Surface Diffusion of Hydrogen on Si(111) 7 × 7

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The diffusion of atomic hydrogen on the Si(111)7×7 surface has been investigated experimentally by means of optical second-harmonic diffraction from a submonolayer grating of adsorbed hydrogen. With submicron grating periods, we are able to measure surface diffusivities $D < 10^{-14}$ cm^{2}s^{-1}. We find a thermally activated diffusion process with a barrier of $E_a = 1.5 \pm 0.2$ eV and a preexponential factor D_0 of 10^{-3} cm^{2}s^{-1}.

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One general result of experiments performed over the past three decades on the diffusion of adsorbates on metals[1,2] is that the surfaces are relatively smooth. As a rule, the corrugation of the potential-energy curves for lateral motion of a chemisorbed atom does not exceed 20% of its total binding energy to the surface.[2] Thus most chemisorbed species exhibit high mobility far below the desorption temperature. A very different behavior is expected for covalently bound adsorbates on the surfaces of semiconductors or insulators. The existence of highly oriented bonds may lead to a large lateral corrugation of the potential. In an extreme case, the depth of the corrugations might even approach the binding energy of the adsorbate, thus virtually eliminating thermally activated lateral motion. To date, however, experimental information on this topic is available mainly indirectly from studies of crystal growth,[3] in which lateral motion of adsorbates plays a key role. Conventional measurements of adsorbate diffusion on clean semiconductor surfaces have so far been restricted to a few highly mobile metallic adsorbates.[4]

In this Letter we present results of a direct determination of the surface diffusivity of a covalently bonded adsorbate on a semiconductor surface. The system investigated, H/Si(111)7×7, has been widely studied as a model for chemisorption on semiconductor surfaces[5] and provides a promising starting point for obtaining a general understanding of the lateral motion of covalently bonded adsorbates. In this work we examine hydrogen in the Si-H monohydride state, in which each hydrogen atom is bound to a single surface atom by a silicon dangling bond.[5-7] While no direct observation of diffusion has been previously reported, thermal desorption from this state occurs recombinatively,[8-10] implying at least some hydrogen mobility near the desorption temperature of ~800 K. The experimental findings presented here demonstrate that lateral motion of hydrogen over hundreds of atomic sites is possible. The surface diffusion process is found to be thermally activated and to be described with an activation energy of $E_a = 1.5 \pm 0.2$ eV and a preexponential factor of $D_0 \simeq 10^{-3}$ cm^{-2}s^{-1}. Chemisorbed hydrogen is thus seen to experience a much larger barrier to lateral motion on the Si(111)7×7 surface than on metals, with the lateral corrugation of the Si-H potential reaching about half of the total binding energy.

The experimental technique employed in these studies consists of a combination of laser-induced desorption[11] (LID) and surface second-harmonic generation (SHG).[12] In this method, first demonstrated by Zhu, Rasing, and Shen for the diffusion of CO on Ni(111),[13] a grating in the adsorbate concentration is created holographically by LID in the field of two interfering beams.[13,14] The decay of the modulation in the adsorbate density is then monitored using the diffracted radiation at the second-harmonic (SH) frequency[13-15] of a probe laser beam. As we show below, this scheme permits one to observe diffusion over distances on the scale of ~1000 Å and to measure surface diffusivities $D < 10^{-14}$ cm^{2}s^{-1}. This high sensitivity is crucial for the present experiment. In a related study of H/Si(111)7×7, Koehler *et al.*[9] were only able to report an upper bound of $D(T = 740\text{ K}) < 10^{-9}$ cm^{2}s^{-1} from a LID-refilling[16] measurement. A further advantage of the SH diffraction scheme is the direct manner in which the surface diffusivity D can be determined from the experimental data. The form of the diffusion equation for the adsorbate density θ, $\partial\theta/\partial t = \nabla\cdot D\nabla\theta$, implies that each Fourier component of the grating profile decays in a simple exponential fashion whenever the density dependence of surface diffusivity D can be neglected. Thus, assuming that the surface nonlinear susceptibility $\chi_s^{(2)}$ varies linearly with adsorbate density,[12] we obtain a time variation in the first-order diffracted SH field of

