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journal or publication title	Physical Review B
volume	65
number	3
page range	033405-1-033405-4
year	2002-01
URL	http://hdl.handle.net/10228/640

doi: 10.1103/PhysRevB.65.033405

Hot-complex-mediated abstraction and desorption of D adatoms by H on Si(100)

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(Received 1 June 2001; revised manuscript received 28 August 2001; published 21 December 2001)

The collision-induced associative desorption (CID) and abstraction (ABS) of D adatoms by H have been studied on the Si(100) surfaces. D₂ CID exhibits a feature common to that of a thermal desorption from a dideuteride phase. HD ABS proceeds along an apparently second-order kinetics rather than a first-order kinetics with respect to surface D coverages. The ABS cross section is about 6 Å², extremely large compared to the theoretical values. Both of the direct Eley-Rideal mechanism and the hot-atom mechanism are ruled out. A hot-complex-mediated reaction model is proposed for ABS and CID.

DOI: 10.1103/PhysRevB.65.033405

PACS number(s): 82.65.+r, 79.20.Rf, 81.05.Cy, 82.30.Hk

The gaseous hydrogen atoms abstract hydrogen adatoms on Si(100) surfaces.¹⁻⁷ The recent kinetic experiments in the reaction system H+D/Si(100) revealed that in addition to abstraction (ABS) of surface adatoms D_{ad} to form HD, collision-induced associative desorption (CID) of D_{ad}, i.e., H+D_{ad}→D₂, also occurs.^{6,7} The kinetic mechanisms so far proposed for ABS and CID reactions are still controversial. Dinger, Lutterloh, and Küppers^{6,8} insist on a so-called hot-atom (HA) mechanism rather than a direct Eley-Rideal (ER) mechanism for both ABS and CID. The HA scenario claims that incident H atoms first weakly chemisorb to the surface retaining the adsorption energy and go across the corrugated potential barriers as hot precursors H* for the abstraction of D_{ad}.⁹ The incident H atoms may generate secondary hot D* atoms that also abstract D_{ad} to form D₂. Therefore, the HA scenario claims a first- and a second-order kinetics for ABS and CID, respectively, with respect to D_{ad} coverage θ_D. Dinger, Lutterloh, and Küppers deduced the second-order kinetics for D₂ CID by comparing the slopes of exponentially decaying HD and D₂ rate curves measured as a function of H admission time.⁶

On the other hand, Shimokawa *et al.*⁷ observe that the reaction order of D₂ CID is approximately four with respect to θ_D, indicating that four adatoms take part in the D₂ desorption process. The fourth-order kinetics in θ_D is quite unexpected, which rules out the HA mechanism. Earlier to this study, Flowers *et al.*¹⁰ admitted that the observed H and D uptake curves are not fit to a Kisliuk model,¹¹ indicating that such a HA mechanism is not operative even for ABS as well. They proposed a thermodynamically quasiequilibrium rate theory that includes not only an ER ABS but also an efficient sticking of H to the terminated Si(100) surface to form transient dideuterides DSiD. The dideuterides were considered to generate D₂ desorption along the same mechanism as for the so-called β₂ TPD (temperature-programed desorption) arising from a dideuteride phase. The nearly fourth-order kinetics in θ_D observed for D₂ CID is not at variance with the Flowers model since the β₂ TPD obeys a second-order kinetics with respect to DSiD coverages^{12,13} involving four D_{ad} in the event. Thus, CID based on the β₂ TPD mechanism is categorized as a Langmuir-Hinshelwood (LH) reaction. HD

CID is also expected to take place in the H and D coadsorption system generated by substitution of D_{ad} with H_{ad} during H admission. Actually, the observed HD rate curves exhibit a bimodal structure particularly at small initial D coverages θ_D⁰, suggesting the occurrence of two distinct channels, i.e., HD CID along the LH mechanism and ABS via the direct ER mechanism.⁷ Khanom *et al.*¹⁴ propose a HD rate equation to fit to the experimental data obtained for θ_D⁰ = 1.0 ML (ML: monolayer, one D atom per surface Si atom),

$$\frac{dN_{HD}}{dt} = k_{ABS}\theta_{DD} + C_1\theta_{HD}\theta_{DD} + 2C_2\theta_{HD}\theta_{HD} + C_3\theta_{HD}\theta_{HH}, \quad (1)$$

where k_{ABS} is the rate constant for the ER type ABS, and C_n ($n = 1 \sim 3$) stands for the rate constants related to the three possible combinations of dideuterides upon their encounters for the LH type CID. For the CID terms in Eq. (1), the coverages of D_{ad} in the prepaired Si dimer, θ_{ij} ($i, j = H, D$), are employed instead of the unmeasured transient dideuteride coverages. Even for the ABS term θ_{DD} is taken instead of θ_D ($= \theta_{DD} + \theta_{DH}$). This means that in the viewpoint of ER scenarios for ABS,^{5,7,10} H abstracts D_{ad} preferentially in the doubly occupied Si dimers DSi-SiD rather than D_{ad} in DSi-SiH.¹⁴ Yet, the significance of this unexpected isotope effect on ABS has not been clarified.

