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Desorption of hydrogen from Si(100)2×1 at low coverages: The influence of π-bonded dimers on the kinetics

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The recombinative desorption of hydrogen from the Si(100)2×1 monohydride state was investigated by means of isothermal measurements using optical second-harmonic generation to monitor the hydrogen coverage. In agreement with previous results, we observe approximately first-order kinetics for hydrogen coverages above 0.1 monolayers. For lower hydrogen coverages, the desorption rate is found to decrease more rapidly. The data are interpreted within the recently developed model of hydrogen pairing at the Si dimers. We relate the observed kinetics to the π bonding of the Si-Si units and deduce an effective π-bond strength of 0.25 eV. The desorption activation energy determined from the present data is 2.48 ± 0.1 eV, with a first-order prefactor of $\sim2\times10^{15}\ \mathrm{s}^{-1}$.

It has been found that the desorption of molecular hydrogen from the monohydride state of H/Si(100)2×1 follows first-order kinetics.[1,2] This experimental observation, unexpected for a recombinative desorption process, has attracted considerable interest.[3–8] In the usual picture of recombinative desorption, the adsorbed atoms diffuse from site to site, occasionally undergoing a collision leading to reaction and desorption. Such a process, absent other complications, yields a desorption rate varying quadratically with coverage. To explain the first-order kinetics of H/Si(100)2×1, a new mechanism was initially proposed for recombinative desorption on covalent materials, one in which an atomic precursor played a key role.[1] However, experimental results on surface diffusion[9] and desorption kinetics[2,3] or H/Si(111)7×7 indicate that such a model is not required to explain the behavior of this Si surface. Current evidence suggests that recombinative desorption of hydrogen from Si(100) also proceeds more conventionally, but in a manner strongly influenced by the distinct structure of this surface.

The main element of the Si(100)2×1 reconstruction is the formation of Si dimers. One of the two dangling bonds of each surface atom of the truncated bulk establishes a strong σ bond with another Si atom. As this pair of atoms move together to form a dimer, the remaining p_z-like dangling bonds interact in a weak π bond.[10] Hydrogen adsorption at low coverage retains the dimerization,[11] but disrupts the π bonds.[12] If the π bond is stronger than the repulsive interaction between two hydrogen atoms on the same dimer, then a *pairwise* occupation of the dimers becomes energetically favorable relative to singly occupied dimers.[5,8] Such a preferential pairing was indeed observed in a recent scanning tunnel microscopy (STM) study of annealed H/Si(100)2×1 surfaces[5] and provides a natural explanation for the observed first-order desorption kinetics.[2,5,8]

In this paper we present new isothermal desorption measurements in the regime of low hydrogen coverages that add quantitative information to the existing qualitative picture. We exploit the high surface sensitivity of optical second-harmonic generation (SHG) to monitor accurately the hydrogen coverage θ to below 0.005 monolayers (ML). Our experiments reveal a kinetic behavior close to first order for $\theta>0.1$ ML, as was observed previously with laser-induced thermal desorption (LITD).[1,2] We find, however, that for $\theta<0.1$ ML, the kinetics depart from first order, with a desorption rate decreasing more rapidly than linearly with coverage. We interpret our data as the statistical mechanical consequence of the finite stabilization energy ε of a pair of hydrogen atoms sharing a dimer site: at low coverages the relative population of singly occupied dimers becomes substantial, diminishing the number of doubly occupied dimers available to participate in the desorption process. From analysis of the desorption rate versus coverage, a value of $\varepsilon=0.25$ eV is deduced for the pairing energy. We have also performed a precise determination of the activation energy and prefactor for desorption in the low-coverage regime. The activation energy of 2.48 ± 0.1 eV agrees well with one of the two recent determinations by the LITD method.[1,2]

The experiments were conducted under ultrahigh vacuum conditions (base pressure $<10^{-10}$ mbar). The experimental setup and sample preparation were similar to those reported for our previous study of H/Si(111)7×7,[3] the major difference being the geometry for the SHG measurement. In the present work the 1064-nm radiation of the *Q*-switched Nd:yttrium aluminum garnet (pulse duration 10 ns, repetition rate 33 Hz, fluence <0.2 J/cm^2) was incident at 45° with respect to the surface normal. The pump radiation was linearly polarized with *s*- and *p*-components chosen to maximize the SH signal. The silicon sample, consisting of lightly *p*-doped material, was oriented to within 1/4° of the (100) plane. The surface exhibited equally weighted domains of both orientations of the 2×1 reconstruction.

