

Site-Specific Measurement of Adatom Binding Energy Differences by Atom Extraction with the STM

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Using a scanning tunneling microscope, single adatoms can be extracted from a Si(111)7×7 surface by field evaporation, when the sample voltage is pulsed at 4 V or more in either polarity. Statistically, adatoms at the center of the 7×7 unit cell are more frequently removed than those near the corner holes, by a ratio of 1.6:1. This difference can be explained by assuming that the binding energy of center adatoms is approximately 0.1 eV less than for corner adatoms. The relationship of this result to previous observations of greater chemical reactivity at center adatom sites is discussed.

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Atomic-scale modification of surfaces by scanning tunneling microscopy (STM) provides a unique means to probe the local physics and chemistry of such surfaces [1], as well as a promising technology for the fabrication of novel electronic devices [2]. Modification of semiconductor surfaces is of particular interest for practical applications. In their pioneering work, Becker, Golovchenko, and Swartzentruber [3] made atomic-scale protuberances on Ge(111) by briefly increasing the bias between tip and sample above 3 V. The proposed mechanism was field ion emission. However, Si(111) could not be modified in the same way, even for biases up to 20 V. Lyo and Avouris [4] have succeeded in manipulating single atoms on Si(111) by moving the tip to within a few Å units of the surface and applying a 3 V pulse. Because of the close proximity of tip and sample, this process is believed to depend on direct chemical interaction as well as electric field.

Recently, grooves several nanometers wide were made on Si(111) at bias voltages in the range 3–6 V, without first moving the tip towards the sample [5]. The process was directly dependent on electric field, rather than on current or voltage, indicating that the mechanism was field evaporation. In this Letter, we show that a similar process can be used to modify Si(111) on the atomic scale and remove single Si adatoms from the surface. The statistics of adatom vacancy creation yield information about the differences of binding energy for different adatom sites in the Si(111)7×7 unit cell. The approach presented here for studying surface energetics, by directly comparing how easily different atoms are extracted from a surface, should prove widely applicable.

The experiments were made with a commercial ultrahigh vacuum (UHV) STM (JEOL JSTM-4000 XV). Samples cut from wafers of *p*-doped Si(111) were cleaned in UHV by repeated flash heating to 1200°C. The base pressure in the chamber was 1×10^{-8} Pa. The STM tip was a 0.1 mm W wire, sharpened by electrolytic etching using a 0.5N solution of KOH. Electron bombardment heating of the tip to above 1200°C was performed in the UHV chamber. This step has been shown

to be critical for obtaining reproducible modification [5].

Silicon adatoms were extracted as follows. A clean, flat area of the surface was imaged at +2 V and –2 V at a tunneling current of 0.6 nA, revealing the regular pattern of Si adatoms of the Si(111)7×7 reconstructed surface. The tip was moved to a point in the imaged region and a voltage pulse of either +6 V or –6 V was applied to the sample for 10 ms in constant current mode [6]. After the pulse was applied, the same area was again imaged at 2 V in both polarities. Figure 1 illustrates the typical result of a single –6 V pulse.

Certain adatom positions are modified, the dominant form of modification being a dark spot in both polarities. Commonly adsorbed gases from the rest gas in the UHV chamber, such as H and O, are known to appear light in one or both polarities [7,8], as are deposited metal atoms [9]. Thus the dark appearance in both polarities is evidence that these modifications are not due to adsorption, but due to vacancy formation. This is also consistent with the observation of groove formation when high voltage is applied for longer periods [5].

Other sorts of defects, which do not appear dark in both polarities, are occasionally generated by the voltage pulse (see Fig. 1). The exact origin of these defects is not known yet, though it is likely that they are due in part to W field evaporated from the tip. In field ion emission studies, the critical field for the onset of W ion emission is 5.7 V/Å compared to 3.0 V/Å for Si [10]. This difference might explain why Si extraction is more likely than W deposition, even though the field at the tip is expected to be larger than at the sample. We note, though, that direct comparison with results for field ion emission from isolated tips is not very reliable, since recent calculations show that the field ion emission process itself is strongly affected by the close proximity of the sample [11].

