Atom-Resolved Surface Chemistry Using Scanning Tunneling Microscopy

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We use scanning tunneling microscopy to investigate the reactivity of the dangling-bond states of Si(111)-(7×7). The reaction with NH_3 is used as a prototype. We find that Si rest atoms are more reactive than Si adatoms and that center adatoms are more reactive than corner adatoms. Using atom-resolved electronic spectra, we probe the dangling-bond states on both clean and NH_3-exposed surfaces. We find significant interactions and charge transfer between sites which strongly influence surface reactivity.

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The study of semiconductor surface electronic structure has been one of the most active areas of surface physics.[1] While the relation between surface electronic structure and the physical properties of surfaces is well established, the relation with surface chemical reactivity, despite its fundamental and technological importance, is not as well understood. Recently it was shown[2,3] that at ambient or lower temperatures the reactivity of Si(100) towards various gases is indeed correlated with the presence of surface dangling-bond (db) states. However, important questions such as the role of the local environment and of interactions among db sites on the reactivity still remain unanswered.

In this work, we use scanning tunneling microscopy[4] (STM) to study the reaction of Si(111)-(7×7) with NH_3. This study provides new insight not only on the relation between db's and surface reactivity, but also on the nature of the db states themselves. The Si(111)-(7×7) surface is particularly appropriate in this respect because it contains db's on several different sites within the surface unit cell, thus allowing us to probe the effects of the local environment on the nature and chemical activity of the db states. By our taking advantage of differences in the energy-level structure of the clean and reacted surfaces, the spatial distribution of the reacted atoms can be directly observed. We find that the different sites of triply coordinated Si in the 7×7 unit cell are not chemically equivalent. Using atom-resolved electronic spectroscopy, we probe the occupation of surface states and thus obtain direct information about the delocalization of db states and charge transfer (CT) between sites. Our results show that CT between sites strongly influences reactivity and suggest a more delocalized picture for surface reactivity than previously thought.

The experiments were performed in an ion-pumped vacuum chamber having a base pressure of $\simeq 1\times10^{-10}$ Torr. The Si crystals were phosphorus-doped (~ 1 Ω cm) Si(111) wafers. Sample cleaning involved prolonged heating of the crystal to 700 °C with subsequent removal of the oxide layer by heating to 1030 °C for about 1 min. STM tips were prepared by electrochemical etching of tungsten wires. The design of our STM is similar to that described by Demuth *et al.*[5] During recording of STM topographs, a feedback circuit controls tip-surface separation and maintains a constant tunneling current ($\simeq 1$ nA). Activation of a sample-and-hold circuit in the feedback loop permits the tip-surface separation to be temporarily fixed, while the bias voltage is linearly ramped so that an *I-V* curve containing atomic-specific spectroscopic information can be obtained in about 1 ms.

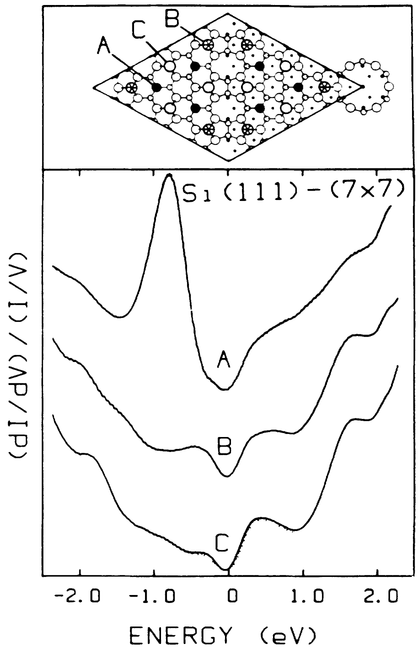

FIG. 1. (Top) Schematic diagram illustrating the Takayanagi model (Ref. 6) of the 7×7 surface reconstruction: Rest atoms (curve *A*), corner adatoms (curve *B*), and center adatoms (curve *C*) are identified by arrows. (Bottom) Atom-resolved electronic spectra obtained over the above surface sites.

