

# Probing the dynamics of hydrogen recombination on Si(100)

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Relatively few state-selective studies have probed recombinative desorption from surfaces.<sup>1-4</sup> These studies, which have focused on desorption from the surfaces of metals, have used bulk permeation or chemical reactions to prepare the desorbing species. In this Communication we report the first state-selective study of recombinative thermal desorption from a semiconductor surface. Our results indicate that the mechanism of recombinative desorption of molecular hydrogen from Si(100) leads to rotational distributions colder than the surface; we conclude that little torque is applied to the molecule in the process of recombination. An accurate model of recombination must include a dynamical constraint that causes an exaggerated population of low rotational states.

The chemisorption and desorption of molecular hydrogen on silicon surfaces has been studied extensively using traditional surface science techniques.<sup>5-12</sup> The sticking coefficient for molecular hydrogen is quite low ( $< 10^{-5}$ ), probably because adsorption is an activated process. Many properties of this system, however, have yet to be determined unambiguously.

A series of experiments<sup>13,14</sup> has shown that desorption from the monohydride phase on the Si(100)-(2×1) surface follows a first-order rate law while confirming that desorption from Si(111)-(7×7) follows a second-order rate law.<sup>9</sup> Recently, another experiment found that desorption from Si(111)-(7×7) at low coverage is described by kinetics that are intermediate between first and second order.<sup>15</sup> First-order desorption of hydrogen has also been observed from diamond,<sup>16</sup> germanium,<sup>17</sup> and tellurium<sup>18</sup> surfaces. Kinetics with an order less than two are inconsistent with conventional hopping models<sup>19</sup> that appear to describe accurately the recombinative desorption of hydrogen from the surfaces of metals. Sinniah *et al.*<sup>13</sup> have proposed a model in which the irreversible excitation of one hydrogen atom into a freely translating state precedes recombination of this atom with a bound atom, while Reider *et al.*<sup>15</sup> have proposed a more conventional diffusion-based model that incorporates recombination via at least two distinguishable sites. Thus, we are led to consider alternative mechanisms of recombinative desorption that must explain not only why recombinative desorption differs on semiconductors versus metals, but also why it is structure sensitive for Si surfaces.

Internal-state distributions of molecular hydrogen are determined using a (2 + 1) resonance-enhanced multiphoton ionization (REMPI) scheme utilizing the  $E, F^1\Sigma_g^+$  state as an intermediate state.<sup>20</sup> This scheme requires ultraviolet radiation in the wavelength range of 200–215 nm to probe  $v=0$  and 1. This light is generated by a

Nd:YAG-pumped dye laser, the output of which is first doubled in a potassium dihydrogen phosphate (KDP) crystal, then mixed with residual dye fundamental in a  $\beta$ -barium borate (BBO) crystal.<sup>21</sup> The laser beam propagates parallel to the crystal face and is focused a few millimeters above the Si surface using a 350 mm lens. Ions produced in the REMPI process are extracted into a time-of-flight (TOF) tube wherein they are counted using a chevron (two-stage multichannel plate) detector. The output of the chevron detector is collected by a gated integrator and stored by a minicomputer for subsequent analysis. This method of state-selective detection has a sensitivity on the order of  $5 \times 10^5$  molecules per quantum state per  $\text{cm}^3$ .

The ultra-high vacuum chamber is evacuated by a turbomolecular pump to a base pressure of  $\sim 2 \times 10^{-10}$  Torr. Surface order and cleanliness are checked with low energy electron diffraction (LEED) and Auger electron spectroscopy (AES). Highly As-doped (0.005  $\Omega$  cm) Si(100) crystals facilitate direct resistive heating. The crystal and manipulator are liquid-nitrogen cooled. Surface temperature is monitored by chromel–alumel thermocouples affixed to the Si.

