random chopper to the ionizer of the QMS was 38.0 cm. The rotation rate of the random chopper disc and the dwell time of the MCS were 200 Hz and 20 \(\mu\)s, respectively. The details of the TOF system have been described elsewhere \cite{32}.

The incident angle of the H beam was 60° and the desorption angle of HD molecules was zero, both with respect to the surface normal. A clean Si(100) surface was obtained by Ar\textsuperscript{+} ion sputtering at 873 K and thermal annealing at 1200 K. The surface cleanliness was periodically checked by AES during repeated data collection. A D-saturated Si(100) surface was first prepared by admitting D atoms onto the clean Si(100) surface. Then the surface was exposed to H atoms to generate HD abstraction. The effect of oxygen mixed with the H\textsubscript{2} gas was negligible because of the very short data collection time of 15 s. One TOF distribution curve was obtained by accumulating one hundred cycles of D-adsorption followed by adatom abstraction by H atoms. At the end of each cycle, the surface was flashed and annealed at 1173 K, and then cooled at a rate of 1 K/s. Figure 2 shows an HD desorption rate versus H exposure time curve (not a TOF distribution curve) measured with the same QMS in the TOF chamber. The desorbed HD molecules in the hatched region were collected for TOF data. This included somewhat large background signals, which originated from the dark noise of the QMS and also from H\textsuperscript{+} ions generated by electron impact with H\textsubscript{2} gas before it entered the QMS. A major fraction of desorbed HD molecules was spread into the reaction chamber and had a chance to enter the TOF detection line as an effusive beam, contributing to the background signals. However, this component was minimized by the buffer chamber placed between the chopper and the QMS chambers. Surface temperatures of 473 and 600 K were chosen to avoid surface etching by H atoms. Even after 100 cycles of data accumulation, the obtained raw convoluted TOF data fluctuated due to the background noise. Therefore, before the cross correlation deconvolution processing the raw TOF data were smoothened by means of a weighted 5-point average along Savitzky-Golay method \cite{33}. The transit time in traversing the QMS field and delay at the counting circuits were calibrated using a 300 K He effusive gas leaked from the reaction chamber, so that the TOF data could be fit by a 300 K Maxwellian.

III. RESULTS AND DISCUSSION

Figure 3 shows plots of the measured TOF distribution of HD molecules desorbed from the Si(100) surface at \(T_s=473\) K. A similar TOF distribution was obtained at
\( T_s = 600 \, \text{K} \) (not shown). The measured TOF curve is clearly much faster than the 473 K effusive HD gas. The mean translational energies can be evaluated by

\[
< E_{\text{trans}} > = \frac{\sum_{i} \frac{1}{2} M(t_i) \frac{1}{T_i} I(t_i)}{\sum_{i} \frac{1}{T_i} I(t_i)}, \tag{1}
\]

where \( M \) is the mass of an HD molecule, \( L (=38 \, \text{cm}) \) is the flight distance, and \( I(t_i) \) is the desorption intensity (density) of the HD molecules at \( t_i = (2 \times i - 1) \, \mu \text{s} \) for \( i=1, 2, 3, \ldots \). If the data were overestimated due to noise, a correction to the flux by a factor \( 1/t_i \) would make the values near \( t=0 \) unreasonably large. To avoid such overestimation of \( < E_{\text{trans}} > \), we intentionally excluded the datum at \( t_i = 10 \, \mu \text{s} \). We then obtained \( < E_{\text{trans}} > = 0.96 \) eV for \( T_s = 473 \, \text{K} \) and 0.95 eV for \( T_s = 600 \, \text{K} \). However, these values remained overestimated, since the TOF data were not deconvoluted with the 20 \( \mu \text{s} \) full slit. Deconvolution of the TOF data will be treated later, using a curve fitting process with a proposed TOF function.

As reviewed in the Introduction, HD desorption occurs via both the ABS and AID pathways. Since the ABS channel reaction may be predominantly direct in nature, the HD desorption along this pathway must be energetic. On the other hand, since the AID channel reaction is of LH type, the HD desorption along this pathway may not be as energetic as the ABS pathway. The measured TOF distribution curves were decomposed into three components, including a background (BG) contribution. The background signals were \( \text{H}_2^+ \) ions, formed in front of the QMS by electron impact of \( \text{H}_2 \) molecules scattered from the surface. During abstraction reactions, abstracted HD molecules may backfill the H-surface reaction chamber and enter the TOF line, also contributing to the BG component. To retain the direct nature of the ABS reaction, we employed a so-called shifted Maxwellian to fit the TOF distributions of the ABS component. On the other hand, taking their thermal nature into consideration, we employed non-shifted Maxwellians for the AID and BG components. Thus, the measured TOF distribution curves were fit with

\[
\begin{align*}
    f(t)dt &= c_{\text{ABS}} t^{-4} \exp\left(-M(L/t-v_0)^2/2k_BT_{\text{ABS}}\right)dt \\
    &+ c_{\text{AID}} t^{-4} \exp\left(-M(L/t)^2/2k_BT_{\text{AID}}\right)dt \\
    &+ c_{\text{BG}} t^{-4} \exp\left(-M(L/t)^2/2k_BT_{\text{BG}}\right)dt. \tag{2}
\end{align*}
\]

Convoluting the above function with the 20 \( \mu \text{s} \) slit function, the six free parameters, \( T_{\text{ABS}}, v_0, T_{\text{AID}}, c_{\text{ABS}}, c_{\text{AID}} \) and \( c_{\text{BG}} \), were determined by the following curve fitting method. Since the number of data points were scarce, the number of free parameters in the least mean squares curve fitting had to be effectively reduced.

