Site-Specific Displacement of Si Adatoms on Si(111)-(7 × 7)

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Tunneling and field-emitted electrons from the tip of a scanning tunneling microscope were used to reversibly displace Si adatoms on Si(111)-(7 × 7) at 30 to 175 K. Displacement rates were determined as a function of current, sample bias voltage, and lateral distance from the tip. The displacement is found to be site specific, with *strong* preference for center Si adatoms in the faulted half of the unit cell. Si adatoms return to the normal site by the same method or by annealing above 155 K with an activation energy of 0.49 ± 0.03 eV and preexponential of $10^{12.2\pm0.9}$ s^{-1}. [S0031-9007(97)04666-8]

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The scanning tunneling microscope (STM) can be used to image and manipulate individual atoms and molecules on metal surfaces [1–4]. A number of atomic scale manipulation experiments have also been carried out on silicon surfaces at room temperature [5–11]. Both inelastic tunneling and higher energy field-emitted electrons have been used to desorb hydrogen atoms from regions as small as a single dimer row of the Si(100)-(2 × 1) surface [5,6]. The desorption of hydrogen from regions of the Si(111) [7] and Si(111)-(7 × 7) [8] surfaces with field-emitted electrons has also been achieved. Similarly, chlorine has been desorbed from Si(111)-(7 × 7) [9]—probably also by the field-emitted electrons. Adatoms of the bare Si(111)-(7 × 7) surface have been removed by a thermally activated field-evaporation mechanism due to the high electric field under the STM tip [10,11]. The tip-induced migration of vacancies on the GaP(110) surface has been attributed to a field-induced reduction of the migration energy barrier [12]. Vacancy migration was also observed on GaAs(110) and attributed to the recombination of carriers injected via the STM tip with carriers from the bulk [13].

Knowledge of the interaction of electrons with silicon surfaces can enhance our understanding of the fundamental energetics of these surfaces. This knowledge is also of great importance to the semiconductor industry where surface chemistry and electron beams are used in device fabrication. In this paper, we report the reversible lateral displacement of specific Si adatoms on the bare Si(111)-(7 × 7) surface under the influence of both tunneling and field-emitted electrons. In the case of tunneling electrons, a single adatom could be reversibly displaced (as an "atomic switch") and its change in position monitored with the tunneling current. Above 175 K, displaced Si adatoms return to their normal positions too quickly to be imaged with the STM. Unlike previous room temperature experiments [10,11], the removal of adatoms from the surface does not occur at these low temperatures.

Instrumentation has been described elsewhere [4]. The two silicon samples used were p-type, boron doped with resistivities of 0.5 Ω cm and 5 Ω cm, respectively. The Si(111) surface was prepared by outgassing at 1000 K for several hours followed by repeated cycles of Ne^+ sputtering and annealing at 1200 to 1500 K to remove all traces of carbon from the surface. STM images were typically scanned at 1 to 2 V sample bias and 0.1 to 1 nA tunneling current.

Atoms were displaced by applying a positive voltage pulse to the sample relative to the STM tip while the tunneling or field emission current was recorded. Atoms could not be displaced with negative voltage pulses. To determine the single atom transfer and return rates with tunneling current, the tip was precisely positioned over the adatom of interest by finding a local maximum in the tip's vertical position with the feedback loop turned on to maintain constant tunneling current. This was done with an "atom tracking" software program and was reproducible to within 0.2 Å. Then the feedback loop was turned off and the voltage pulse was applied. Just before the voltage pulse, the tip was often moved to a predetermined position to give the desired tunneling current during the pulse. Total rates for atom transfer for all other adatoms other than the one directly under the tip were determined by applying a voltage pulse and rescanning the surface to determine the number and distribution of transferred adatoms.