For the isothermal desorption measurements a controlled amount of atomic hydrogen, produced by dissociation of H$_2$ at a hot filament, was adsorbed on the sample. The sample, held at 590 K during dosing, was then stepped to the desired temperature and the SH signal was recorded as hydrogen desorbed. The relation between the SH signal and the hydrogen coverage was established by means of a series of temperature programmed desorption (TPD) measurements using a quadrupole mass spectrometer. For all the low-coverage data discussed in this work, the required conversion is just a linear proportionality between the SH field (the square root of the detected SH signal) and the hydrogen coverage. As an absolute reference for the calibration procedure, we employed the saturated monohydride (β_1) TPD desorption peak, which is identified with a hydrogen coverage of 1 ML$=0.68\times10^{15}$ atoms/cm^2.

Figure 1 displays the hydrogen coverage $\theta(t)$ as a function of time t during the isothermal desorption of hydrogen from Si(100)2×1. Results are shown for several temperatures T in the range of 670 to 730 K. The experimental data allow us to determine θ over almost two orders of magnitude below the initial coverage of 0.15 ML.

For the purposes of analysis, we assume, as suggested by D'Evelyn, Yang, and Suctu,[8] that the recombination process is dominated by reactions at the doubly occupied dimers. This approximation neglects the traditional hopping recombination from singly occupied dimers, as well as reactions from, e.g., hydrogen atoms adsorbed at adjoining sites of different dimers.[6] We further assume that there is only one type of dimer on the surface and thus do not take into account possibly different desorption rates associated with step or defect sites.[13] The desorption rate may then be written as

$$R_d=-\frac{d\theta}{dt}=k\theta_2=\nu_d\exp\left[\frac{-E_d}{k_BT}\right]\theta_2\,, \tag{1}$$

where E_d and ν_d describe the thermally activated recombination process at the doubly occupied dimers. The amount of hydrogen at doubly-occupied dimers θ_2 is determined by the total hydrogen coverage θ and the equilibrium established between singly- and doubly-occupied dimer units.[14] We define the pairing energy ε of the doubly-occupied dimer unit by the energy required to form two singly-occupied dimers from it:

$$\overset{\mathrm{H}}{\mathrm{Si}}\text{-}\overset{\mathrm{H}}{\mathrm{Si}}+\mathrm{Si}\text{-}\mathrm{Si}\xrightarrow{\varepsilon}2\,\mathrm{Si}\text{-}\overset{\mathrm{H}}{\mathrm{Si}}\;. \tag{2}$$

To calculate the density of doubly occupied dimers we adopt a simple lattice-gas model in which different dimer sites are noninteracting. θ_2 is then given directly by elementary statistical mechanics.[8] With $\alpha(\varepsilon,T)=\exp(\varepsilon/k_BT)-1$, the result can be expressed as

$$\theta_2=\theta-\frac{[1+4\alpha\theta(1-\theta)]^{1/2}-1}{2\alpha}\,. \tag{3}$$

We emphasize that this expression is an approximation. A more detailed model would have to go beyond a lattice-gas description in order to take into account effects of clustering,[5] as well as geometrical constraints of the reaction (2) on the surface.

Equations (1) and (3) together determine the desorption kinetics. It is instructive to consider the predicted behavior in different regimes. For a pairing energy ε small compared with the thermal energy k_BT ($\alpha\ll1$) the behavior is trivial: the occupancy of the dimers is random and a second-order rate law ($R_d\propto\theta^2$) holds for all coverages. In the opposite limit of a substantial pairing energy ($\alpha\gg1$), it can be seen that first-order kinetics ($R_d\propto\theta$) apply for coverages $\theta\gg\alpha^{-1}$. In this regime almost all of the hydrogen is accommodated in doubly occupied dimers, with the consequent first-order kinetics. As the coverage falls to $\theta\sim\alpha^{-1}$, the entropy term in the free energy becomes significant and an appreciable concentration of hydrogen appears on singly occupied dimers. This leads to a decreased desorption rate. Finally for coverages low enough to satisfy $\theta\ll\alpha^{-1}$, occupation of the dimers becomes completely random and second-order kinetics are predicted. Thus we see that the form of the desorption kinetics in the low-coverage regime is strongly influenced by the energetics of the hydrogen pairing on dimers.

We have numerically fit our data to the functional form $\theta(t)$ obtained by integrating Eq. (1) with θ_2 given by Eq. (3). The pairing energy that provides the best agreement with data for various temperatures and initial coverages is $\varepsilon=0.26$ eV. The solid lines in Fig. 1 have been constructed using this value of ε together with a temperature dependent rate constant k. Good agreement is obtained for all of the experimental data.