The extent of modification on the Si surface varies with the magnitude of the pulse. Of the order of 10 vacancies are produced by a –6 V pulse to the sample, as shown in Fig. 1, and the result is similar for a +6 V pulse. For a –4 V pulse, fewer vacancies are formed and frequently a single adatom can be extracted from a predetermined po-

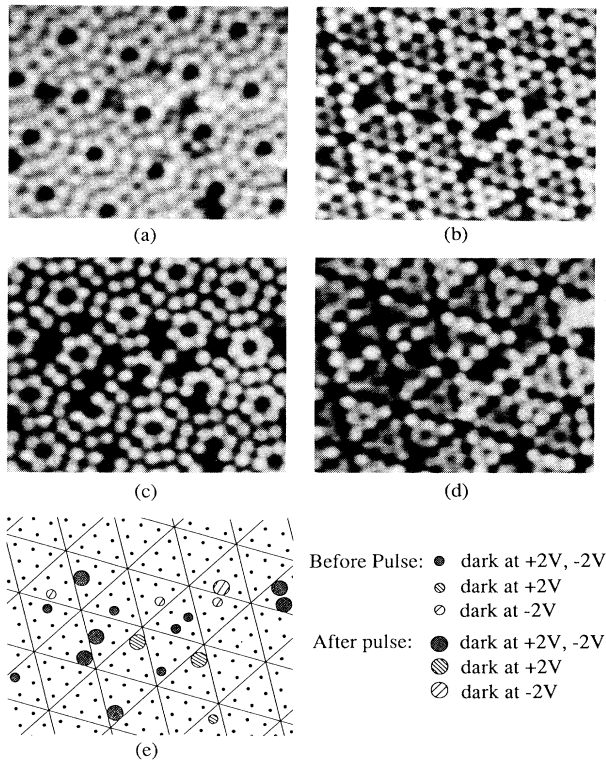


FIG. 1. Si(111)7×7 structure imaged at a sample bias of +2 V [(a) and (c)] and -2 V [(b) and (d)] and a tunneling current of 0.6 nA, before [(a) and (b)] and after [(c) and (d)] a -6 V pulse to the sample. Below the STM images, a sketch of the modified adatom sites is shown. Those that are modified in both polarities appear as filled circles. Note that in the images at -2 V, the stacking faulted side of the 7×7 unit cell appears darker.

sition. Such site-specific manipulations are possible due to the very low thermal drift of the STM (<1 Å per minute). An example where a pulse resulted in the extraction of a single atom is illustrated in Fig. 2(a). For a +4 V pulse to the sample no vacancies are formed. This agrees with the observation that higher voltages are required to form grooves when the tip is biased negatively [5].

Single adatom extraction as in Fig. 2 is successful in about 30% of attempts: Sometimes a pulse will not produce an adatom vacancy, and sometimes several are made at once. This is consistent with field ion emission, which is a thermally activated process [10] where emission of an adatom is a probabilistic event. A feature of Fig. 1 is that adatoms are extracted over a relatively large area of about 100 nm². This is reasonable: Whereas the tunneling current is an exponential function of the tip-sample separation, *s*, and so is concentrated at a single atomic protuberance on the tip, the electric field varies roughly as 1/*s*, and so atom extraction due to field ion emission is effective over a larger area, which depends on the radius of curvature of the tip. A detailed discussion

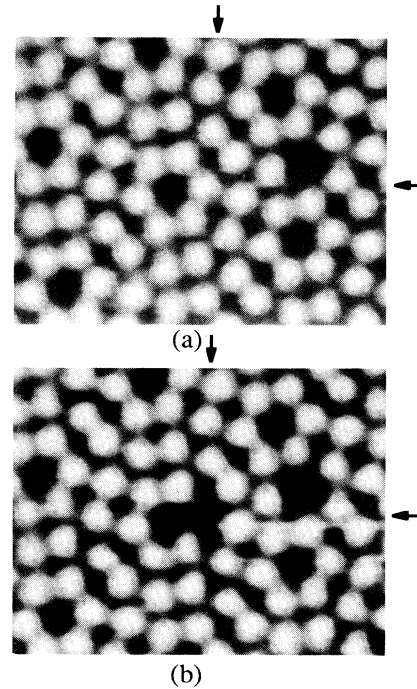


FIG. 2. Image of a single adatom modification. The STM was positioned at the point indicated by the arrow in the first image. After a -4 V pulse to the sample, a single vacancy appears at that point. Both images taken at a sample bias of +2 V and 0.6 nA.

of the dependence of the extraction probability on tip preparation is given elsewhere [12].

