Translational Heating of D$_2$ Molecules Thermally Desorbed from Si(100) and Ge(100) Surfaces

T. Sagara, T. Kuga, K. Tanaka, T. Shibataka, T. Fujimoto, and A. Namiki*

Department of Electrical Engineering, Kyushu Institute of Technology, Kitakyushu 804-8550, Japan
(Received 19 February 2002; published 31 July 2002)

The translational energies of D$_2$ molecules thermally desorbed from the Si(100) and Ge(100) surfaces under a heating rate of 6 K/s have been measured. In contrast to the previous laser desorption study, results show a considerable translational heating; the observed translational temperature is about 3 times higher than the desorption temperature for both surfaces. This fact indicates that energy barriers for adsorption are present even in the desorption pathway. Detailed balance is applicable to the adsorption and desorption dynamics of hydrogen on the Si(100) surface.

In addition to technological relevance to electronic devices, adsorption/desorption of hydrogen on Si surfaces is of fundamental interest because of the so-called "barrier puzzle." The energy barriers for adsorption on Si are supposed to be as high as 1 eV since the observed sticking coefficient is extremely low $\sim 10^{-10}$ at around room temperatures [1]. However, the desorbing molecules seem not to have traversed such high barriers since the translational energies measured in pulsed-laser-desorption (PLD) with an as high as 10^{10} K/s heating rate exhibited no translational heating [2].

So far, the barrier puzzle has been extensively challenged theoretically by evaluating energy barrier for adsorption E_{ad} based on the intradimer prepairing mechanism [3–8], the isolated dihydride mechanism [9,10], and the interdimer mechanism [5]. These mechanisms predicted that $E_{ad} > 0$. As a consequence, dynamical simulations over the potential energy surfaces (PES) for the surface temperature T_s resulted in mean translational energies $\bar{E}_{trans} > 2kT_s$ [6,11,12]. In order to reproduce $\bar{E}_{trans} \simeq 2kT_s$ theoretically, a strong coupling of lattice vibration to desorption was necessary in the proposed model PES so that the main fraction of the energy barrier is located in the degrees of freedom of substrate Si atoms rather than molecules [13].

Recently, Höfer and his collaborators [14] measured sticking coefficients s as a function of T_s and the incident energy E_i. Results showed up a feature of s strongly activated by both E_i and T_s, suggesting that barriers for adsorption are located not only in the degree of freedom of substrate Si atoms but also in the translational degree of freedom of molecules. They fit the data with an S-shaped function,

$$s(E_i, T_s) = \frac{A_0}{2}\{1 + \tanh[(E_i - E_0)/W(T_s)]\}, \quad (1)$$

where A_0 is the saturated sticking coefficient, E_0 the mean barrier height, and $W(T_s)$ the width of the barrier distribution. The best fit results obtained for the three parameters were $E_0 = 0.82$ eV and W $= 0.193$ eV for $A_0 = 10^{-2}$ at

$T_s = 670$ K. They noted that application of detailed balance to a desorption energy flux can yield very low translational energy of 0.27 eV for $T_s = 670$ K, very close to the experimental value of $0.15 \sim 0.2$ eV as measured in PLD [2], however, considerably lower than the mean barrier height $E_0 = 0.82$ eV. Hilf and Brenig [15,16] reproduced this feature in their sophisticated dynamic simulations done over the PES parametrized so as to reproduce the Höfer's sticking data [14]. Nevertheless, they had to admit occurrence of translational heating, since the simulated result $\bar{E}_{trans} = 0.235$ eV or $T_{trans}(= \bar{E}_{trans}/2k) = 1410$ K was considerably higher than the surface temperature for desorption $T_s = 670$ K beyond the experimental error limits noted in PLD [2].