In the two papers,^{6,7} however, the experiments were carried out at a fixed temperature around 600 K without systematic changes of T_s . If ABS and CID proceed along the HA scenario,^{6,8} it can be anticipated that they commonly receive a little T_s effect.⁹ It is thus a dilemma for Dinger *et al.* to see a somewhat strong T_s dependence on CID studied on Si(111).⁸ On the contrary, the CID model based on the LH mechanism^{7,14} predicts a strong T_s dependence as was partly exemplified on Ge(100).¹⁵ In this paper, by examining T_s effects on ABS and CID, we reveal their kinetic mechanisms on Si(100), and propose a hot-complex-mediated reaction model.

The details of the experimental method have been given previously.⁷ Here, the essential points are described briefly. The H(D) beams were obtained from a plasma of H₂(D₂)/Ar

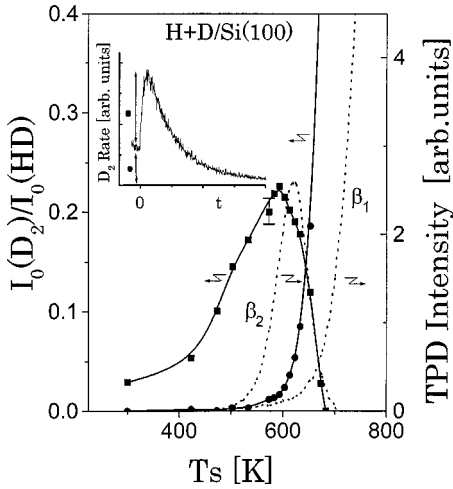


FIG. 1. Plots of D_2 rates $I_0(D_2)$ normalized with HD rates $I_0(HD)$ at the beginning of H admission as a function of T_s . The D_2 rates are decomposed into CID (solid rectangles) and STD (solid circles) as defined in the inset. For comparison, D_2 TPD spectra (rising speed of T_s : 3.3 K/s) decomposed into the β_2 and β_1 TPD spectra arising from the dideuteride and monodeuteride phases are also plotted.

mixed gas. The base pressure of a reaction chamber was 8×10^{-11} Torr, while it was 6×10^{-10} Torr under the beam admission. The flux of H and D beams was evaluated to be $6.5 \times 10^{12}/\text{cm}^2\text{s}$ at the surface. After saturating the Si(100) surface with 1 ML D atoms at 600 K, the H beam was admitted to the Si(100) surface to induce desorption of HD and D_2 at various surface temperatures ranging from 300 to 700 K. The quick temperature rise from 600 K to desired temperatures for $T_s > 600$ K was accomplished within a few seconds by means of a direct resistive heating.

During H admission to the D/Si(100) surface, HD and D_2 molecules were detected with a quadrupole mass spectrometer (QMS), while we failed to detect H_2 because of background H_2 . Spontaneous thermal desorption of D_2 already started before H admission above 600 K, and thus the D_2 rates at $t \approx 0$ can be decomposed into CID (solid rectangles) and spontaneous thermal desorption (STD) (solid circles) as shown in the inset of Fig. 1. Plots of D_2 rates normalized with the initial HD rate [$I_0(D_2)/I_0(HD)$] versus T_s are shown in Fig. 1. The D_2 CID curve exhibits a clear peak around 590 K above which the D_2 CID rates decrease quite rapidly in spite of the sizable amount of residual D_{ad} at the beginning of H admission (the loss of D_{ad} before H admission was at most 0.15 ML at $T_s = 683$ K). On the other hand, STD begins to appear around 600 K and increases quite rapidly with T_s . For comparison, we plot decomposed β_2 and β_1 TPD spectra arising from the dideuteride and monodeuteride phase, respectively. The STD spectrum exhibits a close relation to the β_1 TPD spectrum, which was expected since it occurs from the monodeuteride phase. On the other hand, the D_2 CID spectrum looks similar in line shape to the β_2 TPD spectrum. The peak of the D_2 CID spectrum shifts by about 30 K with respect to the β_2 TPD peak at 620 K, accompanied with tailing down to the lower-temperature region below 300 K. The feature of the CID and STD rate spectra