The adatoms on the Si(111)7×7 surface can be divided into four crystallographically distinct types, according to whether they are corner adatoms or center adatoms, and whether they reside on the faulted or unfaulted half of the 7×7 unit cell. These distinctions are illustrated in Fig. 3. To obtain relative extraction probabilities for these four different groups, pulse experiments similar to those shown in Fig. 1 were repeated many times. The position of the tip during the pulse was chosen at random. In total, 230 adatoms were extracted for -6 V pulses to the sample and 246 for +6 V pulses. The breakdown according to adatom type is given in Table I. There are two

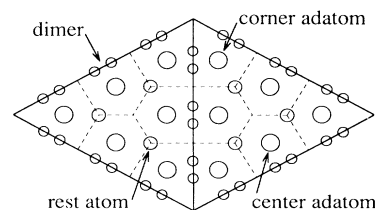


FIG. 3. Sketch of the Si(111)7×7 unit cell, indicating the positions of center and corner adatoms, surface rest atoms, and dimers. The dashed lines are bisectors of lines joining nearest-neighbor adatoms.

TABLE I. Statistics for the adatom vacancy formation. The number of vacancies observed for pulses of +6 V or -6 V to the sample are broken down according to whether a vacancy is at a corner adatom or center adatom site, and whether it is on the faulted or unfaulted side of the 7×7 unit cell. The corresponding percentage of total vacancies for each polarity is given in parentheses.

Corner Si adatom		Center Si adatom	
Faulted half	Unfaulted half	Faulted half	Unfaulted half
Negative voltage pulse: -6 V, 10 msec			
51(21%)	48(19%)	73(30%)	74(30%)
99(40%)		147(60%)	
Positive voltage pulse: +6 V, 10 msec			
41(18%)	46(20%)	79(34%)	64(28%)
87(38%)		143(62%)	

important aspects to the results. First, the probability of extraction from the faulted and unfaulted halves of the unit cell was the same, within errors. Second, center adatoms were more frequently extracted than corner adatoms by a ratio of 1.6 ± 0.2 , for both pulse polarities.

The difference between center and corner adatoms cannot be accounted for by geometrical effects. There are equal numbers of center and corner adatoms in each unit cell. If the unit cell is partitioned by the bisectors of lines joining nearest-neighbor adatoms (dashed lines in Fig. 3), the area associated with corner adatoms is 4% larger than that of center adatoms. Assuming the probability of adatom extraction to be proportional to this "adatom cross section," corner adatom extraction should be slightly preferred. No other reasonable geometrical definition of an adatom cross section can produce the large difference in favor of center adatom extraction that is observed experimentally.

Local variation of the electric field at different adatom sites is also an unsatisfactory explanation of the experimental result. On the basis of simple electrostatic considerations, the field should, if anything, be higher at the corner adatom sites, by virtue of their position at the relatively sharp corners of the 7×7 cells, and also because they are calculated to protrude 0.05 \AA further out of the surface than center adatoms [13].

The configuration of nearest neighbors around a corner adatom and a center adatom is different. Correlation effects, which might make it easier to remove an adatom neighboring a vacancy, and thus possibly skew the statistics, can be eliminated by counting only those vacancies formed in areas isolated from other vacancies or defects. Summing over both +6 V and -6 V pulse experiments, the subtotal of isolated vacancies is 91 for center adatom sites and 60 for corner adatom sites, giving a ratio of 1.5 ± 0.25 . This is the same ratio, within errors, as for all adatom vacancies. We conclude that the preference for center adatom vacancy formation is not due to correlation effects in the formation of vacancy clusters.