$$E_1^{2\omega}(t) \sim \theta_1(t) = \theta_1(0)\exp\left[\frac{-Dt}{(l_g/2\pi)^2}\right] \equiv \theta_1(0)\exp(-\alpha_D t)\,, \quad (1)$$

where θ_1 denotes the first Fourier component of the adsorbate density and l_g the period of the grating.

The measurements were performed in ultrahigh vacuum at a pressure $< 2\times10^{-10}$ mbar. The Si(111) samples, oriented to within $\frac{1}{4}$°, were lightly doped with phosphorus (10-Ω cm resistivity). The samples were mounted on a liquid-nitrogen-cooled holder and could be heated resistively to 1450 K for surface preparation. The cleanliness and structure of the surfaces were checked regularly with Auger electron spectroscopy and low-energy electron diffraction (LEED). Atomic hydrogen was adsorbed on the Si(111)7×7 surface at 620 K to yield a coverage of $\theta_0=0.15$ monolayer (ML) $=1.2\times10^{14}$ cm^{-2}.[10] This sample temperature was chosen to ensure that hydrogen is adsorbed only in the Si-H monohydride state.[10]

The hydrogen adsorbate grating was formed through desorption induced by a single 7-ns pulse of the frequency-doubled output of a Q-switched Nd-doped yttrium-aluminum-garnet (Nd:YAlG) laser ($\lambda=532$ nm). The requisite interference pattern was produced by splitting the laser radiation into two beams of equal intensity which were recombined on the Si(111) surface at angles of $\pm\phi$ with respect to the surface normal. The grating period $l_g=\lambda/(2\sin\phi)$ could be set to values between 380 nm (for $\phi=45°$) and 10 μm (for $\phi=1.5°$). To produce a well-defined adsorbate grating by thermal desorption, a laser energy of 30 mJ was typically required for a spot size of 7 mm diameter (in an annular beam profile). Under these conditions a strong diffracted SH signal could be observed from the adsorbate-covered surface, but no diffracted SH radiation was observable from the clean Si(111)7×7 surface prepared in the same manner. The pump radiation for the SH measurements was supplied by the 1064-nm radiation of the same Nd:YAlG laser, operating at a repetition rate of 20 Hz and a reduced energy for this application. The plane of incidence of the radiation was perpendicular to the grooves of the adsorbate grating and the pump radiation was p polarized. During the experiment we simultaneously monitored the laterally averaged hydrogen coverage θ_0 through the reflected SH signal[10] and the first Fourier component of the grating modulation θ_1 via the diffracted SH signal.

Figure 1 shows data obtained for a grating period $l_g=380$ nm. The measured diffracted SH signal $|E_1^{2\omega}|^2$ is plotted as a function of time for different surface temperatures T. For $T=670$–730 K the diffracted signal decays on a time scale between 100 and 2000 s. A close inspection of the data in Fig. 1 reveals that in addition to a decaying grating amplitude $\theta_1(0)\exp(-\alpha_D t)$ a small nondecaying amplitude δ_1 ($\sim10\%$) contributes to the measured signal. From SHG measurements on clean Si(111)7×7 surfaces, we can exclude the influence of residual gas adsorption. The effect may arise from the presence of a less mobile hydrogen species on the surface.[10] For a rough estimate of the decaying component of the response, we may utilize the initial slope of the data in Fig. 1. For $T=689$ K, e.g., we obtain a decay rate of $2\alpha_D=1.4\times10^{-3}\,\mathrm{s}^{-1}$, which corresponds, according to Eq. (1), to a diffusion constant of $D=2.5\times10^{-14}$ cm^{2}s^{-1}.