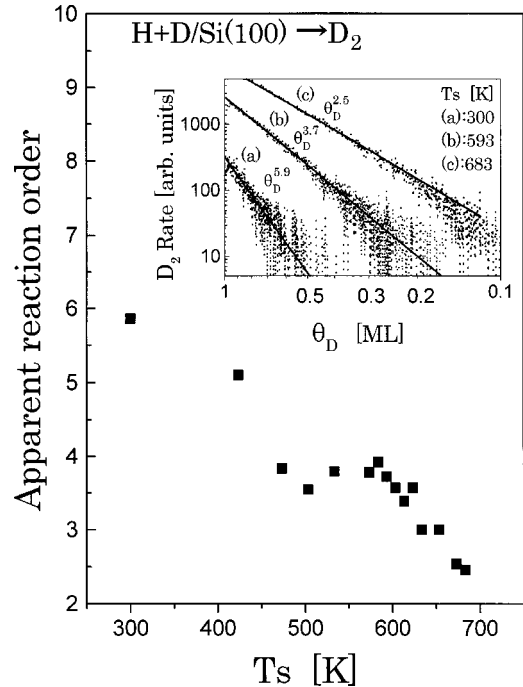


FIG. 2. Plots of apparent reaction order for D_2 CID as a function of T_s . The inset shows the log-log plots of the D_2 rate curves fit to the rate equation, $dN_{D_2}/dt = k\theta_D^m$, where m is the apparent reaction order to be determined by a least-mean-squares method.

manifests an anticorrelation for $T_s \geq 600$ K, indicating the former succumbs to the latter at higher T_s . From $I_0(D_2)/I_0(HD) = 0.23$ at 590 K, we know that about one third of the desorbed D atoms were due to CID on the H_{ad} free D/Si(100) surface.

Reaction orders for the D_2 desorptions were evaluated by fitting the experimental rate curves to a rate equation, $dN_{D_2}/dt = k\theta_D^m$, that consists of a single term characterized with the rate constant k and the reaction order m . However, the actual rates may include not only multiterms of CID as in Eq. (1) but also a term of STD, and the evaluated reaction orders are thus apparent. Figure 2 shows a plot of the D_2 CID reaction orders so determined as a function of T_s . The inset shows the curve fittings based on a least mean-squares method for $T_s = 300, 593,$ and 683 K. Here, the momentary D_{ad} coverages θ_D during H admission were obtained by integrating the HD and D_2 rate curves.^{7,15} The reaction orders for D_2 CID were evaluated to be 3.7 ± 0.3 for the temperature range from 500 to 600 K where the CID rates are high but the STD rates are low, indicating that D_2 CID proceeds along a nearly fourth-order kinetics in θ_D as noted previously for $T_s = 573$ K.⁷ The fourth-order kinetics rules out the HA mechanism for D_2 CID. It is also ruled out even at $T_s = 300$ K because the observed reaction order is about six.

From the facts shown in Figs. 1 and 2, we conclude that D_2 CID on Si(100) proceeds along the same mechanism as for the β_2 TPD arising from the dideuteride phase. In other words, the DSiD species are formed by H on the D/Si(100) surface, however, transiently since T_s is so high that they do not steadily survive. The second-order kinetics with respect

