Evidence of Pairing and Its Role in the Recombinative Desorption of Hydrogen from the Si(100)-2×1 Surface

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A scanning tunneling microscopy and spectroscopy study of the recombinative desorption of hydrogen from the Si(100)-2×1 surface is presented. Initially at room temperature, hydrogen atoms singly occupy the Si dimer units while at higher temperatures (~630 K) these atoms tend to pair up. This pairing phenomenon is due to a π-bonding interaction which favors pairing individual dangling bonds on the dimer units. Following desorption from the saturated surface, pairs of dangling bonds are found localized on the Si dimer units. The significance of these paired-dangling-bond sites is discussed in light of the desorption model recently proposed by Sinniah *et al.*

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The recombinative desorption of hydrogen from silicon surfaces has recently become an area of intense investigation. This interest is largely due to the work of Sinniah *et al.*, who showed that desorption from the Si(100) surface is first order over a wide coverage range [1,2]. The origin of this unusual first-order desorption kinetics remains problematic. Sinniah *et al.* proposed a model in which individual hydrogen atoms are irreversibly excited into a two-dimensional bandlike state. Desorption is then due to the recombination of such mobile hydrogen atoms with the localized atoms on the surface [1,2]. However, the validity of this model remains in question, largely because it ignores the structure and covalent nature of the surface bonding. Here, we present a scanning tunneling microscopy (STM) and spectroscopy (STS) study of recombinative desorption from the Si(100)-2×1 surface. Particular attention is given to the role played by the surface bonding in the desorption process. Evidence is presented for the existence of a pairing mechanism which drives the hydrogen atoms to occupy both sites on the Si dimers. However, rather than being due to an attractive interaction between adsorbed hydrogen atoms, this pairing is the result of an intrinsic π-bonding interaction on the Si(100)-2×1 surface, which favors the remaining dangling bonds to pair up on the dimers. Desorption from the saturated surface also results in the formation of paired dangling bonds which are localized on the dimer units. The significance of these paired-dangling-bond sites is discussed.

The microscope used in this work is similar to that described by Demuth *et al.* [3], and was mounted in a UHV chamber with a base pressure of 8×10^{-11} torr. The sample was a 1-Ω cm phosphorus-doped Si(100) wafer. The clean Si(100)-2×1 surface was prepared by heating the sample to 1350 K for about 30 s. Atomic hydrogen was produced by the decomposition of molecular hydrogen (purity 99.9995%) on a 1800-K tungsten filament. The hydrogen was contained in a glass flask and directly collimated onto the sample. The tip preparation has been described in detail elsewhere [4]. The sample temperature was measured by an IR pyrometer and a thermocouple bonded to the back side of the sample and is accurate to about ±20 K.

Before studying hydrogen recombinative desorption from the Si(100)-2×1 surface, it is necessary to understand the manner in which hydrogen adsorbs on this surface. Figure 1(a) shows the Si(100)-2×1 surface following a 295-K submonolayer exposure to hydrogen atoms. In addition to the bare dimer rows of the clean surface, bright ball-like features are observed that are randomly distributed on the surface and asymmetrically positioned to one side of the dimer rows. Some of the atoms within the dimer rows are well resolved and darker than those that make up adjacent dimer units. Figure 1(b) shows the surface following a brief anneal at 630 K. There is a

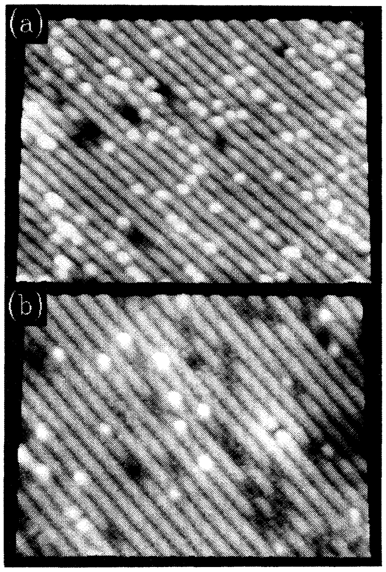

FIG. 1. (a) Si(100)-2×1 surface following a 295-K submonolayer exposure to atomic hydrogen. (b) Room-temperature-dosed surface following a 10-s anneal at 630 K. The areas shown are 180×148 Å and were recorded at a sample bias of +0.8 V. Note the slight uncorrected thermal drift in image (b).

marked reduction in the number of prominent ball-like features while the number of dark well-resolved dimer units has increased. Similar results are obtained by dosing at 630 K.