First we fixed the temperature of the BG component to \( T_{\text{BG}}=380 \, \text{K} \) and 430 K at \( T_s=473 \, \text{K} \) and 600 K, respectively. These values were chosen after taking the results obtained in the scattering experiments for the 300 K D\(_2\) effusive gas from the H-terminated Si(100) surface [34] into account. The other six free parameters were grouped into two categories: one containing the parameters of the Maxwellians, \( T_{\text{ABS}}, v_0 \) and \( T_{\text{AID}} \), and the other containing the coefficients of the three Maxwellians, \( c_{\text{ABS}}, c_{\text{AID}} \) and \( c_{\text{BG}} \). In the first step of the curve fit, under the condition that a reasonably chosen initial value of each parameter in the first category was fixed, the parameters of the second category were determined by the least mean squares method. As a second step, these determined parameters of the second category were fixed while the parameters of the first category were re-determined using the least mean squares method. We repeated this process until the standard deviations reached a minimum. As a result, we obtained \( T_{\text{ABS}} = 4870 \pm 390 \, \text{K} \) and \( v_0 = 2420 \pm 270 \, \text{m/s} \) for the ABS component, and \( T_{\text{AID}} = 1890 \pm 160 \, \text{K} \) for the AID component. The relative values of \( c_i \)'s \( (i=\text{ABS, AID, and BG}) \) are given in the caption of Fig. 3.

One should note that the main peak of the TOF distribution curve was shared by both ABS and AID components, while the BG component was minor. In order to observe more directly the characteristic features of the ABS and AID distributions in the energy domain, the fitted TOF distribution eq.(2) was converted to an energy distribution, i.e., number of desorbed HD molecules having kinetic energies in the range from \( E \) to \( E + dE \),

\[
g(E)dE = c_{\text{ABS}} E \exp\left(-M(\sqrt{2E/M} - v_0)^2/2k_BT_{\text{ABS}}\right)dE + c_{\text{AID}} E \exp\left(-E/k_BT_{\text{AID}}\right)dE. \tag{3}
\]

In Fig. 4 we plotted \( g(E)dE \) for the ABS component, the AID component, and their sum. The yield ratio of the ABS component to the AID component at \( T_s=473 \, \text{K} \) (600 K) was calculated to be 1.86 : 1 (1.64 : 1), in good agreement with the results of the decomposition of the HD rate vs. \( \theta \) curves obtained in the previous kinetics experiments [9, 10]. The mean translational energies of the ABS and AID components were evaluated to be \( < E_{\text{ABS}} > = 1.15 \pm 0.20 \, \text{eV} \) and \( < E_{\text{AID}} > = 0.33 \pm 0.05 \, \text{eV} \). The errors were evaluated by taking the errors in \( T_{\text{ABS}}, v_0 \) and \( T_{\text{AID}} \) into consideration. As predicted, the mean kinetic energy of the all HD molecules (ABS plus AID) at \( T_s=473 \, \text{K} \) (600 K) was \( < E_{\text{trans}} > = 0.86 \, \text{eV} \), a bit smaller than that (about 0.96 eV) evaluated directly from the raw TOF distribution data.

The value of \( < E_{\text{trans}} > = 1.15 \pm 0.20 \, \text{eV} \) was very close to the corresponding value of 1.2 eV reported by Buntin [23, 24], although the energies of the H atoms were different in the two experiments: we used ~0.05 eV H atoms while Buntin used 1.1-3.2 eV H atoms. There was another difference in the experimental conditions. In our case, the TOF data were acquired during the most complete depletion of the saturated adlayer (slightly larger than 1.0 ML). In contrast, Buntin collected the TOF data for the period when the adlayer depletion was 1/8 - 1/4 ML for \( < E_{\text{trans}} > = 1.3-3.2 \, \text{eV} \) [24]. According to the kinetics studies, during the early stages of H exposure when \( \theta_H \) was still low, HD desorption was dominated by the ABS channel reaction. Since this is proportional to \( \theta_H^2 \), the rate of HD desorption along the AID pathway
became measurable as $\theta_D \leq 0.8$ ML and $\theta_H \geq 0.2$ ML, as shown in Fig. 3 of Ref. [9]. Therefore, we believe that the TOF data obtained at $<E_H> = 1.1$ eV were mainly due to the ABS channel reaction. On the other hand, if the TOF data at $<E_H> = 3.2$ eV were collected during the period when the adlayer depletion became 1/4 ML, a fraction of the desorbed HD molecules must have been generated along the AID pathway. This component would give rise to increased desorption of the low-energy molecules. Thus, the experimental results obtained by us and by Buntin can be interpreted in terms of the same HC mechanism. H atoms with energy as high as 1 eV may lose their energy upon collision with the surface via an electronic excitation rather than lattice phonon excitations, and become easily trapped in an excited state of the chemisorption potential as a hot complex. Hence, the mean kinetic energy of desorbed HD molecules remains fixed, independent of $<E_H>$ for a wide range of $<E_H>$.