Alternatively, a solution for the barrier puzzle was sought for in a new interdimer mechanism; Heinz et al. [17] discovered that hydrogen molecules adsorb easily on a pair of dangling bonds of two adjacent singly occupied Si dimers (4H site), suggesting that $E_{ad} = 0$. Zimmermann and Pan [18] found that sticking increases with hydrogen coverage θ_H, and results were analyzed with the interdimer mechanism including H free (2H) sites with $E_{ad} = 0.68$ eV and 4H sites with $E_{ad} = 0$. They noted that the isothermal desorption at $T_s = 690$ K is dominated by the 4H pathway for 0.07 ML $\leq \theta_H \leq 1.0$ ML (ML: monolayer). Quite recently, the new interdimer mechanism was supported by the site selective sticking experiment [19,20], *ab initio* calculation [21], and scanning-tunneling-microscopy [22]. If the desorption pathways were really barrierless for $E_{ad} = 0$, the new interdimer mechanism could be rationalized to reconcile the barrier puzzle.

It is intended to remeasure $\bar{E}_{trans}$ not with PLD but with a temperature-programmed-desorption (TPD) by which a thermoequilibrium desorption can be assured under a condition of slow heating rate well below 10 K/s. Actually, the dynamic desorption experiments done by means of TPD [23,24] seem to be inconsistent with results obtained in PLD [2]; it has been found that the angular distribution of D$_2$ molecules is peaked around the surface normal

characterized with $Y(\theta) = \cos^n\theta$ with $n = 4 \sim 5$, which can be attributed to barriers for adsorption [23]. Besides, the vibrational heating observed in the laser spectroscopy experiments for TPD [24] seems to be incompatible with the translational accommodation, since the two motions are usually coupled. In this Letter we report time-of-flight (TOF) distributions of D_2 molecules desorbed in TPD from the Si(100) and Ge (100) surfaces. For both surfaces we find a considerable translational heating, indicating that barriers for adsorption are present even in the desorption pathways.

TOF distributions of D_2 molecules desorbed from Si(100) (p-type, 7.8 Ω cm) and Ge(100) (p-type, 0.02 Ω cm) surfaces were measured in an ultra high vacuum (UHV) system with a cross-correlation method [25]. The miscut angle of the samples is $\leq 0.5°$, and thus almost no biatomic steps are present [26], assuring major desorptions occur on double domained 2×1 and 1×2 terraces. The UHV system consists of four differentially pumped chambers: the first is for TPD equipped with an Auger electron spectrometer, an Ar^+ ion gun, and a sample manipulator, the second for a quasirandom chopper, the third for a buffer chamber to reduce effusive gases from the desorption chamber, and the fourth for a quadrupole mass spectrometer (QMS). The base pressures for all these chambers except for the chopper chamber are in 10^{-10} Torr range, and that of the chopper chamber is $\sim 5 \times 10^{-9}$ Torr. The desorbing molecules pass through in total four fixed slits plus one rotating slit during their flight from the sample to an ionizer of the QMS. Two same sets of 255 open and blank slits were made so as to fulfill a quasirandom condition along the periphery of a wheel (outer diameter: 9.4 cm) rotatable with 200 Hz. The signals from the QMS were fed into a multi-channel-scaler (MCS, dwell time: 10 μs) which is triggered at each cycle of the random chopper. A cross-correlation spectrum between the MCS data and the random slit function is a TOF spectrum to be obtained. The TOF distance L was usually 33.2 cm long. In order to evaluate transit time across the QMS and to check the TOF system, TOF curves of an effusive D_2 beam from the backfilled desorption chamber were measured for $L = 33.2$ and 63.2 cm. The TOF data could be well fit to a Maxwellian density function, $f(t) \propto t^{-4}\exp[-m(L/t)^2/2kT_{\text{trans}}]$ characterized with $T_{\text{trans}} = 300$ K. Here, m is the mass of a D_2 molecule. The clean Si and Ge(100) surfaces were subjected to D atoms generated by flowing D_2 gas through a heated W tube to prepare a D-covered surface. The desorption angle was 0° with respect to the surface normal and the heating rate for TPD was 6 K/s for both surfaces. Collections of TOF data were done by gating a temperature window of ± 30 K around the maximum of β_1 peaks, or in a coverage window from $\simeq 0.8$ ML($\simeq 0.85$ ML) to $\simeq 0.1$ ML ($\simeq 0.1$ ML) on the Si(100) [Ge(100)] surface. Each TOF spectrum was obtained after accumulating 100 TPD scans. The surfaces were thermally annealed and then

cooled down with a speed of 1 K/s for Si and 0.5 K/s for Ge after each TPD scan.

