Adsorption, Abstraction, and Pairing of Atomic Hydrogen on Si(100)-(2 × 1)

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Using thermal desorption mass spectrometry, we have shown unambiguously that the adsorption of atomic hydrogen on Si(100)-(2 × 1) leads to hydrogen pairing on silicon dimers at surface temperatures as low as 150 K and coverages as low as 0.2 monolayer. A detailed study of the adsorption kinetics shows a high probability of an abstraction reaction together with a coverage-dependent adsorption probability which is greater than expected for Langmuirian adsorption. These results, together with the known saturation coverage, are unified within the context of a “hot-precursor” mechanism for the adsorption of atomic hydrogen.

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The adsorption of atomic hydrogen on various semiconductor surfaces has been the subject of many studies [1]. On Si(100), which reconstructs to a (2 × 1) superstructure by forming surface dimers, the singly occupied dangling bonds on each silicon atom form an additional weak π bond between the dimer atoms [2]. At low hydrogen coverages the atomic hydrogen breaks the weak π bond, and reacts with the silicon dangling bonds to form a monohydride phase. At temperatures near 600 K, the surface saturates with approximately one hydrogen adatom per silicon atom, maintaining the (2 × 1) dimerized reconstruction. It is this well-ordered, (2 × 1)-reconstructed monohydride phase which is the subject of this Letter. Detailed studies of the thermally activated desorption of molecular hydrogen from this phase have revealed unusual first-order desorption kinetics [3,4] which were attributed to the pairing of adsorbed hydrogen atoms on the silicon dimers prior to desorption [5,6]. This pairing has been observed directly by scanning-tunneling microscopy (STM) [1] and was argued to result from hydrogen diffusion at elevated temperatures driven by a thermodynamically favored configuration which maintains the maximum number of Si-Si π bonds (0.2–0.5 eV/π bond [7]), i.e., a configuration of empty and doubly hydrogen-occupied silicon dimers.

Here, we address the issue of this hydrogen pairing as a function of adsorption temperature, together with a detailed study of the adsorption kinetics of atomic hydrogen on the Si(100)-(2 × 1) surface. We show that the adsorption of atomic hydrogen leads to hydrogen pairing on silicon dimers at surface temperatures as low as 150 K, and we propose that the observed independence of surface temperature is a result of the adsorption kinetics rather than any thermodynamic equilibrium. Our data show, for the first time to our knowledge, that atomic hydrogen adsorption does not obey the widely assumed Langmuirian kinetics, and that hot-precursor-mediated adsorption [8] is necessary to account for the totality of our experimental findings.

The experiments were carried out in an ultrahigh vacuum chamber (base pressure of 5 × 10⁻¹¹ Torr) equipped with a high-resolution electron energy loss (HREEL) spectrometer, low-energy electron diffraction optics, an Auger electron spectrometer (AES), and a differentially pumped quadrupole mass spectrometer [9]. The n-type Si(100)-oriented sample (10¹⁹ cm⁻³ Sb doped) was cleaned by Ar⁺ sputtering and annealing to 1100 K, followed by a 30 s flash to 1350 K and slow cooling (2 K/s) to 700 K. Atomic hydrogen or deuterium was generated by dissociation of the respective diatomic molecules with a hot (1800 K) spiral tungsten filament. The different relative mass spectrometric sensitivities for H₂, HD, and D₂ were carefully calibrated based on the hydrogen saturation coverage on Si(100) at 600 K. A 5-μm pin hole doser was used for exposures to acetylene. An estimated fluence of 8 × 10¹⁴ molecules/cm² of acetylene was used for the temperature-programmed desorption (TPD) experiments, which is sufficient to saturate the surface at 100 K.

