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Substantially low desorption barriers in recombinative desorption of deuterium from a Si(100) surface

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ABSTRACT

We have studied desorption kinetics of deuterium molecules from a Si(100) surface by means of temperature-programmed desorption (TPD) spectra and isothermal desorptions. Three desorption components, denoted as $\beta_{1,A}$, $\beta_{1,B}$, and C, can be distinguished in semi-logarithmic plots of the TPD spectra. Their peak positions and intensities are strongly affected by the surface preparation methods employed, either with or without annealing to control the initial D coverage θ_D^0. Peak C appears at the leading edge of the TPD peak. It accounts for only about 5% of the TPD peak at $\theta_D^0 = 1$ ML and it diminishes rapidly with decreasing θ_D^0, vanishing at $\theta_D^0 = 0.5$ ML. In contrast, together the $\beta_{1,A}$ and $\beta_{1,B}$ peaks account for the whole TPD peak at any θ_D^0 less than 1.0 ML. The maximum of the $\beta_{1,A}$ peak is nearly constant at around the maximum temperature of the TPD peak. On the other hand, the $\beta_{1,B}$ peak appears on the high-temperature side of the TPD peak and it systematically shifts to higher temperatures with decreasing θ_D^0. These results imply that first- and second-order kinetics are operating for the $\beta_{1,A}$ and $\beta_{1,B}$ desorptions, respectively. Isothermal desorption experiments confirm the above predicted kinetics for a limited region, namely $\theta_D^0 < 0.5$ ML. From the results for the rate curve analysis, the desorption barriers are evaluated to be 1.6 ± 0.1 eV and 1.8 ± 0.1 eV for the $\beta_{1,A}$ and $\beta_{1,B}$ desorptions, respectively. These values are substantially lower than the widely accepted value of ~2.5 eV. To reproduce the measured TPD spectra we take the Arrhenius-type rate equation containing the first- and second-order rate terms for the $\beta_{1,A}$ and $\beta_{1,B}$ desorptions. The TPD spectra measured for $\theta_D^0 < 0.4$ ML can be reasonably fit with the proposed rate equation when the values given above for $E_{d,A}$ and $E_{d,B}$ are used. For $\theta_D^0 > 0.4$ ML, however, the TPD curves are not fit with the same values; rather, the best-fit curves require values for $E_{d,A}$ and $E_{d,B}$ larger than those given above. Combining the present kinetics results with those obtained by STM along with the studies, the $\beta_{1,A}$ and $\beta_{1,B}$ peaks may be attributed to desorption along the 2H path, while peak C may be attributed to desorption along the 4H path. The atomistic desorption mechanism as well as the energy relationship between the desorption barrier and isosteric heat of adsorption are discussed.

1. Introduction

The recombinative desorption of $H_2(D_2)$ molecules from Si(100) surfaces has been extensively studied, both from a Si device technology perspective and as a prototypical reaction of hydrogen with a covalent solid surface. In contrast with metal surfaces, where surface atoms are rather static during adsorption/desorption reactions, surface reconstruction, including buckling and debuckling of Si dimers, is expected to contribute to the desorption of hydrogen from Si(100) surfaces. Kinetic and dynamic studies of hydrogen desorption were reviewed by Doren [1], focusing on two unexpected observations: an apparent breakdown in the principle of detailed balance [2], and a desorption that followed first-order kinetics [3]. The new measurements done after this review demonstrated that adsorption [4] and desorption [5] dynamics of hydrogen on Si(100) are well related each other via detailed balance. Advancements in getting the solution of the barrier puzzle were recently reviewed from a desorption perspective [6] and an adsorption perspective [7] as well as from a theoretical viewpoint [8]. In contrast to the advancements in the study of dynamics, despite extensive theoretical and experimental efforts, we have not understood the kinetic mechanism of hydrogen desorption from a Si(100) surface.