Prior to TOF experiments we measured angular distributions of each TPD peak. As a consequence, we reconfirmed the forward peaked distribution [23] $Y(\theta) = \cos^n\theta$ with $n = 5.2 \pm 0.3$ for the β_1 peak in Si(100). On the other hand, the angular distribution of the β_1 peak in Ge(100) exhibited a somewhat broader distribution with $n = 2.3 \pm 0.2$.

Figures 1 and 2 show the measured TOF density distributions of D_2 molecules desorbing from the Si and the Ge(100) surface, respectively. The average translational energies of D_2 are $\bar{E}_{\text{trans}} = 0.35 \pm 0.05$ eV ($T_{\text{trans}} = 2040 \pm 300$ K) and 0.28 ± 0.04 eV ($T_{\text{trans}} = 1630 \pm 250$ K) on Si(100) and Ge(100), respectively. These TOF results are summarized in Table I. In contrast to the results in PLD [2], the observed TOF distributions in TPD are found to be considerably faster than those expected for desorptions accommodated with the surface (dotted lines in Figs. 1 and 2), indicating that non zero energy barriers for adsorption are present even in the desorption pathways. Therefore, at least for the D coverage range 0.1 ML $\leq \theta_D \leq 0.8$ ML, the 4H pathway in the new interdimer mechanism [17–22] cannot be the major channel for D_2 desorption on the Si(100) surface.

The measured TOF curves are not fit with a single Maxwellian function but need at least two Maxwellian functions. For Si(100), the faster component is characterized with $T_{\text{trans}} = 2200 \pm 300$ K, and the slower one with $T_{\text{trans}} = 800 \pm 200$ K, with their intensity ratio 100:13 after correcting the density data to flux. For Ge(100), the observed TOF curve can be also fit with two Maxwellian functions characterized with $T_s = 1700 \pm 250$ K, and 500 ± 200 K with their intensity ratio of
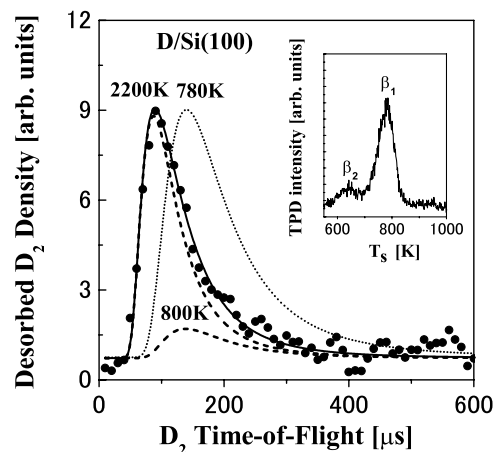

FIG. 1. TOF density spectra of D_2 molecules desorbing from the D(1.1 ML)/Si(100) surface. The experimental curve (solid circles) is deconvoluted into two Maxwellians (dashed lines) characterized with $T_{\text{trans}} = 2200$ and 800 K with the intensity ratio 10 : 2. The dotted line is a 780 K Maxwellian function. The inset shows the D_2 TPD spectrum.
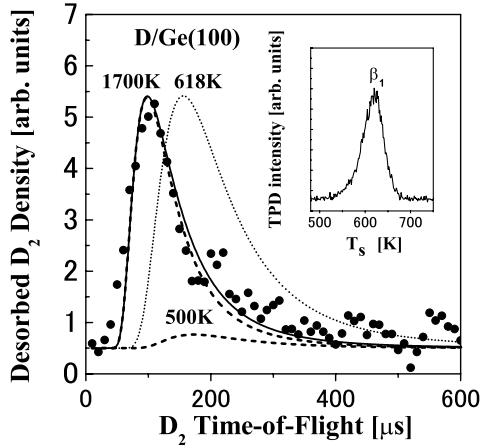
FIG. 2. TOF density spectra of D_2 molecules desorbing from the D(1.0 ML)/Ge(100) surface. The experimental curve (solid circles) are deconvoluted with 1700 and 500 K Maxwellian functions (dashed lines) with the intensity ratio 10 : 1. The dotted line is a Maxwellian function characterized with $T_{trans} = 618$ K. The inset shows the D_2 TPD spectrum.