Experiments are performed by dosing the Si(100)-(2×1) surface to saturation using a pulsed, skimmed, and collimated molecular beam of disilane ( $\text{Si}_2\text{H}_6$ ). Disilane decomposes to form adsorbed silicon hydride species. Disilane has a sticking coefficient of  $\sim 10^{-1}$ ,<sup>22</sup> making it a much more practical source of surface hydrogen than  $\text{H}_2$ . In addition, we find disilane more convenient to use than atomic hydrogen. Disilane adsorption and subsequent  $\text{H}_2$  desorption under our experimental conditions result in the epitaxial growth of silicon. The surface is in the (2×1) reconstruction at the start and end of an experiment, but we cannot probe the surface structure at the time of  $\text{H}_2$  desorption. Recent STM studies,<sup>23</sup> however, have shown that ordered (2×1) islands of monohydride-capped Si result from disilane adsorption after heating the surface to 670 K, i.e., ordering occurs at a surface temperature far below the desorption temperature of the monohydride. A crystal temperature of  $\approx 400$  K is typically used during adsorption. Such elevated temperatures ensure that the Si surface is predominantly covered by the monohydride. We note that at saturation coverage all of the surface dangling bonds are capped with adsorbed hydrogen,  $\text{H}_{(a)}$ .<sup>24,25</sup> Therefore, if we assume complete dissociation of  $\text{Si}_2\text{H}_6$ ,  $\frac{1}{3}$  of the surface is covered with newly deposited Si, and the ratio of  $\text{H}_{(a)}$  on 'original' sites to  $\text{H}_{(a)}$  on newly deposited Si is 2:1.

After dosing the crystal, temperature programmed desorption (TPD) is performed. We use the REMPI/TOF



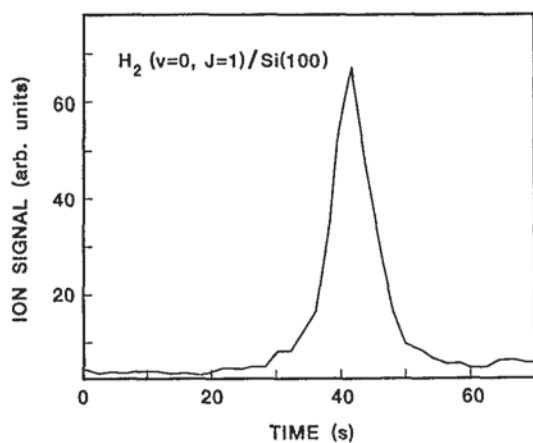


FIG. 1. Thermal desorption spectrum for  $\text{H}_2(\nu=0, J=1)$  desorbed from Si(100) after a saturation dose of  $\text{Si}_2\text{H}_6$ . The surface temperature during adsorption  $\approx 400$  K. The temperature was linearly ramped from 300 to 1000 K at a heating rate of  $10 \text{ K s}^{-1}$ . The time of the peak maximum corresponds to a surface temperature near 800 K.

scheme to collect the desorption spectrum one rovibrational quantum state at a time. In this procedure, the laser is tuned to a transition corresponding to a  $(\nu=0, J)$  level. Ions created in the REMPI process are then collected as a function of crystal temperature. The heating rate is  $10 \text{ K s}^{-1}$  and 20 laser shots are averaged into one bin. The maximum in the thermal desorption flux occurs in the range 780–800 K.<sup>26</sup> The thermal desorption spectra are then integrated and reduced to rotational populations. The reduction of spectral data obtained by  $(2+1)$  REMPI through the  $E, F$  state to accurate populations has been well established.<sup>20</sup>

Using this method, we have obtained data for the thermal desorption from Si(100) of both  $\text{H}_2$  (by dosing  $\text{Si}_2\text{H}_6$ ) and  $\text{D}_2$  (dosing  $\text{Si}_2\text{D}_6$ ). A typical thermal desorption spectrum of  $\text{H}_2(\nu=0, J=1)$  is shown in Fig. 1. This raw data must be corrected for two distinct background contributions, ambient hydrogen present in the vacuum chamber and hydrogen that has thermally desorbed from the Si(100) surface and entered the laser focal volume *after having undergone a number of collisions with the chamber walls*.

The former type of background signal is constant over a desorption spectrum and is easily accounted for by simply setting the baseline for integration at an appropriately offset value. The second type of background signal requires a more elaborate subtraction technique in which independent experiments are performed to determine the temperature of the background gas and the fraction of the signal caused by background. We have determined that the background gases are equilibrated to room temperature. Furthermore, we have determined that nascent  $\text{H}_2$  ( $\text{D}_2$ ) constitutes 70% of our signal, i.e., 30% of our signal is from collisionally relaxed  $\text{H}_2$  ( $\text{D}_2$ ).