We suggest that the difference in extraction probabili-

ties reflects a difference in the activation energy for field ion emission of the center and corner adatoms. At room temperature, thermal activation dominates the field ion emission process, and the evaporation rate can be expressed by an Arrhenius equation of the form [10]

$$R = \nu \exp(-Q/kT), \quad (1)$$

where ν is the vibrational frequency of the adatom, which is dependent on temperature and field, Q is the field-dependent activation energy, k is the Boltzmann constant, and T is the temperature. Given that corner and center adatoms have identical bonding geometries, their vibrational properties should be very similar, so it is unlikely that the exponential prefactor can account for the relatively large difference in evaporation rates. On the other hand, a small difference in activation energy will produce a large effect. Defining Q_{corner} and Q_{center} as the activation energies of corner and center adatoms, and equating the observed ratio of extracted corner and center adatoms to the ratio of evaporation rates, then from Eq. (1), $Q_{\text{corner}} - Q_{\text{center}} = kT \ln(1.6) \cong 0.01 \text{ eV}$, assuming that the sample remains at 297 K during the process.

Several models for the field ion emission process exist [11,14-20]. In the simple image-hump model, the activation energy Q of a positive ion is expressed as [10]

$$Q = E_b + I_n - n\phi - (n^3 e^3 F / 4\pi\epsilon_0)^{1/2} + 0.5(\alpha_n - \alpha_i)F^2, \quad (2)$$

where E_b is the binding energy of the neutral atom, I_n is the energy needed to ionize the atom into an n^+ ion, and $-n\phi$ is the energy gained returning n electrons to the Fermi level of the sample, ϕ being the work function of the sample. The term $-(n^3 e^3 F / 4\pi\epsilon_0)^{1/2}$ is the "image-hump" reduction of the potential barrier, due to the overlap of the applied potential, $-neFx$, and the image potential, $-n^2 e^2 / 16\pi\epsilon_0 x$, near the emitting surface, where F is the applied field, e is the electronic charge, ϵ_0 is permittivity of free space, and x is measured relative to the image plane of the surface. For negative ion emission, I_n is replaced by χ_n , the electron affinity, and the sign of $-n\phi$ is reversed [21]. The last term in Eq. (2) represents the difference in polarization energy between the neutral and ionized states, with polarizabilities α_n and α_i , respectively.

The observation that the extraction probability ratio is identical for both polarities suggests that the difference between the corner and center adatoms is related to the polarity-independent binding energy term E_b in Eq. (2), rather than the ionization or polarization energy terms, which should depend on the ion type and hence on polarity. Other models of field ion emission, such as the charge-exchange model [10,15], are considered to be more rigorous than the image-hump model. However, a physically intuitive feature common to all models is that the activation energy depends directly on the binding energy. Thus, while other effects cannot be entirely ruled

out, a small 0.01 eV difference in binding energy between corner and center adatoms provides the simplest explanation compatible with all aspects of the experimental results.

This binding energy of Si adatoms is calculated as 0.84 eV/adatom for the case of a $\sqrt{3}\times\sqrt{3}R30$ adatom structure [22], so the binding energy difference between two similar adatoms should be much smaller than this. Recently, first principles calculations of the full Si(111)7×7 structure have been made, though the difference in the binding energies between center and corner adatoms is not reported [13]. Calculations of Si adatom structures with different local bonding geometries [23], such as 1×1, $\sqrt{3}\times\sqrt{3}R30$, and 2×2, show energy differences as small as 0.03 eV per 1×1 unit cell, comparable to the difference between center and corner adatoms estimated here.

Recent results for the chemical reactivity of adatom sites on Si(111)7×7 display an intriguing trend, which suggests a relation to the adatom extraction discussed here. For NH₃ reacting with a Si(111)7×7 surface, the center adatom sites are more reactive than the corner adatom sites by a ratio of more than 4:1 [24]. Similar behavior is seen for H₂O [25]. Enhanced chemical reactivity of center adatoms has also been seen for several metals adsorbed in small amounts on Si(111), for example, Cu [9], Ag [9], and Pd [26]. In the case of metals, in contrast to NH₃, there is a preference for reaction with one-half (the faulted half) of the unit cell. A notable exception to this trend is the reaction with oxygen, which shows a preference for corner adatoms [7]. However, the mechanism is believed to be quite different in this case, with the O atom absorbed in a corner adatom backbond, rather than reacting with a dangling bond [7].