To gain further insight into this adsorption process, STS spectra were recorded at specific points on the surface. STS spectrum i of Fig. 2, recorded over the unreacted dimer rows of the surface in Fig. 1(a), is characteristic of the clean 2×1 surface. This spectrum consists of a strong occupied state located about -0.9 eV below the Fermi energy (E_F) and a weaker unoccupied state at $+0.5$ eV. These states are derived from a π interaction between the dangling bonds on each of the Si dimer atoms and represent the bonding (π_b) and antibonding (π_a^*) combinations, respectively [5,6]. The splitting between these states is responsible for the band gap observed on this surface [6]. In addition to these peaks, a strong feature at $+1.5$ eV is observed, which earlier was attributed to a backbond state [7,8]. STS spectrum ii, recorded over the bright ball-like features in Fig. 1(a), consists of a pair of intense peaks that are symmetrically positioned (±0.5 eV) about E_F. We attribute this spectrum to the isolated dangling bond that remains following reaction of a single hydrogen atom with the dimer π bond. This reaction disrupts the π bond, causing the remaining isolated dangling bond to be shifted up in energy towards E_F. Unlike the π_b and π_a^* states observed at the bare-dimer sites, these isolated-dangling-bond sites have true dangling-bond character, consistent with the uniform distribution of states about E_F. Thus, STS spectrum ii identifies dimmer units that have reacted with a single hydrogen atom. STS spectrum iii, on the other hand, was recorded over the well-resolved dimer units observed in Fig. 1. This spectrum is characterized by the presence of a strong unoccupied state located at $+1.2$ eV above E_F, that was shown earlier to be indicative of the Si(100)-2×1 monohydride surface [5,7]. The well-resolved dimer units are therefore dimers that have reacted with two hydrogen atoms.

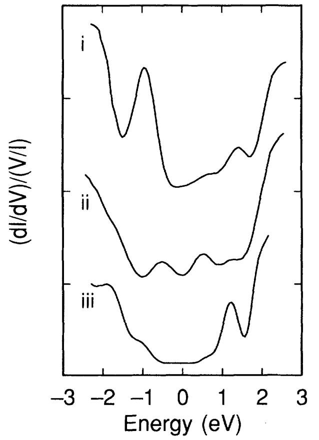

FIG. 2. STS spectra recorded at curve i, unreacted Si(100) dimer sites; curve ii, bright ball-like sites; and curve iii, the dark well-resolved dimer sites. The feedback stabilization conditions were $+0.8$ V and 0.15 nA.

At low temperatures, adsorption initially involves the reaction of single hydrogen atoms with the Si dimer π bonds, resulting in the formation of Si-H bonds and isolated dangling bonds. Annealing to higher temperatures causes the hydrogen atoms to pair up on the dimers, yielding structures similar to the 2×1 monohydride phase. These observations suggest that the paired structure is thermodynamically favored. The initial random distribution of hydrogen atoms is due to a large reactive sticking coefficient and a barrier to surface diffusion. The stability of this paired structure reflects the natural tendency for isolated dangling bonds to pair on this surface, resulting in π-bond formation. The exact nature of this pairing interaction depends on the detailed structure of the dimers; dynamic buckling induces charge transfer between the dangling bonds [9], resulting in an instantaneous polarization of the π bond. Thus the interaction between isolated dangling-bond states is enhanced by the surface buckling mode which serves to vibronically couple these states. However, regardless of its origin, hydrogen pairing is a direct result of this interaction between isolated dangling bonds. Evidently, the repulsive steric interaction between Si-H bonds on the same dimer is not sufficient to offset this favorable π interaction.

Figure 1(b) also shows that there is a strong attractive interaction between these hydrogen-paired units, resulting in the formation of chain structures which extend along the [011] direction, i.e., along the dimer rows. This behavior becomes even more pronounced at higher temperatures, ultimately extending in the $[01\bar{1}]$ direction as well. In each case we note that the pairs at the ends are qualitatively different from those that make up the remainder of the chains. The exact origin of this behavior is unclear at present but is probably related to differences in the 2×1 structures of the clean and monohydride surfaces. Formation of the monohydride surface eliminates the π bond and increases the Si dimer bond length [10]. This results in a relaxation of the subsurface strain [10]. Evidently these relaxed monohydride units favor clustering, the units at the end of the chains having structures which reflect a transition from a relaxed to a strained and perhaps buckled 2×1 structure. Such substrate strain effects may also play a role in pairing dangling bonds since there may be a significant strain energy associated with isolated-dangling-bond sites.