100:6. It was reported that about 10% of the D_2 molecules desorbed from Si(100) surfaces are in the vibrationally first excited state [24]. We tentatively assign the fast and slow components to molecules in the vibrationally ground and the first excited state, respectively.

As was reported in the hydrogen adsorption experiments [14] and in the simulation [15,16], application of detailed balance is successful to predict such low translational energies. Indeed, taking $W(780 \text{ K}) = 0.195$ eV in Eq. (1), the energy flux function for desorption $F(E) \propto E \exp[-E/kT_s] s(E, T_s)$ can reproduce the experimental result $\bar{E}_{trans} = 0.35$ eV. Yet, the physical meaning of E_0 and $W(T_s)$ in Eq. (1) is still unclear since we do not know how they are related to energy values such as $\bar{E}_{trans}$ and activation energy for the lattice vibration or Arrhenius energy E_{Arr} defined in adsorption [11,15]. The principle of detailed balance which claims the adsorption and desorption reactions proceed overcoming the same potential barrier for adsorption, is now the real clue to extracting physics underlying in the two reactions. Since $(E_i - E_0)/W(T_s) < -1$ in the present condition, Eq. (1) can be expanded with $e^{(E_i - E_0)/W(T_s)}$. Preserving only the first term in the series expansion, we obtain

$$s(E_i, T_s) \simeq A_0 e^{-2(E_0 - E_i)/W(T_s)}. \qquad (2)$$

In order to evaluate E_{Arr}, Eq. (2) is equated to an Arrhenius type sticking function described as $A_0 e^{-E_{Arr}/kT_s}$. Thence, E_{Arr} is expressed as

$$E_{Arr} = \frac{2kT_s}{W(T_s)} (E_0 - E_i). \qquad (3)$$

For a wide width regime of the distributed barriers, $W(T_s) \geq 3kT_s$ [27], a Maxwellian energy flux weighted

by Eq. (2) allows us to derive the following energy relation

$$\frac{1}{\bar{E}_{trans}} = \frac{1}{2kT_s} - \frac{1}{W(T_s)}. \qquad (4)$$

From Eq. (4), for $\bar{E}_{trans} = 0.35$ eV, $W(780 \text{ K})$ is evaluated to be 0.21 eV ($\simeq 3.1kT_s$), which is slightly overestimated compared to the value of 0.195 eV as obtained before by Eq. (1). After taking $E_0 = 0.82$ eV [14], $W = 0.20$ eV, and $E_i = \bar{E}_{trans} \simeq 0.35$ eV along the principle of detailed balance, Eq. (3) yields $\bar{E}_{Arr} \simeq 0.31$ eV coming from the lattice heat bath as the mean Arrhenius energy around 780 K. Here, one should keep in mind that a somewhat large error of ± 0.2 eV evaluated for E_0 in the sticking experiment [14] results in ± 0.1 eV uncertainty in the value of $\bar{E}_{Arr}$ evaluated above.

Taking mean vibrational energy $\bar{E}_{vib} = 0.14$ eV [24] into account, we are aware of that $\bar{E}_{trans}$, $\bar{E}_{Arr}$, and $\bar{E}_{vib}$ for the mean desorption temperature of 780 K approximately fulfill the expected energy relation $E_0 = \bar{E}_{trans} + \bar{E}_{vib} + \bar{E}_{Arr}$. In the average regime of the distributed desorption events in TPD, the ~ 0.8 eV barrier for adsorption is disposed to the degrees of freedom of both the molecule and the lattice, i.e., ~ 0.5 eV to the former for both translation and vibration, and ~ 0.3 eV to the latter for phonon excitation. As shown in Eq. (4) for the wide width regime of the distributed energy barriers, the translational heating is determined not by E_0 but rather by $W(T_s)$, indicating that $W(T_s)$ really plays a key role in the adsorption/desorption dynamics.