Currently, the most generally accepted model for the Si(111)-(7×7) reconstruction is that of Takayanagi *et al.*[6] (for a schematic diagram, see the top portion of Fig. 1). According to this model, there are only nineteen db's in the 7×7 unit cell. Of these, six are located on the first layer "rest atoms" (labeled *A* in Fig. 1, top), twelve are on the Si "adatoms," and one on the atom at the bottom of the "corner hole" (vacancy). For reasons that will become apparent later, we separate the adatoms into two groups. Those next to corner holes we refer to as "corner adatoms" (labeled *B*), while the rest are referred to as "center adatoms" (labeled *C*). In Fig. 2(a), we show a topograph of the clean surface obtained with the sample biased at +0.8 V. Under these conditions, STM probes the unoccupied states of the sample up to 0.8 eV above E_F. The twelve Si adatoms in the 7×7 unit cell are clearly seen. The topograph of the surface, also at +0.8 V, obtained after exposure to $\simeq 1$ L (1 langmuir $\equiv 10^{-6}$ Torr s) of NH_3 is shown in Fig. 2(b). We see that about half of the adatoms appear to be missing. However, the reaction of NH_3 with Si is not an etching reaction. Electron energy-loss[7] and photoemission[3] studies show that the surface reaction involves the dissociation of NH_3 to NH_2 with H, with both Si-H and Si-NH_2 species present at the surface. The "disappearance" of the adatoms is the result of changes in electronic structure upon reaction with NH_3 (see subsequent discussion). When the bias is increased to +3 V, all adatom sites become visible again [Fig. 2(c)]. The 7×7 reconstruction appears to have been preserved, although there are some distortions from the clean-surface topography. Nitrogen-derived states are not directly detectable with the STM because their binding energy is higher than about 4 eV,[3] i.e., they are located beyond the STM "tuning range." The preservation of the 7×7 reconstruction suggests that the reaction with NH_3 has primarily saturated existing db's with limited, if any, Si—Si bond breaking. This behavior is analogous to that observed[2] in the case of Si(100)-(2×1) and underscores the notion that db's control the low-temperature reactivity of Si surfaces.

It is clear that STM topographs at different energies [e.g., Figs. 2(b) and 2(c)] provide the unique ability to follow the spatial distribution of the surface reaction on the atomic scale. Thus, by analyzing topographs of partially reacted Si(111) surfaces, we always find that most of the unreacted adatoms are corner adatoms. For example, after $\simeq 1$ L NH_3 exposure there are $\simeq 3.5$ times more unreacted corner adatoms than center atoms [see Fig. 2(b)]. This preferential reactivity is particularly interesting given that both types of adatoms represent triply coordinated Si sites of very similar structure.

To obtain insight into the reasons for the above behavior, we studied the electronic spectra of the clean and reacted surfaces with atomic resolution using the STM. The quantity $(dI/dV)(I/V)^{-1}$ is approximately proportional to the local density of states.[8] In Fig. 1 we show atom-resolved spectra of the clean surface. These spectra are, in general, in agreement with conventional photoemission and inverse-photoemission spectra[9] and current-imaging STM results.[10] Curve *A* shows a spectrum obtained over a rest-atom site. The characteristic feature is a strong occupied band at $\simeq 0.8$ eV below E_F. The energy and intensity of this band suggests that the corresponding rest-atom db state is fully occupied. Curve *B* is obtained over a corner adatom. It shows an occupied band at $\simeq 0.4$ eV below E_F and an unoccupied band at $\simeq 0.5$ eV above E_F. These bands correspond to the occupied and unoccupied parts of the corner-adatom db state. Following theory,[11] we ascribe the band at $\simeq 2$ eV below E_F as an adatom back-bond state. The band at $\simeq 1.5$ eV above E_F is also primarily an adatom back-bond state. The center-adatom spectrum (curve *C*) shows important differences from that of the corner adatom (curve *B*). The intensity of the occupied db state has decreased while, correspondingly, the intensity of the unoccupied state has increased. The filling of the rest-atom db state and the small occupation of the adatom state suggests an adatom to rest-atom CT process.[11] In addition, our spectra (Fig. 1, curves *B* and *C*) show that most of this charge is contributed by the center adatoms. This is most likely because center adatoms have two rest-atom neighbors while corner adatoms have only one. The above differences in the occupation of the db states could be the cause of the observed differences in the reactivity of center and corner adatoms. We will return