Figure 2 displays the results of a single isothermal desorption measurement in greater detail. On this semilogarithmic plot, the exponential decay in coverage associated with a first-order rate law appears as a straight line. For $\theta>0.1$ ML, the experimental data conform well to the predictions of a first-order rate law, in accordance with previous reports.[1,2] At lower coverages, however, the desorption rate clearly becomes slower than expected for a first-order process. Comparing the experimental results with the predictions of the model, we find the best fit for $\varepsilon=0.25$ eV. As can be seen from Fig. 2, small changes in ε lead to noticeable departures from the experimental data. From these and other data, we estimate an uncertainty of ±0.05 eV in our determination of the pairing energy ε. This experimental error does not include possible effects of the various simplifications introduced in the

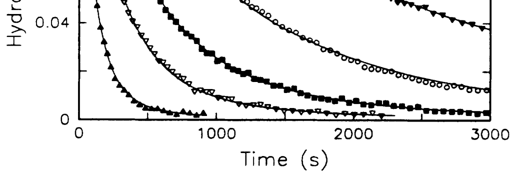

FIG. 1. Hydrogen coverage as a function of time for isothermal desorption of H_2 from Si(100)2×1. The symbols indicate the H coverage obtained from the measured SH signal for various surfaces temperatures. The solid lines are the results of best fits to the model described in the text using a pairing energy of $\varepsilon=0.26$ eV.

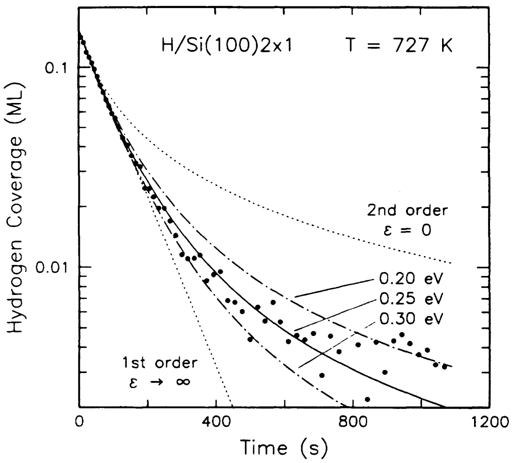

FIG. 2. Semilogarithmic plot of isothermal desorption data obtained at a surface temperature of 727 K together with predictions of the desorption model for different pairing energies ε. The best fit, indicated by a solid line, is obtained for $\varepsilon=0.25$ eV. Two curves for $\varepsilon=0.20$ and 0.30 eV are shown for comparison. The results for $\varepsilon=0$ and $\varepsilon \to \infty$ correspond to second- and first-order kinetics, respectively.

model.

As was indicated above, the origin of the attractive interaction of two H atoms on a Si dimer unit can be understood in terms of disruption of the π bonding of the dangling bonds existing in the unreacted Si(100)2×1 surface. The π bond gives rise to a surface state at about 0.7 eV below the Fermi level[15] that is found to be quenched upon hydrogen adsorption.[12] While spectroscopic data on the position of the electronic states may be used to estimate the stabilization energy ε for a doubly occupied dimer, such a comparison is far from direct. In addition to relaxation and correlation energies associated with the breakup of the π bond, any weak (repulsive) interaction between the two H atoms of the doubly occupied dimer or (attractive) interaction between the H atom and the empty dangling bond of the singly occupied dimer enter into ε and are difficult to account for in spectroscopic measurements. It is therefore not surprising that Boland[5] estimates a much higher pairing energy of ~ 0.8 eV from his STM spectroscopic data than observed here.

It is interesting to compare our measurement with two recent *ab initio* calculations in which the Si(100)2×1 dimers were represented by modified Si_9H_{12} clusters.[6,7] Assuming the validity of the model developed to describe the desorption data, our experimental determination of ε should provide an important test for these calculations. The pairing energy ε can be compared with the computed difference in energy required to remove the first and second H atoms from a doubly occupied dimer. From the calculations of Wu and Carter[6] one estimates $\varepsilon \approx 0.08$ eV, while the work of Nachtigall, Jordan, and Janda[7] gives $\varepsilon \approx 0.22$ eV, both of which appear to agree with experiment to computational accuracy.