The rotational populations for  $\text{H}_2$  and  $\text{D}_2$  after background subtraction are presented as Boltzmann plots in Fig. 2. Because of curvature in the high- $J$  region, we prefer

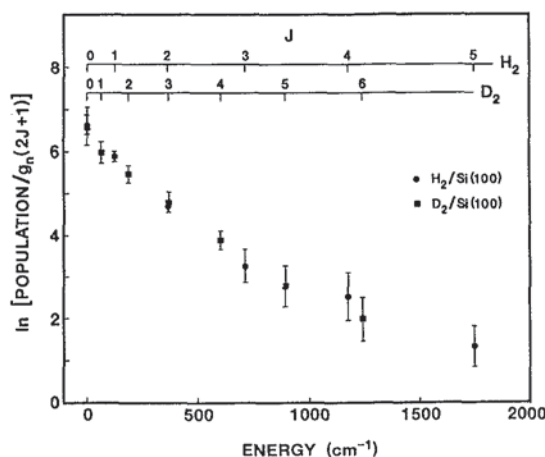


FIG. 2. Boltzmann plot (natural logarithm of the degeneracy weighted population vs rotational energy) of  $\text{H}_2$  and  $\text{D}_2$  thermally desorbed from Si(100). The data have been corrected for background contributions as explained in the text.  $T_s \approx 780\text{--}800$  K.

to characterize the distributions using an average rotational energy,  $\langle E_{\text{rot}} \rangle$ , rather than a rotational temperature. The observed average rotational energies are  $\langle E_{\text{rot}}(\text{H}_2) \rangle = 368 \pm 67 \text{ K}$  and  $\langle E_{\text{rot}}(\text{D}_2) \rangle = 348 \pm 65 \text{ K}$ . Note that (1) both  $\text{H}_2$  and  $\text{D}_2$  exhibit significant rotational cooling in desorption (compared to  $T_s \approx 780\text{--}800$  K), (2)  $\langle E_{\text{rot}}(\text{H}_2) \rangle$  and  $\langle E_{\text{rot}}(\text{D}_2) \rangle$  are essentially the same, (3) deviations from a Boltzmann distribution are manifested by curvature in the high- $J$  region, and (4) ortho and para states are populated statistically.

Rotational cooling in desorption has been observed for molecular hydrogen desorption from Cu (Ref. 1) and Pd.<sup>27,28</sup> In the case of Cu, rotational cooling was slight ( $\langle E_{\text{rot}} \rangle \approx 0.8\text{--}0.9$  of  $kT_s$ ) and Kubiak *et al.*<sup>1</sup> concluded that the rotational degree of freedom did not play a major role in the recombinative process. On S-covered poly-Pd surfaces,  $T_{\text{rot}}$  remained fairly constant at  $\approx 490$  K over the range  $500 \text{ K} < T_s < 1050 \text{ K}$ . Rotational-to-translational energy transfer as in the case of NO desorption (see, for example, Ref. 29, and references therein) was offered by Zacharias *et al.*<sup>27,28</sup> as a possible mechanism. In neither system has any isotopic effect been observed in the rotational distribution.

It is unlikely that rotational-to-translational energy transfer is responsible for the rotational cooling observed here. The hydrogen molecule has almost no interaction with a Si surface, experiencing only an extremely weak van der Waals attraction. Momentum transfer is further hindered by the large mass mismatch between molecular hydrogen and Si, the large rotational energy spacing of molecular hydrogen, and the  $\Delta J = \text{even}$  selection rule that rotational-state-changing collisions of  $\text{H}_2$  and  $\text{D}_2$  must obey. Little energy transfer<sup>30,31</sup> is to be expected between the surface and a newly formed hydrogen molecule; thus, it is unlikely that the energy distribution of the hydrogen molecule is significantly perturbed by the Si surface once the molecule has formed. Therefore, we regard the rotational distribution as reflecting the dynamics of the recom-



binative event rather than an exit channel effect.