Equation (3) predicts that E_{Arr} increases linearly with decreasing E_i. This fact suggests that at the transition state for adsorption, energies are interchangeable between the degrees of freedom of the Si lattice and the molecules. Such equivalency in the role of E_{Arr} and E_i in promoting adsorption has been also found on Cu(111) where the sticking coefficient curves exhibit also S-shaped one with E_i and T_s [28,29], and it was found that E_{Arr} linearly decreases with E_i, while $W(T_s)$ linearly increases with T_s [29]. Although an erf(x) instead of the tanh(x) for $x = (E_i - E_0)/W(T_s)$ has been employed for $s(E_i, T_s)$ on metal surfaces, we can notice that the fundamental physics of adsorption/desorption dynamics is quite analogous on both the Cu(111) and Si(100) surfaces, particularly on the molecule-phonon interaction which may determine the nature of $W(T_s)$. It has been pointed out by Hodgson [29,30] that a modified surface oscillator (MSO) model formulated by Dohle and Saalfrank [31] after taking a linear coupling

TABLE I. Mean translational energy $\bar{E}_{trans}$ and translational temperature $T_{trans}(= \bar{E}_{trans}/2k)$ for mean desorption temperature T_s around β_1 TPD peak.

Surface	$\bar{E}_{trans}$ (eV)	T_{trans} (K)	T_s (K)
Si(100)	0.35 ± 0.05	2040 ± 300	780
Ge(100)	0.28 ± 0.04	1630 ± 250	618

between displacement of a surface oscillator and the barrier height can explain the basic features in the T_s effect on sticking and $W(T_s)$ on Cu(111). The MSO model could be also applicable to Si(100) if we could choose appropriate phonon modes.

The D_2 desorption from the Ge(100) surface also exhibits a marked translational heating as shown in Fig. 2. From Eq. (4), the width of the barrier distribution can be estimated to be $W(618 \text{ K}) \simeq 0.17 \text{ eV}$ ($\simeq 3.2kT_s$). Translational energy barrier for adsorption is evaluated to be $0.18 \text{ eV} (= \bar{E}_{\text{trans}} - 2kT_s)$, which is slightly lower by 0.05 eV than the corresponding value on Si(100). From TPD lineshape analysis, we evaluate the activation energy for D_2 desorption of $1.85 \pm 0.05 \text{ eV}$ and the preexponential factor of $5.7 \pm 0.5 \times 10^{13} \text{ s}^{-1}$ (not shown). Both values are also smaller compared to the corresponding values on Si(100), $\sim 10^{15}/\text{s}$ and $\sim 2.5 \text{ eV}$ [32]. The binding energies E_B of hydrogen with two surfaces are nearly the same ($E_B = 3.1 \text{ eV}$ and 3.4 eV for H-Ge and H-Si, respectively, [33]), but Debye temperature Θ_D is quite different on the two surfaces. Since $\Theta_D = 374 \text{ K}$ for Ge while 645 K for Si, the Ge substrate is much softer than the Si lattice. Therefore, the observed differences in the values of the TPD parameters between the two surfaces may be caused mainly by the lattice parameters. The angular distribution of D_2 desorbing the Ge(100) surface is also forward peaked, however, apparently broader than that on Si(100). We speculate that the two associating D atoms in transition states are farther away on Ge(100) than on Si(100), receiving less repulsive force. In the context of detailed balance, we predict that $s(E_i, T_s)$ for the $D_2/\text{Ge}(100)$ system is shifted in lower values of both T_s and E_i compared to the case on Si(100). Sticking experiments as well as dynamical simulations on Ge(100) are highly desirable.

---

*Electronic address: namiki@ele.kyutech.ac.jp

[1] P. Bratu and U. Höfer, Phys. Rev. Lett. **74**, 1625 (1995).

[2] K. W. Kolasinski, W. Nessler, A. de Meijere, and E. Hasselbrink, Phys. Rev. Lett. **72**, 1356 (1994).

[3] P. Kratzer, B. Hammer, and J. K. Nørskov, Phys. Rev. B **51**, 13 432 (1995).

[4] E. Pehlke and M. Scheffler, Phys. Rev. Lett. **74**, 952 (1995).