To investigate the temperature dependence of hydrogen pairing on the silicon dimers, the adsorption site correlation was investigated using acetylene as a “chemical probe.” Acetylene adsorbs on the Si(100) surface with an initial probability of essentially unity at temperatures below 300 K. Chemisorption occurs by insertion into the dimer bond and formation of two carbon-silicon σ bonds [9,10]. Preadsorbed hydrogen is known to block the adsorption of unsaturated hydrocarbons, with the saturated silicon monohydride completely inert to their adsorption [11]. It is this site blocking by preadsorbed hydrogen together with the known adsorption site of acetylene which permits a study of the local adsorption site correlation of hydrogen. At a given temperature the clean Si(100)-(2 × 1) surface is exposed to atomic deuterium and then cooled to 90 K. The surface is then exposed to acetylene (C₂H₂), resulting in a saturation acetylene coverage which depends on the initial deuterium coverage. The acetylene and deuterium coverages are subsequently determined by monitoring the time-integrated TPD intensities of H₂, HD,
and D₂, the only desorption products. The acetylene coverages, relative to saturation coverage on the clean surface, were also determined by AES, monitoring the carbon (KLL) and silicon (LVV) peak intensities. Additional HREELS results show clearly that the effect of preadsorbed hydrogen on adsorbed acetylene at 90 K is limited to site blocking, and there is no chemical reaction between the coadsorbates [11].

The saturation coverage of acetylene at an adsorption temperature of 90 K is shown in Fig. 1 as a function of the preadsorbed deuterium coverage for various deuterium preparations. Coverages determined by TPD are denoted with open symbols and by AES with filled symbols. The preparation of the preadsorbed deuterium overlayer was effected either by partial desorption of the saturated monohydride, shown as triangles, or by atomic deuterium adsorption at surface temperatures of 600, 300, and 150 K, indicated by circles, diamonds, and squares, respectively. The data show clearly that preadsorbed deuterium blocks the subsequent adsorption of acetylene, and within the experimental error bars there is no dependence on the deuterium adsorption temperature. The saturation acetylene coverage is linearly reduced with increasing deuterium precoverage, with essentially complete passivation by the fully saturated silicon monodeuteride.

We now show that the observed site blocking of Fig. 1 is explained by a surface temperature-independent hydrogen pairing on silicon dimers and, therefore, implicates adsorption kinetics with an unexpected adsorption site correlation. Complete pairing of adsorbed hydrogen would lead to silicon dimers with either two adsorbed hydrogen atoms or none. In this case the saturation acetylene coverage θ₄ is proportional to the fraction of empty dimers. Depending on the hydrogen coverage θ₄ the probabilities of doubly occupied, singly occupied, and empty dimers prior to acetylene adsorption are simply θ₄, 0, and 1 − θ₄, respectively. Hydrogen pairing on the silicon dimers leads therefore to a linear coverage dependence of the site blocking for subsequent acetylene adsorption, θ₄ ∝ 1 − θ₄. On the other hand, for a random distribution of hydrogen adatoms, the probability of finding an empty silicon dimer is (1 − θ₄)². Allowing acetylene adsorption only on empty dimers leads to a quadratic coverage dependence of the site blocking, θ₄ ∝ (1 − θ₄)². Assuming the same random distribution of hydrogen but allowing acetylene adsorption on both empty and singly occupied dimers leads to a different site blocking behavior θ₄ ∝ 1 − θ₄². All three site blocking models are plotted in Fig. 1. The experimentally observed linear dependence of the saturation coverage of acetylene on the coverage of preadsorbed hydrogen indicates hydrogen pairing, at least for θ₄ ≈ 0.2, at surface temperatures as low as 150 K.

For adsorption at high temperatures where adatom diffusion occurs, one expects—indeed, independent of the details of the initial adsorption mechanism—complete hydrogen pairing [1]. Our data for hydrogen adsorption at 600 K as well as overlays prepared by partial desorption of a saturated monohydride are consistent with pairing based on this argument. However, for hydrogen adsorption at a surface temperature of 150 K, we find identical site blocking, implying hydrogen pairing also at low temperatures. In this case, hydrogen adatom diffusion with an activation barrier of ~1.3–2 eV [12,13] is negligible, and, hence, arguments based on small energy differences for different adsorption sites can be ruled out as an explanation of the observed pairing. Under these conditions the kinetics of adsorption must be otherwise unique phenomenon. We propose that it is the probability to encounter several adsorption sites (hot-precursor mechanism) together with a higher probability of adsorption at preferred sites which leads to the observed pairing. Deviations from the commonly assumed picture of Langmuirian (random) adsorption of atomic hydrogen, which are necessary to permit hydrogen pairing, should also be reflected in the coverage-dependent adsorption probability.