The desorption of hydrogen is generally expressed by an Arrhenius-type rate equation,

$$R = \nu \exp[-E_d/k_B T]\theta_{H(D)}^m, \quad (1)$$

where R is the rate of desorption, ν is the frequency factor, E_d is the desorption barrier, k_B is the Boltzmann constant, T is the surface temperature, $\theta_{H(D)}$ is the hydrogen(deuterium) coverage, and m is

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the desorption order. It has been observed that although a first-order rate law ($m = 1$) appropriately describes desorption from a high-coverage regime ($\theta_H \geqslant 0.1$ ML), desorption from a low-coverage regime ($\theta_H < 0.1$ ML) tends to have a nonintegral order of $1 < m < 2$ [1,7]. Historically, the physical meaning of this nonintegral order has been discussed in terms of an intra-dimer mechanism, by which first-order kinetics arises from a recombination of two H(D) atoms in prepaired (thus doubly occupied) Si dimers (DODs), while second-order kinetics ($m = 2$) is caused by singly occupied Si dimers (SODs) [9]. Recently, however, evidence of an inter-dimer mechanism, rather than the above-mentioned intra-dimer mechanism, has been observed in scanning-tunneling-microscopy (STM) images [10]. The inter-dimer mechanism includes the cases of 2H (a *cis* configuration of two SODs), 3H (a pair of SOD and DOD), and 4H (two neighboring DODs). Thus, desorption kinetics should be coverage dependent. Indeed, in TPD measurements, three desorption components were discriminated in the energy domain for various coverage windows, and these were tentatively attributed to 2H, 3H, and 4H desorptions [11]. Despite being by far the richest configuration, owing to clustering of DODs even at coverages as low as 0.5 ML [12], the 4H path was observed to be active only above 0.9 ML, whereas the 2H desorption was predominant over a wide range of surface coverages ($0 < \theta_H \leqslant 0.8$ ML). Desorption barriers must therefore be substantially lower for the 2H path than for the 4H path. However, no clues to spectral decomposition into possible kinetic channels were found in the measured TPD spectra, since, as shown in Fig. 1, the generally employed normal plots of TPD spectra do not allow discrimination of the peak components involved.

Moreover, the values reported for E_d are not well established, since they vary from 1.8 eV to 2.8 eV [13–18]. Among these, the value of 2.5 eV [16–18] is currently favored [1,7]. This value was evaluated from the rate of decrease in surface coverage measured by optical second harmonic generation (SHG) [17] and laser-induced thermal desorption (LITD) [16], and from curve fitting of TPD spectra with a kinetic equation based on an intra-dimer mechanism [18]. Low E_d values of 2.0 eV and 2.2 eV were also obtained by the LITD method [13] and by direct counting surface dangling bonds with STM [15]. The smallest value, 1.8 eV, was reported based on a best-fit curve to a D_2 TPD spectrum, using first-order desorption kinetics [14]. In Fig. 1, we compare the fit results obtained for the two extreme values of $E_d = 1.8$ eV and 2.5 eV on a 1 ML D-covered Si(100) surface, where first-order kinetics is assumed in the numerical integration of Eq. (1). The fit using $E_d = 2.5$ eV cannot reproduce the measured TPD spectrum, since the fit curve is much sharper than the measured one. In contrast, using $E_d = 1.8$ eV can give a better fit, although the curve is slightly broader than the measured TPD spectrum in the main temperature region. Moreover, both of the fit curves seriously deviate from the measured curve at their leading and trailing edges. As long as desorption data are analyzed on the basis of a single, first-order kinetics, the TPD spectrum cannot be reasonably reproduced using any kinetic parameters. To validate the observed desorption kinetics, the consistency between isothermal desorption and TPD spectra should be thoroughly evaluated.