[5] A. Vittadini and A. Selloni, Chem. Phys. Lett. **235**, 334 (1995).

[6] A. Gross, M. Bockstedte, and M. Scheffler, Phys. Rev. Lett. **79**, 701 (1997).

[7] E. Penev, P. Kratzer, and M. Scheffler, J. Chem. Phys. **110**, 3986 (1999).

[8] E. S. Tok and H. C. Kang, J. Chem. Phys. **115**, 6550 (2001).

[9] M. R. Radeke and E. A. Carter, Phys. Rev. **54**, 11 803 (1996).

[10] P. Nachtigall, K. D. Jordan, and C. Sosa, J. Chem. Phys. **101**, 8073 (1994).

[11] P. Kratzer, R. Russ, and W. Brenig, Sur. Sci. **345**, 125 (1996).

[12] A. J. R. da Silva, M. R. Radeke, and E. A. Carter, Surf. Sci. **381**, L628 (1997).

[13] P. Bratu, W. Brenig, A. Gross, M. Hartmann, U. Höfer, P. Kratzer, and R. Russ, Phys. Rev. B **54**, 5978 (1996).

[14] M. Dürr, M. B. Raschke, and U. Höfer, J. Chem. Phys. **111**, 10 411 (1999).

[15] M. F. Hilf and W. Brenig, J. Chem. Phys. **112**, 3113 (2000).

[16] W. Brenig and M. F. Hilf, J. Phys. Condens. Matter **13**, R61 (2001).

[17] A. Biedermann, E. Knoesel, Z. Hu, and T. F. Heinz, Phys. Rev. Lett. **83**, 1810 (1999).

[18] F. M. Zimmermann and X. Pan, Phys. Rev. Lett. **85**, 618 (2000).

[19] M. Dürr, M. B. Raschke, E. Pehlke, and U. Höfer, Phys. Rev. Lett. **86**, 123 (2001).

[20] M. Dürr and U. Höfer, Phys. Rev. Lett. **88**, 076107 (2002).

[21] E. Pehlke, Phys. Rev. B **62**, 12 932 (2001).

[22] M. Dürr, Z. Hu, A. Biedermann, U. Höfer, and T. F. Heinz, Phys. Rev. Lett. **88**, 046104 (2002).

[23] Y.-S. Park, J. -Y. Kim, and J. Lee, J. Chem. Phys. **98**, 757 (1993).

[24] K. W. Kolasinski, S. F. Shane, and R. N. Zare, J. Chem. Phys. **96**, 3995 (1992).

[25] D. J. Auerbach, *Atomic and Molecular Beam Methods*, edited by G. Scoles, D. Laine, and U. Valbusa (Oxford University Press, New York, 1988), Vol. 1, p. 369.

[26] J. Dabrowski and H. J. Müssig, *Silicon Surfaces and Formation of Interfaces* (World Scientific, Singapore, 2000), Chap. 3.

[27] According to Eq. (4) $\bar{E}_{\text{trans}}$ converges to $2kT_s$ as $W(T_s) \longrightarrow \infty$, while it diverges as $W(T_s) \longrightarrow 2kT_s$. The latter is physically unreasonable since Eq. (1) yields that $\bar{E}_{\text{trans}}$ converges to $E_0 + kT_s$ as $W(T_s) \longrightarrow 0$ (also see the discussion of Ref. [30]). We admit that Eq. (4) is applicable only for $W(T_s) \gtrsim 3kT_s$.

[28] C. T. Rettner, H. A. Michelsen, and D. J. Auerbach, J. Chem. Phys. **102**, 4625 (1995).

[29] M. J. Murphy and A. Hodgson, J. Chem. Phys. **108**, 4199 (1998).

[30] A. Hodgson, Prog. Surf. Sci. **63**, 1 (2000).

[31] M. Dohle and P. Saalfrank, Surf. Sci. **373**, 95 (1997).

[32] M. L. Wise, B. G. Koehler, P. Gupta, P. A. Coon, and S. M. George, Surf. Sci. **258**, 166 (1991).

[33] M. P. D'Evelyn, Y. L. Yang, and L. F. Sutcu, J. Chem. Phys. **96**, 852 (1992).