Deuterium coverage as a function of atomic exposure is shown in Fig. 2 for adsorption temperatures of 600 (circles) and 150 K (squares). The atomic deuterium exposure is proportional to the product of the uncorrected ion gauge pressure for D₂ and the exposure time. The coverages were determined from time-integrated TPD spectra and normalized to the saturated monohydride which showed a reproducibility of ±5% over a period of weeks. Since the (steady-state) saturation coverage of the monohydride is near unity, the ordinate of Fig. 2 may be regarded as essentially equal to the absolute fractional surface coverage. As may be seen in Fig. 2, the deuterium uptake is identical for adsorption at 600 and 150 K for

![FIG. 1. Saturation coverage of acetylene as a function of preadsorbed deuterium coverage for various deuterium preparations. See text for details.](image)
coverages below 0.8, where only the monodeuteride phase is formed. Identical results were obtained for atomic hydrogen.

The adsorption of atomic hydrogen on Si(100)-(2 × 1) has heretofore been assumed, either implicitly or explicitly, to obey Langmuirian kinetics [1]. The deuterium coverage, calculated for Langmuirian adsorption where the adsorption probability is proportional to the number of empty sites (ignoring for the moment any abstraction), is shown as the dashed curve in Fig. 2, \( \theta_D = \theta_s[1 - \exp(-F_D P_{a,0} t)] \), where \( \theta_s \) is the saturation coverage, \( F_D \) is the flux of atomic deuterium on a site basis, and \( P_{a,0} \) is the initial probability of adsorption. Since the saturation fractional coverage is known to be near unity [1], this leaves only a single parameter \( (F_D P_{a,0}) \) which is determined uniquely by the initial slope in Fig. 2. Clearly, this model (dashed curve of Fig. 2) underestimates the adsorption probability and disagrees with the data.

The adsorption of atomic hydrogen (or deuterium) on Si(100)-(2 × 1) is complicated by abstraction, i.e., the reaction of gas-phase atomic hydrogen with adsorbed hydrogen to produce \( \text{H}_2 \) which desorbs. Although hydrogen abstraction on the Si(100)-(2 × 1) surface has been observed earlier [3,14–16], the implications for the adsorption kinetics and the saturation coverage have been largely ignored. Figure 3 shows the dependence of the deuterium and hydrogen coverages of the saturated silicon monohydride exposed to atomic deuterium at a surface temperature of 600 K, a temperature at which no recombination thermal desorption occurs [3]. The hydrogen coverage decreases with exposure to atomic deuterium, whereas the deuterium coverage increases. The total coverage is constant, as expected for an isotope-independent saturation coverage. Reversed experiments, the abstraction of adsorbed deuterium by incident hydrogen atoms, revealed the same rate of abstraction within experimental uncertainties, implying no isotope effect for the abstraction reaction, in agreement with Refs. [14–16].

The observed abstraction reaction shown in Fig. 3 is well described by an exponential decay of the hydrogen coverage with atomic deuterium fluence. This is expected for a direct, first-order abstraction reaction, i.e., an Eley-Rideal mechanism for which

\[
\dot{\theta}_H = -F_H P_r \theta_H. \tag{1}
\]

For a known flux of atomic deuterium, the reaction probability \( P_r \) can be extracted. Independent of the exact atomic deuterium flux, which is not known with great accuracy, the reaction probability can be determined relative to the probability of abstraction on the clean surface. A direct comparison of the deuterium uptake on both a clean and a saturated Si(100)-(2 × 1) monohydride surface (i.e., a comparison of the initial slopes in Figs. 2 and 3) gives a reaction probability on the saturated monohydride surface of 0.5 ± 0.1 relative to the adsorption probability on the clean surface.