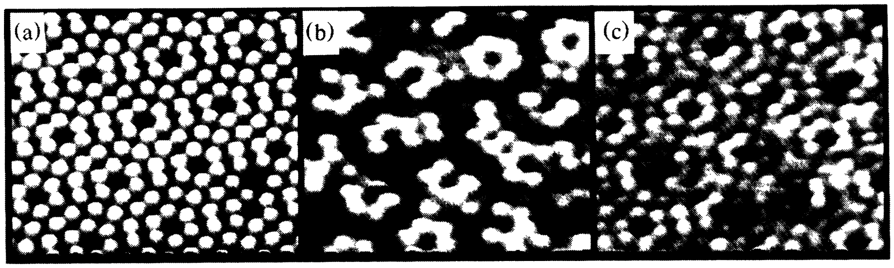

FIG. 2. Topographs of the unoccupied states of (a) clean Si(111)-(7×7) surface ($V_{bias}=0.8$ V), (b) partially reacted surface ($V_{bias}=0.8$ V), and (c) partially reacted surface ($V_{bias}=3.0$ V).

to this point.

While the reaction of the adatoms can be directly seen by inspection of the topographs, the rest-atom reaction must be followed with atom-resolved spectroscopy. In Fig. 3, we show spectra obtained on a partially reacted surface. Spectrum *A* is obtained over a rest-atom site. We see that the characteristic state at $\simeq 0.8$ eV has been eliminated. Adatom spectra (curve *B*, dashed line) show that the corresponding surface states are also eliminated upon reaction. The elimination of the surface states is the reason for the "disappearance" of the reacted adatoms in Fig. 2(b). By a systematic study of the spectra of reacted surfaces, we find that rest atoms are much more reactive than adatoms. Upon NH_3 exposure, rest atoms react first, and under conditions such as those of Fig. 2(b) where about half of the adatoms are still unreacted, we find no unreacted rest atoms remaining. The high reactivity of rest atoms appears surprising since, as we concluded earlier, the rest-atom db state is filled on the clean surface. It is thus not clear how the reaction would occur at a closed-shell or nearly closed-shell Si site. The spectra *B* (full line) and *C* of *unreacted* corner and center adatoms which are adjacent to *reacted* rest atoms provide additional information. On the clean surface the center-adatom db state is nearly empty (Fig. 1, curve *C*), but on the surface where the rest atoms have reacted (Fig. 3, curve *C*) it shows a much higher occupation with a simultaneous decrease in the intensity of the unoccupied part at +0.5 eV. The above results suggest that during reaction a rest atom to adatom reverse CT takes place which allows the rest atom to transfer the extra charge and react with NH_3. Further examination of Figs. 1 and 3 reveals other spectroscopic changes at *unreacted* adatom sites induced by the reaction of nearby rest atoms. These changes are consistent with the above picture. The adatom back-bond state at -1.8 eV (Fig. 1, curves *B* and *C*) is eliminated and a new band appears at -1.5 eV (Fig. 3, curves *B* and *C*). We believe that this new band is due to the back-bond state on the reacted surface. The adatom–rest-atom coupling involves the back bonds. Upon reaction, the rest-atom db state is eliminated, leading to the decreased binding energy and increased intensity of the back-bond band.

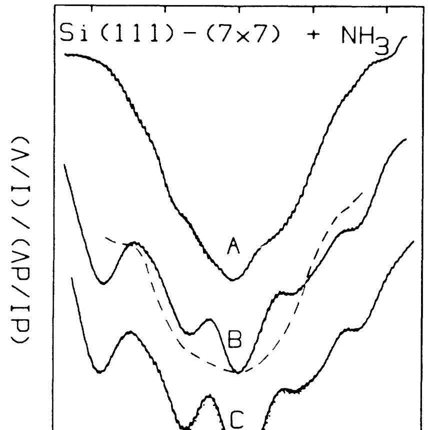

FIG. 3. Atom-resolved electronic spectra obtained at an NH_3-exposed surface: curve *A*, spectrum over a *reacted* rest-atom site; curve *B* (dashed line) spectrum over a *reacted* corner-adatom site; curves *B* (solid) and *C*, spectra obtained over *unreacted* corner- and center-adatoms sites, respectively, adjacent to reacted rest atoms.

While these observations can explain how the rest atoms can react with NH_3, they do not explain why they are more reactive than adatoms. We suggest that the reason for this behavior may be found in the more delocalized nature of the adatom db state. While adatoms are thought of as triply coordinated Si atoms, much as the rest atoms are, the STM spectra (Fig. 1) show a lower density of states at adatom sites. This is true even after the rest atoms have reacted (Fig. 3, curves *B* and *C*). A low density of states at adatom sites is consistent with a recent cluster calculation,[12] which suggested a strong bonding interaction between an adatom and the Si atom directly below it. We propose that the reduced density brought about by the delocalization of the adatom db state is responsible for the reduced reactivity of adatoms as compared to rest atoms.