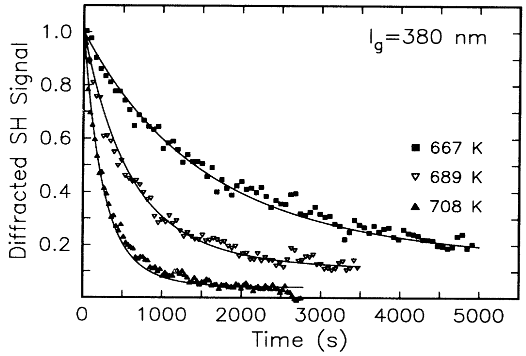

FIG. 1. First-order diffracted SH signal from a hydrogen grating of 380-nm period of 0.15-ML initial coverage as a function of time. Data points are measured intensities for different surface temperatures; solid lines are fits assuming a time dependence of the form $|E_1^{2\omega}|^2=\mathrm{const}\times[\theta_1\exp(-\alpha_D t)+\delta_1]^2$.

Up to this point we have assumed that the grating decays only as a result of diffusion. While this condition can be achieved if the adsorbate becomes mobile far below desorption temperatures, we find that at the temperatures required for reasonable decay rates of the diffracted signal some hydrogen desorption also occurs. Since the desorption rate is generally coverage dependent, the influence of desorption on the modulation $\theta_1(t)$ may be rather complex. Fortunately the necessary correction can be identified experimentally by changing the grating spacing l_g. The decay caused by desorption should be independent of l_g, whereas the decay rate α_D arising from diffusion is expected to vary as $1/l_g^2$. Furthermore, from the SH reflected signal we have at our disposal the mean hydrogen coverage $\theta_0(t)$, which is affected only by desorption and not by diffusion.

Figure 2 shows data for various grating periods taken at a surface temperature of 708 K. The mean hydrogen coverage θ_0 is plotted in the top part of the figure. These data look very similar for the different gratings and are shown only for $l_g=380$ nm. The amplitudes θ_1 derived from the diffracted signal are displayed in the bottom portion of the figure. For $l_g=10$ μm (not shown) and $l_g=5$ μm, $\theta_1(t)$ follows $\theta_0(t)$ rather closely. θ_1 decays slightly faster in the case of a 1.2-μm grating. For the shortest grating period of 380 nm we observe a strong increase in the decay rate of θ_1. For this grating the initial rate is 3 times higher than the normalized desorption rate $\alpha_{\mathrm{des}}=(1/\theta)d\theta/dt$; the decay of this grating is obviously dominated by diffusion. The various rates are collected in the inset of Fig. 2. As shown by the solid line, the functional dependence $\alpha_g=\alpha_{\mathrm{des}}+\alpha_D=\alpha_{\mathrm{des}}+D/(l_g/2\pi)^2$ fits the data fairly well. This good agreement and the relatively minor influence of desorption for the case of $l_g=380$ nm suggests that we may correct the measured grating decay rate α_g rate by simply subtracting α_{des}.[17]

We now analyze the entire set of data taken with the 380-nm grating at various surface temperatures. Two Arrhenius plots are displayed in Fig. 3. The measured decay rates for the grating α_g (solid triangles) and for the mean hydrogen coverage α_{des} (open circles) are shown in Fig. 3(a). The coverage data are fitted by a straight line corresponding to an activation energy for