The available energy can be evaluated by $E_{\text{avail}} = \Delta E_{\text{rxn}} + E_0$, where $E_0 = 0.3$ eV is the zero point vibrational energy of the Si-D bond. Kratzer further added a thermal energy of 0.29 eV at $T_s = 700$ K. Taking this term into account, we may obtain $E_{\text{avail}} = 2.0$ eV. If all of this energy was given to the translational degree of freedom of the molecule, the desorbed HD molecules would carry away a maximum kinetic energy of 2 eV. This is approximately fulfilled in the energy distribution curve plotted in Fig. 4. The long tail over 2 eV could be due to the assumed shifted Maxwellian. The Fig. 4 exhibits an apparent maximum in the energy distribution for the ABS component around 0.7 eV. In the framework of the HC scenario for the ABS pathway, we expect that an H atom in the hot complex would dissipate energy to the lattice or to the adsorbates, which means that the available energy would be reduced by the amount of dissipated energy. This would in turn reduce the kinetic energy of the desorbed HD molecules. The manner of such a bound H atom-adatom recombination may be different from the free H atom-adatom recombination. The H atom in the HC well would steer to abstract the adatom so that energy disposal to the internal degrees of freedom of the molecule would be somewhat restricted, compared to the free atom-adatom recombination. To further rationalize this HC mediated ABS picture, experiments on internal state distributions of desorbed HD molecules may be worth measuring.

Finally, we briefly discuss the AID channel reaction. The mean translational energy of the HD molecules desorbed along the AID pathway ($<E_{\text{trans}}^{\text{AID}}>$ = 3.2 ± 0.05 eV) was only one third of the mean translational energy along the ABS pathway ($<E_{\text{trans}}^{\text{ABS}}>$ = 1.15 ± 0.20 eV). As a possible AID mechanism, our group has proposed a model of thermodynamic instability of the local (1x1) dihydride domain in the (3x1) dihydride/methylene phase [12, 13, 19]. This mechanism may be related to the thermal desorption (TD) of the (3x1) dihydride/methylene phase, or the so-called $\beta_2$-TD [30, 35–39]. The TOF distributions of thermally desorbed $D_2$ molecules from a Si(100):(3x1)-D surface were measured by Niida et al. [40], and a mean translational energy of 0.27 eV was reported. Thus, molecules desorbed along the AID pathway are more energetic than those desorbed along the $\beta_2$-TD pathway. According to the proposed AID mechanism, four neighboring dihydrides, one of which has a dangling bond, are present at the AID desorption sites [12, 19]. On the other hand, two neighboring dihydrides are present at the $\beta_2$-TD sites [30, 36–39]. Thus, the surface energy must be higher at the sites responsible for the AID reaction than at those responsible for the $\beta_2$-TD.

IV. SUMMARY

We measured time-of-flight (TOF) distributions of HD molecules generated by D adatom abstraction by $\sim$0.05 eV H atoms under experimental conditions the same as were used in previous kinetics studies. The measured TOF distributions were found to be faster than those of desorption accommodated by the surface. Relating to the ABS and AID channels well-elicited by the kinetics studies, the TOF curves were decomposed into their ABS and AID components. Based on curve fits, the relative ratio of the ABS to AID components for $T_s = 473$ K (600 K) was 1.86 : 1 (1.64 : 1), in good agreement with the results obtained in the kinetics studies. The mean kinetic energies of the HD molecules were 1.15±0.20 eV and 0.33±0.05 eV for the ABS and AID components, respectively. The former value was close to the mean kinetic energy of the HD molecules generated by the 1.1-3.2 eV H atoms [24]. Hence the mean kinetic energy of
The HD molecules desorbed along the ABS channel is independent of the H incident energy over a wide range, from 0.05 eV to 3 eV. This can be explained using the hot complex mediated abstraction scenario proposed in the kinetics studies [9].

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[31] Using the same cross correlation TOF system, our group measured the TOF distribution of H atoms which were generated in H₂ plasma discharged by microwave (4.25 GHz) power. As a result, \( E_H = 0.047 \) eV was evaluated. Since the condition of H₂ gas in the plasma was almost the same, the mean energy of H atoms generated in the RF plasma may be \( \sim 0.05 \) eV.