To study recombinative desorption from the Si(100)-2×1 surface, a saturated monohydride surface, prepared by exposure to atomic hydrogen at 600 K [11], was annealed to 690 K for 10 s. The results are shown in Fig. 3. The surface consists of a well-ordered monohydride structure which exhibits the characteristic hydrogen-derived state at $+1.2$ eV (see spectrum iii). On this surface in-

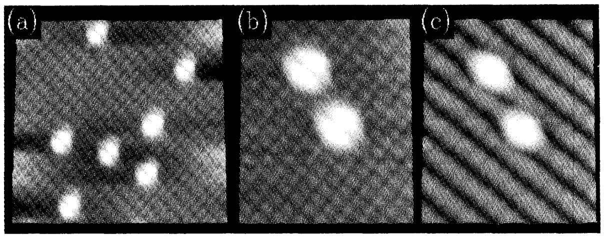

FIG. 3. (a) Si(100)-2×1:H monohydride surface following a 10-s anneal at 690 K. Area shown is 125×130 Å. (b),(c) Closeup images of paired-dangling-bond sites recorded at sample biases of +1.7 and −2 V, respectively. Closeup images are 46×62 Å. Shadows are an artifact of the background subtraction.

tense dangling-bond sites are observed that exhibit a distinct nodal structure. Figure 3(b) shows a closeup of two such sites recorded at a sample bias of +1.7 V. This image clearly shows that the unoccupied states are localized on a single dimer unit and that the nodal plane falls exactly along the middle of the dimer row. The corresponding occupied-state image, recorded at a bias of −2 V, is shown in Fig. 3(c). A nodal structure is not observed under these bias conditions; the occupied states are symmetrically distributed about a single dimer unit. STS spectra recorded over these sites are similar to those observed on the clean 2×1 surface (see spectrum i). Each site consists of two individual dangling bonds that are paired up on a single dimer unit. The unoccupied-state image in Fig. 3(b) is the π_a^* state derived from the asymmetric combination of these dangling bonds. This antibonding state exhibits a characteristic node between the Si dimer atoms [6]. The nodal properties of this π_a^* state are readily seen due to the passivated nature of the surrounding surface. Such nodes can also be observed on the clean surface [5], albeit with poorer contrast, and in general, require a very good tip. The occupied-state image in Fig. 3(c), on the other hand, reflects the spatial character of the π_b state derived from the bonding combination of these dangling bonds [6]. Other dangling-bond sites are occasionally observed on this surface but appear to be clusters of these paired-dangling-bond units.

The observation of π-bonded dangling-bond states localized on single dimer units does not definitively prove that the first-order desorption kinetics is due to pairing of hydrogen atoms from these dimer units. Given that isolated dangling bonds have a propensity to pair on this surface, the pairing observed following the anneal *may* reflect a postdesorption rearrangement. In an attempt to address this issue, room-temperature tip-induced desorption was studied [4,12]. The presence of the low-lying hydrogen-derived antibonding state at +1.2 eV facilitates desorption from this surface [13]. The dangling bonds produced in this manner were always paired and identical to those shown in Fig. 3. Thus, while there is no *a priori* reason for the thermal and electronic desorption pathways to be related, the possibility of a common final state is intriguing. However, Sinniah *et al.* [2] rejected a concerted pairing mechanism because in that case the activation energy for desorption is 75 kcal/mol, i.e., $2D(\text{Si-H})-D(\text{H-H})$, where D is the bond strength, significantly larger than the 47–58-kcal/mol barrier observed experimentally [1,14,15]. This is true of all pairs *except* those that originate from the same dimer unit since in the latter case π-bond formation must be considered in the final state. Based on STS spectra i and ii, this π-bond stabilization is estimated to be about $2(0.9-0.5)$ eV or 18 kcal/mol and hence the activation energy for paired recombinative desorption from the same dimer should be 57 kcal/mol. (This estimate neglects differences in the relaxation and correlation energies at the bare and singly occupied dimer sites.) Thus if desorption involves prepairing, it is likely due to pairing of atoms on the same dimer, since other pairing schemes yield activation barriers that are necessarily larger.

Despite the fact that we are unable to uniquely identify the mechanism of desorption, these observations place severe constraints on any proposed mechanism. Since no isolated-dangling-bond sites are observed, the band model of Sinniah *et al.* [1,2] can be reconciled with the present results only if all such dangling bonds are paired immediately upon formation. This seems unlikely, given that Fig. 1(b) shows an appreciable number of isolated dangling bonds following a 630-K anneal. STS spectra i and ii indicate that the energy difference between isolated- and paired-dangling-bond sites is about 0.4 eV, so that there remains a nonequilibrium distribution of dangling bonds between these sites even after the anneal. This is presumably due to a significant barrier to diffusion and suggests that care must be taken in interpreting the isotopic mixing studies of Sinniah *et al.* [2] since the results depend on the initial conditions. For instance, desorption studies which start with a submonolayer coverage are likely to be different from those observed from a surface that was initially saturated and then annealed to obtain the desired coverage. This is particularly true at low coverages and temperatures where pairing of isolated dangling bonds is slow and potentially rate limiting. Indeed, recent desorption results show a departure from first-order kinetics at very low coverages [15]. For surfaces that were initially saturated, this is never an issue, since the dangling bonds remain paired down to zero coverage. In any case, regardless of the exact desorption mechanism, it is clear that pairing of isolated dangling bonds, together with the concomitant pairing of hydrogen atoms, must play an important role in the desorption process.