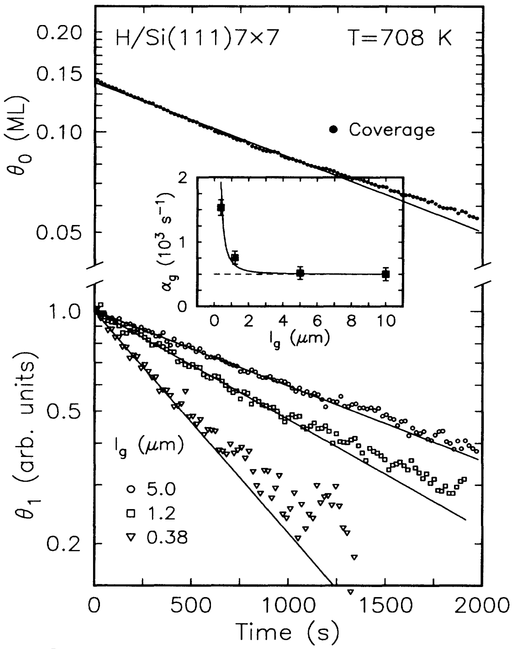

FIG. 2. Comparison of the decay of the mean hydrogen coverage θ_0 (top) and the grating amplitude θ_1 (bottom) for different grating periods $l_g = 5$ μm, 1.2 μm, and 380 nm as a function of time. The points show the measured signals and solid lines indicate the initial exponential decay. Inset: Dependence on grating period l_g for the normalized desorption rate $\alpha_{\text{des}} = (1/\theta) d\theta/dt$ (dashed line), the measured grating decay rate α_g (squares), and the functional form $\alpha_{\text{des}} + D/(l_g/2\pi)^2$ (solid line).

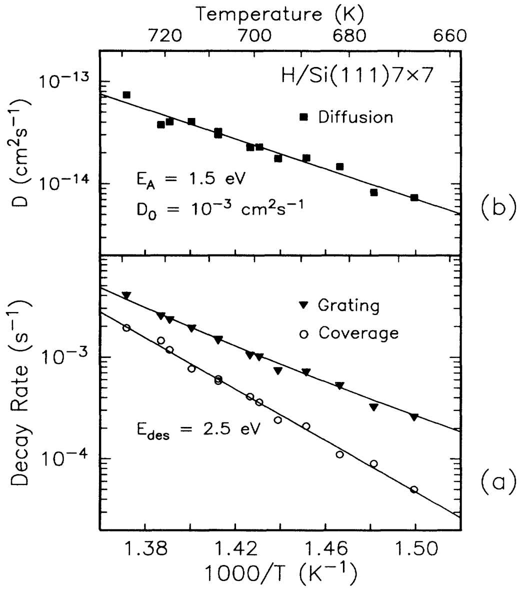

FIG. 3. Arrhenius plot of data taken with a grating of period $l_g = 380$ nm. (a) The measured initial grating decay rates α_g and desorption rates α_{des}. (b) The diffusion constant D derived from the data in (a) using the relationship $D/(l_g/2\pi)^2 = \alpha_D = \alpha_g - \alpha_{\text{des}}$. The curves drawn through the desorption rates α_{des} and the diffusivities D are straight-line fits to the data points; the curve through the grating decay rates α_g is obtained by adding these two lines.

desorption of 2.48 eV, in accord with the result 2.40 ± 0.1 eV obtained previously for homogeneous hydrogen layers of similar coverage.[10] Also note that the relative contribution of desorption to the grating decay varies with temperature. At $T = 670$ K, e.g., α_g and α_{des} differ by a factor of 5, whereas at $T = 730$ K, the grating decays only twice as fast as the total coverage. Figure 3(b) displays the decay rate of the grating modulation θ_1 from diffusion, $\alpha_D = \alpha_g - \alpha_{\text{des}}$. In this plot we have converted α_D into a diffusion constant D using the relation $\alpha_D = D/(l_g/2\pi)^2$ of Eq. (1). Writing $D = D_0 \exp(-E_a/k_B T)$, we then deduce an activation energy for the diffusion of $E_a = 1.5$ eV and a preexponential factor of $D_0 = 0.7 \times 10^{-3}$ cm^{2}s^{-1}. The error in E_a associated with the scatter of the data is ±0.1 eV. Since a small systematic error also may arise from the correction for desorption, the overall uncertainty of the activation energy is probably higher, but less than ±0.2 eV.