The reason for the greater reactivity of center adatoms is not yet understood fully. It may be related to a greater degree of charge transfer from the center adatoms to the surface rest atoms shown in Fig. 3 [25]. Strain relaxation may also play a role, since corner adatoms are adjacent to two Si dimers, while center adatoms are adjacent to only one. Clearly, such differences will also affect the adatom binding energies. An interesting theoretical challenge is to calculate the effect of such differences on the adatom binding energies, and compare with the present experimental result.

In conclusion, we have modified Si(111)7×7 by a field evaporation process using an STM. A difference in the emission probabilities of the center and corner adatoms of the Si(111)7×7 unit cell was observed. This has been interpreted in terms of a 0.01 eV smaller binding energy for center adatoms. We have suggested that this difference is related to the enhanced chemical reactivity of center adatoms relative to corner adatoms, as observed in previous

STM investigations. We have demonstrated that extraction by field ion emission can be achieved with single atom precision. As a result, extraction statistics can in principle be gathered one site at a time, rather than by the process of random vacancy formation used here. Examples where this option could prove important include studies of low concentration adsorbates or kink sites on steps, where the random approach cannot be relied on to produce sufficient data.

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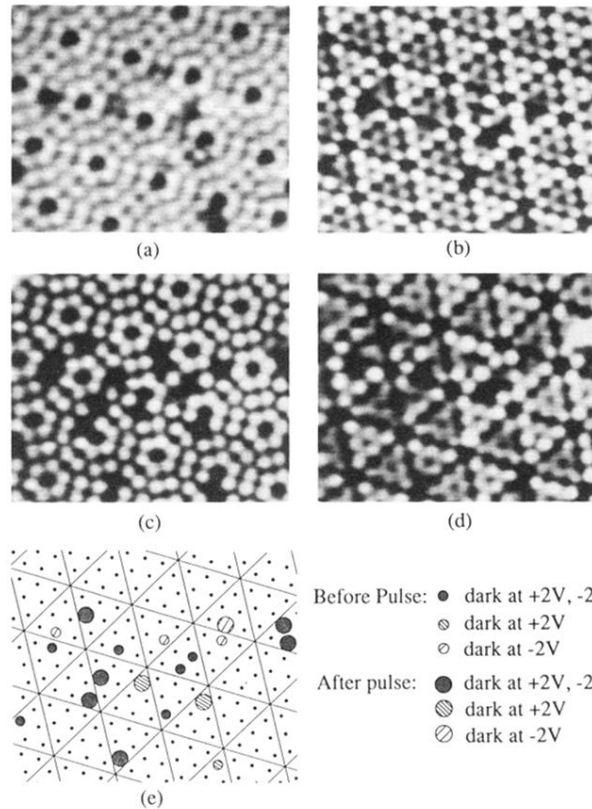


FIG. 1. Si(111)7×7 structure imaged at a sample bias of +2 V [(a) and (c)] and -2 V [(b) and (d)] and a tunneling current of 0.6 nA, before [(a) and (b)] and after [(c) and (d)] a -6 V pulse to the sample. Below the STM images, a sketch of the modified adatom sites is shown. Those that are modified in both polarities appear as filled circles. Note that in the images at -2 V, the stacking faulted side of the 7×7 unit cell appears darker.

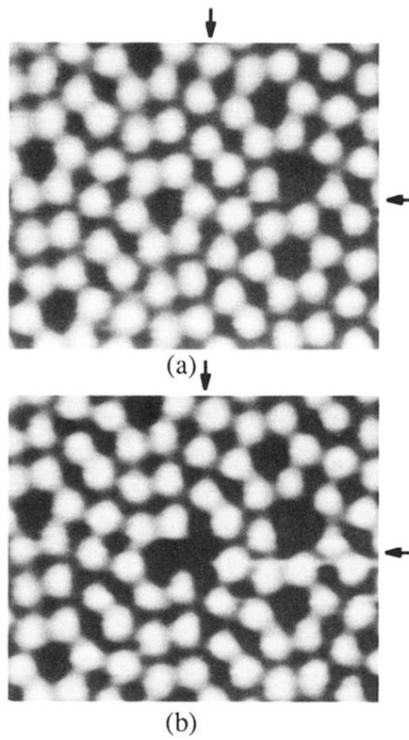


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