Because we can neglect the possibility of rotational-state-changing events after molecular formation, low rotational excitation demands that little torque is applied to the molecules during recombination. Thus, we can rule out recombination from a highly asymmetric transition state or recombination from collisions with large impact parameters. The low rotational excitation must result from some dynamical constraint on the recombination of molecular hydrogen. It is unlikely that this constraint arises from the interatomic interaction potential of hydrogen. Theoretical calculations<sup>32,33</sup> on the three-body, gas-phase recombination of H<sub>2</sub> do not support the idea that only collisions with low impact parameters lead to molecular formation. A more likely explanation is that the recombination occurs on a potential energy surface that does not resemble the gas-phase H–H interaction potential because of the presence of the Si surface. Rotational distributions colder than the surface will result if the surface is able to bias reactive trajectories toward low-torque pathways. These pathways would be characterized by low impact parameters (engendered either by constraining diffusion to certain crystallographic directions or by favoring recombination across or between dimer pairs) and/or by high symmetry between the H–H bond axis and the potential energy surface (i.e., both ends of the molecule are in regions of roughly equal potential energy during formation).

Recall that Sinniah *et al.* proposed a mechanism involving the collision of one diffusing hydrogen atom with one bound atom to explain the first-order rate law for recombination.<sup>13</sup> Based on the present result, their model must be modified. If the diffusing atom is unaffected by the surface corrugation, this model can only be consistent with low rotational temperatures if we demand that the H–H interaction potential itself strongly favors recombination through low-impact-parameter collisions. As we have stated above, this is unlikely. In addition, the Sinniah model gives us no apparent reason to expect desorption from the (100) surface to behave differently than desorption from the (111) surface, yet the kinetics are clearly different.<sup>14</sup> For the model of Sinniah *et al.* to be consistent with our results, we must assert that diffusing hydrogen atoms experience some of the surface corrugation because the surface can then force the diffusing atoms into the head-on collisions that are required for low rotational excitation.

Alternatively, we might consider a model involving a concerted reaction, in which the recombination takes place between hydrogen atoms that are bound to two adjacent Si atoms. Our data may then be interpreted as resulting from a transition complex which is characterized by a high degree of symmetry with respect to the potential felt by both H atoms. A unique feature of the reconstructed Si(100)-(2×1) surface is the presence of rows of dimers. Dimer rows and first-order kinetics are also present on the Ge surface noted above, but are absent on the Si(111)-(7×7) surface. It is suggestive to consider the presence of dimer rows, and the geometric and energetic corrugation introduced by them, as a possible influence on the recombina-

tion dynamics. This influence may stem either from diffusion along the rows of dimers or from recombination across a dimer or between adjacent dimer pairs.<sup>34</sup>

A comparison with the kinetic model proposed by Reider *et al.*,<sup>15</sup> to describe desorption of H<sub>2</sub> from Si(111)-(7×7), while making no specific predictions about the recombination dynamics, cannot be made until rovibrational-state distributions have been obtained from this surface.

Experiments are now underway in our laboratory to obtain vibrational-state distributions for hydrogen desorbed from Si(100)-(2×1) as well as rovibrational-state distributions for hydrogen desorbed from Si(111)-(7×7) surfaces which may, as suggested by the results of the kinetic measurements, involve a different mechanism of recombination. Preliminary results indicate that vibrational-state distributions for hydrogen desorbed from Si(100)-(2×1) exhibit superthermal excitation.

In conclusion, we have obtained rotational distributions for H<sub>2</sub> and D<sub>2</sub> thermally desorbed from Si(100) surfaces. The average rotational energies (expressed in temperature units) are significantly lower than the surface temperature and exhibit no isotopic dependence. The observed low rotational excitation requires some dynamical constraint in the recombinative process which demands an exaggerated preference for low-torque trajectories during recombination and desorption of molecular hydrogen from Si(100).