What then are the implications of the observed adsorption kinetics and abstraction reaction on the mechanism of adsorption and the observed saturation coverage? The change in surface coverage during the adsorption of hydrogen can be expressed as

\[
\dot{\theta}_H = -F_H P_r \theta_H + F_H P_{a}(\theta_H). \tag{2}
\]

The first term on the right-hand side describes the abstraction reaction as in Eq. (1). The second term accounts for chemisorption, where \( P_{a}(\theta) \) is the coverage-dependent probability of adsorption. Assuming the linear \( P_{a,0}(1 - \theta) \) Langmuirian form, the steady-state saturation hydrogen coverage in the presence of abstraction is given by \( \theta_s = 1/(1 + P_r/P_{a,0}) \), which is ∼0.66, cf. the dotted curve of Fig. 2, whereas the experimentally observed saturation coverage is close to unity [1]. Clearly, the
adsorption of atomic hydrogen on Si(100)-(2 × 1) does not obey Langmuirian kinetics.

To explain and unify the data, we propose a hot-precursor mechanism of adsorption. The incident hydrogen atom excites surface phonons during the initial collision and becomes dynamically trapped in highly excited vibrational states above the barrier for adatom diffusion. The hydrogen atom translates on the surface during the time necessary for energy dissipation until it is finally localized by the diffusion barrier. A higher probability of “inelastic scattering” and, consequently, chemical bonding at a singly occupied dimer is what leads to hydrogen pairing in this picture. At coverages lower than 0.2, not accessible with our experimental methods, we expect the pairing to break down due to a finite lifetime or “diffusion” length of the hot precursor. Low-coverage STM data (θH ≈ 0.07), which show the absence of complete hydrogen pairing at room temperature [1], can be understood in these terms.

There are many different precursor-mediated adsorption models which can lead to enhanced adsorption probabilities at high surface coverages. For the purpose of discussion, we employ a functional form for the adsorption probability of

\[ P_a(\theta) = P_{a,0}[1 + \kappa \theta/(1 - \theta)]^{-1} \]

to account for the hot precursor [17]. The hydrogen atom samples several adsorption sites (number on the order of \(1/\kappa\)) prior to localized chemisorption at an empty site. We use this approximate model to simulate the “lifetime” of the excited hydrogen atom prior to chemisorption. The solid line in Fig. 2 shows the calculated hydrogen uptake as a function of exposure, generated by solving Eq. (2) with the adsorption probability given above and \(\kappa = \frac{1}{20}\). The agreement between the experimental data and this approximate model strongly suggests that a hot-precursor mechanism can explain both the uptake and the abstraction data. This mechanism leads to a (steady-state) saturation coverage which is near unity and explains the observed high saturation coverage in the presence of abstraction. Note that the detailed form of \(P_a(\theta)\) is not important; it is rather the large value of \(-\partial P_a(\theta)/\partial \theta\) near saturation coverage (here \(P_{a,0}/\kappa\)) which determines the adsorption probability at the higher coverages and the saturation coverage in the presence of abstraction.

To summarize, we have presented two different experimental results—hydrogen pairing on individual silicon dimers at low surface temperatures and the kinetics of hydrogen adsorption taking proper account of abstraction—which can both be explained by a hot-precursor mechanism of atomic hydrogen adsorption on Si(100)-(2 × 1). The incident hydrogen atom, which is initially bound in excited vibrational states above the diffusion barrier of the hydrogen adatom, encounters several adsorption sites which leads to a higher adsorption probability than in a Langmuirian model. The interrogation of several adsorption sites together with a higher probability of adsorption at a site adjacent to an already chemisorbed hydrogen adatom accounts both for the observed hydrogen pairing on silicon dimers well below room temperature and for saturation fractional coverages approaching unity in the presence of the abstraction reaction.

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