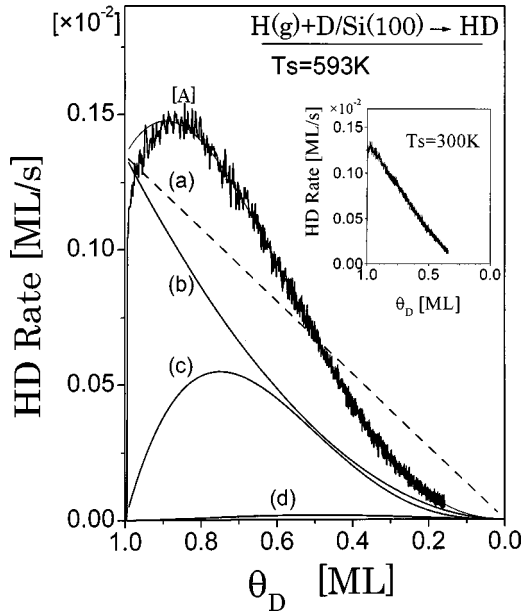


FIG. 3. Plots of HD rate curves measured at $T_s = 593$ K and 300 K (inset) as a function of θ_D . The dashed line (a) shows the first-order kinetics with respect to θ_D expected in the direct ER or HA scenario. The experimental rate curve is fit to the rate equation, $dN_{HD}/dt = k_{ABS}\theta_D^2 + C_1\theta_H\theta_D^3 + 2C_2\theta_H^2\theta_D^2 + C_3\theta_H^3\theta_D$, which is derived from Eq. (1) in the text after taking $\theta_{ij} = \theta_i\theta_j$ for $i, j = H, D$. For $\theta_H + \theta_D = 1$, the best fit curve [A] is obtained for the rate constants, $k_{ABS} = 1.35 \times 10^{-3} \text{ s}^{-1}$ [curve (b)], $C_1 = 5.2 \times 10^{-3} \text{ ML}^{-1} \text{ s}^{-1}$ [curve (c)], and $C_2 = 0.27 \times 10^{-3} \text{ ML}^{-1} \text{ s}^{-1}$ [curve (d)]. The third term of CID is negligibly small.

to dideuterides $DSiD$ implies that the surface dideuterides do not make stable clusters, but they are rather repulsive to each other.¹³ For such second-order D_2 desorptions, the dideuterides have to migrate across the surface to make binary collisions among them. For higher T_s , where STD takes place efficiently, the migrating dideuterides will terminate the dangling bonds created by STD before CID, which causes the reduction in D_2 CID at higher T_s . On the other hand, for $T_s \leq 400$ K their migration across the surface is limited because of the insufficient thermal activation, and thus D_2 CID becomes inefficient as observed in Fig. 1.

Figure 3 shows the HD rate curve as a function of θ_D for $T_s = 593$ K where the D_2 rate becomes maximum. The curve has a clear maximum around $\theta_D = 0.85$ ML, after which the HD rate superlinearly tends to the (0,0) point. For $T_s = 300$ K, on the other hand, the HD rate curve shows a tiny peak around $\theta_D \approx 0$, and exhibits a roughly first-order decrease with decreasing θ_D as shown in the inset. However, the rate curve does not tend to the (0,0) point again likely in Fig. 3. In order to get to the (0,0) point, the HD kinetics must be characterized with a reaction order higher than unity. This is evident as the HD rate curve is compared to the straight line along the first-order kinetics in θ_D [curve (a) in Fig. 3]. The HD rate is clearly lower than the line for $\theta_D \leq 0.5$ ML. Therefore, we conclude that neither the HA mechanism nor the direct ER one are operative for the D_{ad} abstraction by H because the two mechanisms commonly claim a first-order kinetics in θ_D . Besides, taking into account the feature that

the ABS rate curve is a simply decreasing function with decreasing θ_D on the saturated surface, the maximum in the HD rate around $\theta_D = 0.85$ ML is attributed to HD CID overlapping ABS. With the light of the present results and the rate-curve analysis done at $T_s = 573$ K,¹⁴ we confirm that Eq. (1) and the physics and chemistry behind it are valid. Since the relation that $\theta_{ij} = \theta_i\theta_j$ ($i, j = D, H$) is held on the surface saturated with randomly mixed H_{ad} and D_{ad} ,¹⁴ the ABS term in Eq. (1) can be recast as $(dN_{HD}/dt)_{ABS} = k_{ABS}\theta_D^2$. Thus, the HD ABS reaction on the saturated Si(100) surface follows an apparently second-order kinetics in θ_D . Using the relation that $\theta_D + \theta_H = 1$ during H admission,³ Eq. (1) is recast as a function of θ_D (see the figure caption), and the HD rate curve is decomposed into ABS and CID as shown in Fig. 3. We notice that the rates for both ABS and CID are comparable after the middle stages of H admission.

Taking into account the balance between the uptake on and loss from the surface keeping the 1 ML saturation coverage, we can evaluate ABS efficiency ξ at $t \approx 0$ as $\xi = I_0(HD)/[2I_0(HD) + 2I_0(D_2) + I_{ref}]$ for $T_s \sim 600$ K. Here, $I_0(HD)$ and $I_0(D_2)$ are the initial HD and D_2 rates, respectively, and I_{ref} is the reflected H flux. Taking the reflection probability of 0.05 as evaluated theoretically by Hansen and Vogl,¹⁶ and employing $I_0(D_2)/I_0(HD) = 0.23$ for $T_s = 593$ K as plotted in Fig. 1, we obtain $\xi = 0.39$. This value corresponds to a sticking probability $s = 0.56$, and yields an abstraction cross section $\sigma \approx 6 \text{ \AA}^2$ as evaluated from the relation $\sigma = \xi \cdot S$ ($S: 1 \times 1$ unit cell area). This is extremely large compared to the size of a hydrogen molecule. According to the recent quantum-mechanical calculations based on a flat surface model avoiding sticking,¹⁷ cross sections of the direct ER abstraction, σ_{ER} , becomes small with increasing H-substrate binding energy E_B . For $E_B = 3$ eV, close to the value $E_B = 3.4$ eV on Si,¹⁸ it has been estimated that $6 \times 10^{-5} \leq \sigma_{ER} \leq 0.025 \text{ \AA}^2$.¹⁷ Thus, there exists a serious discrepancy between the theory and the experiment on the ABS cross sections.