Extending the anneal time or increasing the temperature results in a dramatic increase in the surface dangling-bond density. Figure 4 shows the result of a further 10-s anneal at 750 K. The surface is now covered with π-bonded dimer units, the spatial distribution of

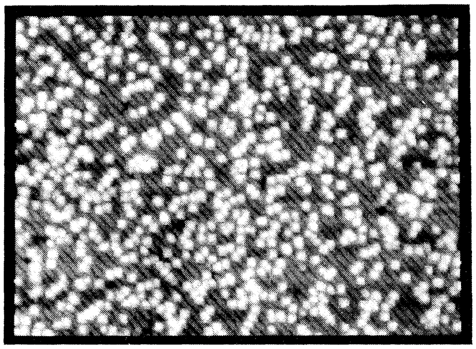

FIG. 4. Monohydride surface following a 10-s anneal at 750 K. Area shown is 485×365 Å and was recorded at a sample bias of −1.5 V.

which depends on the desorption rate. Slow desorption rates allow these dimer units to cluster together resulting in spatially delineated regions of the surface which exhibit either the 2×1 clean or monohydride structures. Further desorption results in the growth of these bare 2×1 regions at the expense of the monohydride surface. This behavior is analogous to the clustering of hydrogen-paired dimer units discussed earlier [see Fig. 1(b)].

In conclusion, there is a significant π-bonding interaction on the Si(100)-2×1 surface which favors isolated dangling bonds pairing up on the dimer units. While in principle the π-bonded dangling-bond sites observed following desorption may reflect a postdesorption rearrangement, the present results suggest that this is unlikely. In any case, these observations place severe constraints on any proposed desorption model and suggest that under some conditions the pairing step itself may become rate limiting. Such π-bonded dangling bonds are characteristic of the clean Si(100)-2×1 surface, and their presence following desorption suggests that the structure and bonding of the clean surface plays an important, if not dominant, role in the desorption process. Indeed one might expect such pairing phenomena to be important whenever the clean surface exhibits a band gap, since the final state of the desorption process must reflect the properties of the clean surface.

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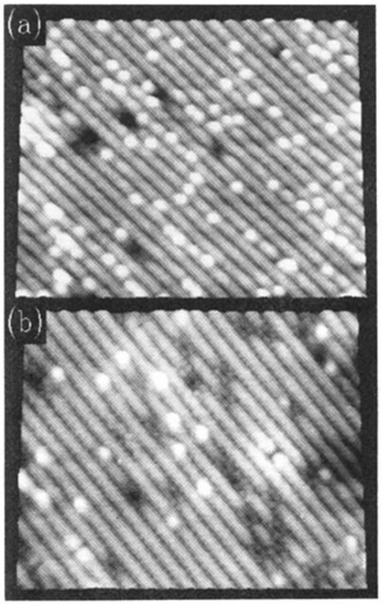

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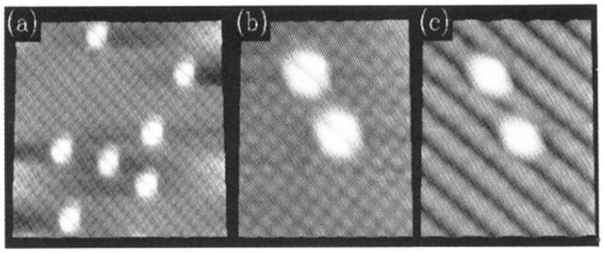

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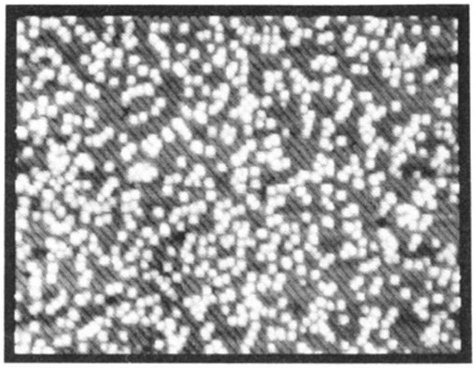

FIG. 4. Monohydride surface following a 10-s anneal at 750 K. Area shown is 485×365 Å and was recorded at a sample bias of −1.5 V.