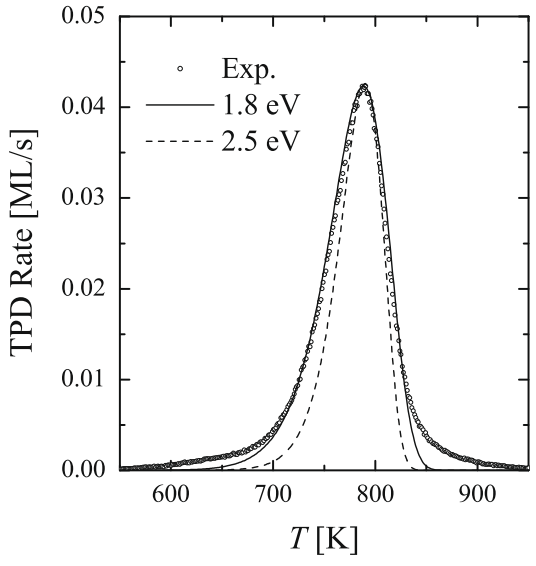

Fig. 1. Fits of a β_1 TPD spectrum obtained on a 1 ML D/Si(100) surface (open circle) by the rate equation (1) in the text assuming first-order kinetics with $m = 1$. Solid and dotted lines indicate the "best" curve fits obtained with fixed $E_d = 1.8$ eV and $E_d = 2.5$ eV and ν's as free parameters in curve fitting. The values of 3.7×10^{10} s^{-1} and 1.4×10^{15} s^{-1} for ν were chosen for the 1.8 and 2.5 eV desorption barriers, respectively.

In this paper, we report the desorption kinetics of deuterium from a Si(100) surface measuring TPD spectra and isothermal desorptions. We intend to show that semi-logarithmic plots of TPD spectra are detailed enough to be decomposed into three desorption components. Isothermal desorption experiments revealed that two main desorption components follow first- and second-order kinetics with respect to θ_D and both are characterized with a desorption barrier substantially lower than the conventionally accepted value of ~2.5 eV.

2. Experiment

Kinetic experiments on D_2 desorption from Si(100) surfaces were conducted in an ultra-high vacuum reaction chamber equipped with a quadrupole mass spectrometer (QMS). A commercially available Si(100) wafer (p-type, 10–15 Ω cm) was cut into a $15 \times 24 \times 0.3$ mm^3 specimen. The specimen was cleaned in the reaction chamber by thermal flashing at 1373 K followed by annealing at 873 K for 10 min. The cleanliness of the surface was verified by Auger electron spectroscopy (AES). We found that the C(KLL) and O(KLL) AES intensities were less than 1% of the Si(LVV) intensity. Clean Si(110) and Si(111) surfaces were also prepared following the above procedure. D_2 desorption from these surfaces was studied to validate the measurement capability of the system. D atoms were generated in a radio-frequency plasma of D_2 mixed with Ar (1:1 pressure ratio) and admitted to the reaction chamber through three differentially pumped chambers. The resulting D flux at the surface was about 1.5×10^{13}cm^{-2}s^{-1} or 0.02 ML/s (ML: monolayer). In order to control the surface temperature T for TPD or isothermal desorptions, direct resistive heating was employed. A personal computer (PC) set current I of a power supply and then it read voltage V to control and regulate injected power. The PC also evaluated electrical resistance of the sample $R(= V/I)$ from which temperature of the surface was determined referencing a T vs. R curve calibrated by an infrared pyrometer. D_2 TPD spectra (heating rate of 3.4 K/s) were measured by the QMS. To record isothermal desorption rate curves, signal pulses from the QMS were fed into a multichannel scaler. The temperature for the isothermal desorption experiments was generally set prior to D deposition, to avoid unsteady desorption that could result from a rapid temperature rise after D deposition at a lower temperature. To investigate isothermal desorption from the high-coverage regime, the surface was exposed to the D beam for 1 min at various desorption temperatures that affect θ_D^0 due to desorption during D dosing. Hence, θ_D^0 becomes smaller with T, yet larger than 0.1 ML at $T < 750$ K. Desorption rates were measured for 14 min at various temperatures below 750 K. To study isothermal desorption from the low-coverage regime at $T > 870$ K, we used a rotating chopper