Since it was observed in this work that the ABS reaction is neither of a direct ER type nor of a HA one, a new model for the ABS mechanism is needed to solve the ABS puzzle, i.e., the large cross section and the apparently second-order kinetics for ABS. We seek a hint in the high reactivity of H with the substrate, since the formation of dideuterides is quite facile on Si(100) as confirmed by the β_2 TPD. In other words, the sticking probability of H to the D/Si(100) surface is much larger than that of the direct ER type ABS. The classical molecular-dynamics simulation¹⁶ in the same system showed that in addition to the high ABS probability of about 0.4 the adsorption probability of H is as high as 0.6. Although the adsorption in the simulation does not necessarily mean dihydrides, the simulated feature of the H reaction with D_{ad} is thus quite close to the present results. Such high reaction probability may be assured by three mechanisms:¹⁶ (1) the potential felt by the incident H is attractive on almost the entire surface, (2) the corrugation of this potential prolongs the interaction time and confines the event locally, and (3) the efficient momentum and energy transfer take place to the Si lattice as well as to the adsorbates. If we look at this

feature from a quantum-mechanical point of view, the chemisorbed hydrogen before full relaxation is in vibrationally excited states rather than in free conduction-band states. Here, such a vibrationally excited H-chemisorbed system is called a hot complex, and is invoked to explain a new mechanism for ABS other than an ER mechanism and a HA one. The following is proposed as a new mechanism of hot-complex-mediated ABS and CID on Si(100): Major fractions of incident H atoms first get trapped in the chemisorption potential not as a hot atom H* but as a hot complex (H+DSi-SiD)*, where based on the fact that $(dN_{\text{HD}}/dt)_{\text{ABS}} = k_{\text{ABS}} \theta_{\text{DD}}$ in Eq. (1), the doubly occupied Si dimers DSi-SiD (including DSi-SiH and HSi-SiH for $t > 0$) is chosen as a skeleton of the complex. This hot complex does not allow us to release the H atom into the mobile states or H*. The generation of ABS and formation of HSiD take place from the hot complex competitively;



The exothermicities of the relevant reactions are evaluated to be -1.1 and -2.6 eV for Eqs. (2) and (3), respectively, for the bond energies of HD (4.5 eV), H-Si (3.4 eV, Ref. 18) and Si-Si dimer (1.9 eV, Ref. 19). Therefore, the HSiD formation is facile compared to ABS, which is not at variance with the experiment. The HSiD species formed along Eq. (3) are precursors for CID that subsequently proceeds along the same mechanism as for the β_2 TPD.¹³ Hence, the HD desorptions

consist of ABS via Eq. (2) and CID initiated by HSiD formed via Eq. (3). The HD desorption via Eq. (2) is a non-thermal process and thus expected to show a dynamic feature⁵ similar to those theoretically predicted in the ER and HA scenarios.^{16,20} The fate of the hot complex either to ABS or to dihydride followed by CID may be determined by potential-energy surfaces at impact sites, phases of vibrations relevant to reaction coordinates, mass of the adatoms, etc. A hot complex (H+HSi-SiD)* arising from H sticking to HSi-SiD has a chance to generate either H₂ ABS or formation of HSiH, competing with HD ABS and formation of HSiD. This competition could cause the less efficient HD ABS at the late stages of H admission. In the ER scenario, the isotope effect on ABS is interpreted in terms of kinematics upon collision.^{10,21,22} In the present hot-complex model, it is explainable in terms of quantum effects upon relaxation of the hot complex, including a zero-point vibrational energy effect, an attempting frequency factor to transition states, tunneling through barriers, etc. Generally speaking, lighter atoms are superior to heavier ones in such quantum-mechanical transitions. Therefore, the preferential D_{ad} abstraction from DSi-SiD rather than from DSi-SiH, i.e., the first term in Eq. (1), could be reconciled with such quantum effects on the reaction in the hot complex.

This work was financially supported by CREST (Core Research for Evolutional Science and Technology) of Japan Science and Technology Corporation.

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