Reconsidering the issue of the different reactivity of center and corner adatoms, we note that the proximity and interactions between rest atoms and adatoms can affect the reactivity of adatoms in more than one way. On the clean surface, the preferential center-adatom to rest-atom CT could lead to differential adatom reactivity. As the reaction proceeds and the rest atoms are reacted, reverse CT results in similar populations of the center- and corner-adatom db states (Fig. 3, curves *B* and *C*). Geometric factors may also play a role. When an NH_3 molecule is dissociated at a rest-atom site, only one of the products, H or NH_2, will saturate the rest-atom db. The other product can either break a Si–Si bond, a possibility not supported by topographs such as Fig. 2(c), or be scavenged by other db's. Given that each rest atom has two center-adatom neighbors but only one corner adatom, a preferential reaction of center-adatom db's will result. Our results show that reaction at center adatoms is preferred by more than a 2-to-1 ratio, indicating that differences in electronic structure are indeed important. Such differences may arise, for example, from differences in strain energy.

In conclusion, we have been able to follow the spatial distribution of the reaction of Si(111)-(7×7) with NH_3 at the atomic level. We have shown that, in this reaction surface, rest atoms are more reactive than adatoms and, moreover, center adatoms are more reactive than corner adatoms. We have been able to observe the interactions and charge transfer between surface sites and the changes in these interactions induced by the surface reaction. We found that the db states show significant delocalization and that this delocalization greatly influences surface reactivity. The use of atom-resolved scanning tunneling spectroscopy to study surface electronic structure while chemically "titrating" various surface sites promises to be a new and powerful way for the study and the understanding of surface chemistry.

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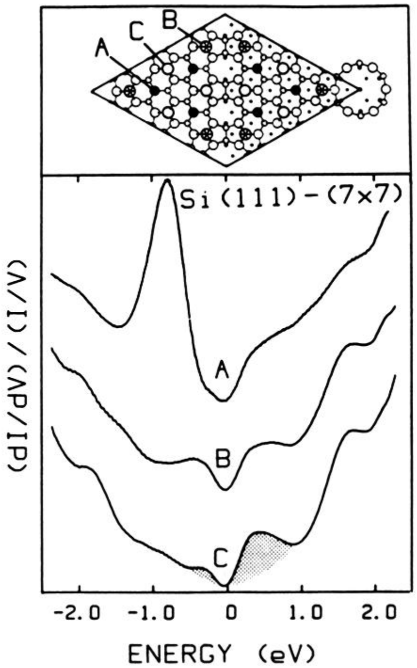

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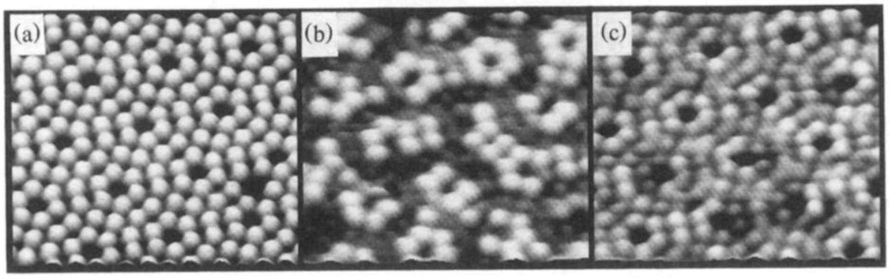

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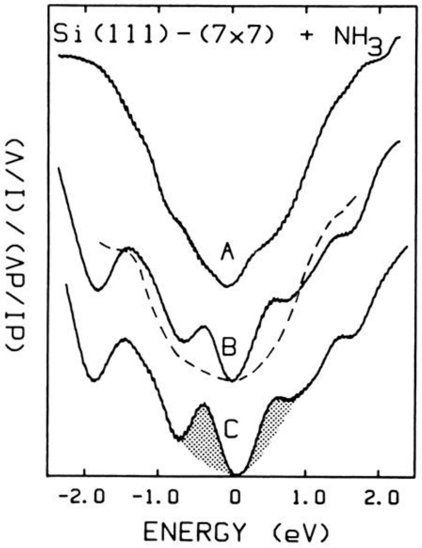

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