In addition to the detailed analysis of the kinetic order of the desorption process, i.e., of its variation with hydrogen coverage, our data allow us to extract accurate values for the temperature dependence of the desorption rate and to establish thereby the activation energy for desorption. This issue is of particular interest in light of the conflicting results obtained in recent LITD and TPD studies.[1,2] In analyzing our data, we make use of the fitting procedure described above to determine the desorption rate $k_d = R_d/\theta_2$ of the doubly occupied dimers as a function of temperature. The rates from a series of measurements are displayed in Fig. 3 as an Arrhenius plot. The activation energy deduced for desorption from the doubly occupied dimers is $E_d = 2.48 \pm 0.1$ eV, with a prefactor of $\nu_d \sim 2\times 10^{15}\ s^{-1}$. These values are in excellent agreement with the recent work of Wise *et al.*,[2] but are at variance with the significantly lower activation energy (2.0–2.1 eV) and prefactor ($2\times 10^{11}\ s^{-1}$) reported by Sinniah *et al.*[1] We note that in our description the desorption rate is treated as proportional to θ_2, rather than to the usual total coverage θ.[1,2] This distinction is negligible in the limit of high coverage and is *not* relevant for the comparison with the LITD results. For $\theta = 0.15$ ML this treatment introduces a minor correction, increasing the activation energy by 0.05 eV.

The values obtained for the activation energy ($E_d = 2.5$ eV) and the pairing energy ($\varepsilon \simeq 0.25$ eV) can be combined with the known H_2 dissociation energy ($E_{\text{H-H}} = 4.5$ eV) and the calculated Si-H bond strength ($E_{\text{Si-H}} = 3.5$–3.8 eV) (Refs. 6 and 7) to examine the overall energetics of the hydrogen desorption process from the Si(100)2×1 surface. The energy balance relation $2E_{\text{Si-H}} - \varepsilon \simeq E_d + E_{\text{H-H}}$ is seen to be roughly satisfied.[16] The failure of this relationship based on a higher $E_{\text{Si-H}}$ and a lower E_d was one important motivation for the initial rejection of the pairing model by the authors of Ref. 1.

In conclusion, the present investigations of recombinative desorption of the monohydride species of H/Si(100)2×1 in the low-coverage regime reveal a somewhat complex behavior, despite the apparent simplicity of the system and reaction under study. For hydrogen coverages exceeding 0.1 ML, the rate for recombinative desorption is found to obey first-order kinetics, while a sharper

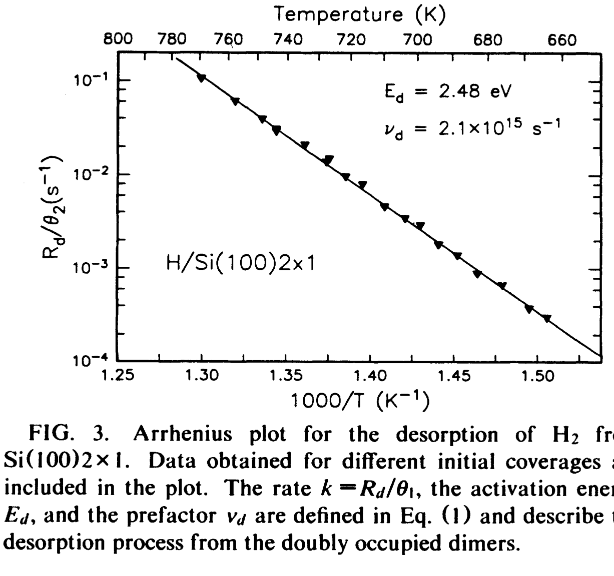

FIG. 3. Arrhenius plot for the desorption of H_2 from Si(100)2×1. Data obtained for different initial coverages are included in the plot. The rate $k = R_d/\theta_1$, the activation energy E_d, and the prefactor ν_d are defined in Eq. (1) and describe the desorption process from the doubly occupied dimers.

fall in the rate with decreasing coverage is observed at lower coverages. These desorption kinetics can be understood in a straight forward manner on the basis of a prepairing model. In this scheme hydrogen atoms preferentially form doubly occupied dimer units from which desorption occurs. At high coverage essentially all of the hydrogen is accommodated in the paired state and first-order kinetics are predicted. At sufficiently low hydrogen coverages, however, a non-negligible fraction of the hydrogen appears on singly occupied dimers, leading to a decrease in the desorption rate. Quantitative agreement with the experimental data is obtained using a statistical model with a stabilization energy for the doubly occupied sites of $\varepsilon=0.25$ eV. This attractive interaction arises from the energy required to disrupt the π bond formed between the two dangling bonds of an unreacted dimer. The result demonstrates the limitation of a picture of the surface in which the interactions between dangling bonds are neglected and clearly has implications for other reactions on the Si(100)2×1 surface.

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