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- <sup>1</sup>G. D. Kubiak, G. O. Sitz, and R. N. Zare, *J. Chem. Phys.* **83**, 2538 (1985).
- <sup>2</sup>L. Schröter, H. Zacharias, and R. David, *Phys. Rev. Lett.* **62**, 571 (1989).
- <sup>3</sup>R. P. Thorman and S. L. Bernasek, *J. Chem. Phys.* **74**, 6498 (1981).
- <sup>4</sup>H. Zacharias, *J. Mod. Phys. B* **4**, 45 (1990).
- <sup>5</sup>S. Ciraci, R. Butz, E. M. Oellig, and H. Wagner, *Phys. Rev. B* **30**, 711 (1984).
- <sup>6</sup>H. Froitzheim, U. Köhler, and H. Lammering, *Surf. Sci.* **149**, 537 (1985).
- <sup>7</sup>U. Jansson and K. Uram, *J. Chem. Phys.* **91**, 7978 (1989).
- <sup>8</sup>H. Kobayashi, K. Edamoto, M. Onchi, and M. Nishijima, *J. Chem. Phys.* **78**, 7429 (1983).
- <sup>9</sup>B. G. Koehler, C. H. Mak, D. A. Arthur, P. A. Coon, and S. M. George, *J. Chem. Phys.* **89**, 1709 (1988).
- <sup>10</sup>S. Maruno, H. I. Wasaki, K. Horioka, S.-T. Li, and S. Nakamura, *Phys. Rev. B* **27**, 4110 (1983).
- <sup>11</sup>D. Muller, F. Ringeisen, J. J. Koulmann, and D. Bolmont, *Surf. Sci.* **189/190**, 364 (1989).
- <sup>12</sup>G. Schulze and M. Henzler, *Surf. Sci.* **124**, 336 (1983).
- <sup>13</sup>K. Sinniah, M. G. Sherman, L. B. Lewis, W. H. Weinberg, J. T. Yates, Jr., and K. C. Janda, *J. Chem. Phys.* **92**, 5700 (1990).
- <sup>14</sup>M. L. Wise, B. G. Koehler, P. Gupta, P. A. Coon, and S. M. George, *Surf. Sci.* (to be published).
- <sup>15</sup>G. A. Reider, U. Höfer, and T. F. Heinz, *J. Chem. Phys.* **94**, 4080 (1991).
- <sup>16</sup>A. V. Hamza, G. D. Kubiak, and R. H. Stulen, *Surf. Sci.* **237**, 35 (1990).
- <sup>17</sup>J. E. Crowell (private communication).
- <sup>18</sup>D. A. Outka, *Surf. Sci.* **235**, L311 (1990).

- <sup>19</sup>K. Christmann, Surf. Sci. Rep. **9**, 1 (1988).
- <sup>20</sup>K.-D. Rinnen, M. A. Buntine, D. A. V. Kliner, R. N. Zare, and W. M. Huo, J. Chem. Phys. **95**, 214 (1991).
- <sup>21</sup>The  $\beta$ -barium borate crystal was supplied by R. S. Feigelson and R. K. Route and grown as part of a research program sponsored in part by the Army Research Office, Contract No. DAAL03-86-K-0129, and in part by the NSF/MRL Program through the Center for Materials Research, Stanford University.
- <sup>22</sup>S. M. Gates, Surf. Sci. **195**, 307 (1988).
- <sup>23</sup>J. J. Boland, Phys. Rev. B **44**, 1383 (1991).
- <sup>24</sup>F. Bozso and P. Avouris, Phys. Rev. B **38**, 3943 (1989).
- <sup>25</sup>Y. Suda, D. Lubben, T. Motooka, and J. E. Greene, J. Vac. Sci. Technol. B **7**, 1171 (1989).
- <sup>26</sup>During data acquisition the computer controls the heating rate, but does not directly monitor the crystal temperature and, thus, our desorption spectra are taken versus time. The desorption temperature we quote here is based on the work of Ref. 13 and is consistent with our own less accurate measurements.
- <sup>27</sup>H. Zacharias and R. David, Chem. Phys. Lett. **115**, 205 (1985).
- <sup>28</sup>L. Schröter, H. Zacharias, and R. David, Appl. Phys. A **41**, 95 (1986).
- <sup>29</sup>D. C. Jacobs, K. W. Kolasinski, S. F. Shane, and R. N. Zare, J. Chem. Phys. **91**, 3182 (1989).
- <sup>30</sup>L. M. Raff, I. NoorBatcha, and D. L. Thompson, J. Chem. Phys. **85**, 3081 (1986).
- <sup>31</sup>B. M. Rice, J. Chem. Phys. **86**, 1608 (1987).
- <sup>32</sup>N. C. Blais and D. G. Truhlar, J. Chem. Phys. **66**, 772 (1977).
- <sup>33</sup>N. C. Blais and D. G. Truhlar, J. Chem. Phys. **74**, 6709 (1981).
- <sup>34</sup>We note that the concerted reaction involving the Si dimers which we describe here would encompass the "pre-pairing" model which has recently been proposed (see Ref. 14) to explain the first-order rate.