The observed barrier to lateral motion of 1.5 eV for H/Si(111)7×7 corresponds to roughly half the estimated binding energy of atomic hydrogen on the Si surface of 3.1 eV.[18] It is instructive to compare this behavior with that found for hydrogen diffusion on metals, which has been examined for a wide variety of surfaces[2] such as W(110), W(111), Ru(100), Ni(100), Pt(111), and Rh(111). Although the binding energy of atomic hydrogen is similar in these systems to that of H/Si, the diffusion barrier does not exceed 0.3 eV. A diffusion barrier of ~50% of the total binding energy is also significantly higher than that reported for metallic adsorbates on clean semiconductor surfaces.[4] The measured prefactor $D_0 \simeq 10^{-3}$ cm^{2}s^{-1} for H/Si(111)7×7, on the other hand, is comparable to that found for hydrogen on metal surfaces and is indicative of diffusion by thermally activated hopping. In a random-walk diffusion process, the surface diffusivity is given by $D_0 = \frac{1}{4} a^2 \nu$, with a being the distance per jump and ν the attempt frequency. For a distance $a \simeq 4$ Å between two dangling bonds on the 7×7-reconstructed surface,[19] $D_0 \simeq 10^{-3}$ cm^{2}s^{-1} corresponds to $\nu \simeq 2.5 \times 10^{12}$ s^{-1}. Our results are thus consistent with a classical diffusion process and the anticipated high barriers for lateral motion due to oriented covalent bonds.

For hydrogen on W(110) and W(111) surfaces, in addition to classical diffusion a nonactivated diffusion process associated with site-to-site tunneling has been observed with $D \simeq 10^{-13}$ cm^{2}s^{-1}.[2] While we cannot exclude a contribution of quantum diffusion for H/Si(111), our experimental results show that any nonactivated contribution to the diffusivity cannot exceed 10^{-15} cm^{2}s^{-1}. A much lower contribution of tunneling processes would be expected for H/Si(111) in view of the large potential barriers for lateral motion deduced in this work. Our data also provide no evidence for a bandlike diffusion process of the type proposed by Sinniah *et al.*[20] to explain the measured desorption kinetics for H/Si(100).

To our knowledge, adequate models of the potentials for hydrogen on the 7×7-reconstructed Si(111) surface are not currently available. Monte Carlo calculations for hydrogen diffusion on an *unreconstructed* Si(111) surface by Rice, Raff, and Thompson[18] have resulted in an activation energy for classical diffusion of ∼2.6 eV, which is considerably higher than our experimental value. It is hoped that the present work will stimulate further theoretical studies of the surface potential. We should note that our diffusion measurements, although performed on a submicron length scale, still involve motion over many atomic sites. In relating this information to microscopic processes, one must then consider the presence of various adsorption sites on the Si(111)7×7 surface, as well as the possible influence of steps[21] and surface disorder. In regard to steps, the sample misorientation of $\leq \frac{1}{4}°$ implies that only 1–2 steps are present over the observed diffusion length of ∼1000 Å. This fact taken together with the smooth decay of the diffracted SH signal observed experimentally suggests that steps have only a minor effect on the diffusion data. With respect to the influence of surface disorder, recent STM studies[7] indicate that the underlying 7×7 reconstruction remains intact upon hydrogen adsorption for the low coverages used in this experiment.

In summary, we have measured the surface diffusivity of a covalently bound adsorbate on a semiconductor surface in the model system of H/Si(111)7×7. Employing the method of second-harmonic diffraction from adsorbate gratings, we have been able to measure surface diffusion occurring over a length scale of ∼1000 Å. The results indicate that diffusion occurs by a thermally activated mechanism with an activation energy of $E_a = 1.5 \pm 0.2$ eV and a prefactor of $D_0 \simeq 10^{-3}$ cm^{2}s^{-1}. This barrier to lateral motion of ∼50% of the total binding energy of hydrogen reflects the presence of the highly localized bonds formed on the surface and stands in marked contrast to the usual behavior of adsorbates on metal surfaces.

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