The displacement of single adatoms of the Si(111)-(7 × 7) surface at 52 K is shown in Fig. 1. An STM image of this surface is shown in Fig. 1(a) and a schematic of the surface is shown in Fig. 1(e). In the dimer–adatom–stacking-fault (DAS) model for the Si(111)-(7 × 7) surface unit cell [14], there are six Si atoms on "center" sites and six Si atoms on "corner" sites in the top adatom layer which is visible in STM images. Each adatom lies on a threefold site (T_4 site) of the second, "rest atom," layer which contains a stacking fault in one half of the unit cell. The STM tip was first positioned as described above over a center site adatom in the faulted half of the Si(111)-(7 × 7) unit cell (tip-sample distance ~6 Å). The faulted half was determined from negative sample bias images which are known to show the faulted-half adatoms more brightly than unfaulted-half adatoms. The voltage was stepped from 1.5

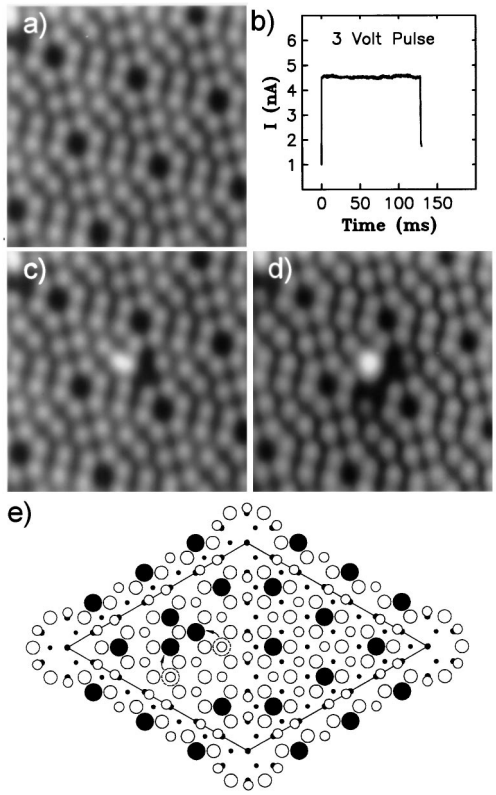

FIG. 1. (a) STM image of the Si(111)-(7 × 7) surface at 52 K. (b) Tunneling current during a 3 V sample bias pulse applied directly above the center site adatom in the middle of (a). (c) Rescan shows the adatom in one of the two equivalent metastable T_4 sites. (d) After a 3 V pulse directly over another center site adatom in the same unit cell, both atoms are found in metastable positions. (e) DAS model for the surface [14] showing the site occupied by the two adatoms before and after transfer in the faulted half of the unit cell.

to 3 V and the tunneling current recorded [Fig. 1(b)]. The sudden drop in current is due to the transfer of the adatom. To prevent the return of the adatom to the normal site under the influence of the tunneling electrons, the computer was directed to end the voltage pulse as soon as the drop in current was detected. The STM image in Fig. 1(c) shows the atom has moved to a site halfway toward one of the other two neighboring center adatoms in the same unit cell. A second pulse was applied in the same manner over the remaining center adatom resulting in its transfer as shown in Fig. 1(d). It was found that the displaced atoms would return to their normal locations with tunneling or field-emitted electrons or after warming the sample above 155 K and were therefore metastable. When two center adatoms were in metastable positions in the same half of the same unit cell as shown in Fig. 1(d), the atoms were metastable at 50 K but unstable at 90 K or above. Transferring center adatoms in the unfaulted half of the unit cell was also possible but transfer rates were approximately 100 times lower. These unfaulted-half transferred atoms were at least as stable as those in the faulted half and were imaged as high as 166 K. Displacement of corner adatoms was not observed.

To obtain rates of atom transfer and rates of return to the normal site, tunneling current was recorded for a period of time while the atom hopped between these two positions. The distribution of times spent in each site was an exponential function and so the characteristic lifetime and rate were determined. Examples for 2.25 and 3 V are shown in Fig. 2(a). The high current state corresponds with the normal position while the low current state corresponds with the metastable position. As can be seen, the transfer rate is higher than the return rate at 3 V while the opposite is true at 2.25 V (this is also true for the same current). For the metastable "double hop" states of Fig. 1(d), return rates were approximately 30 times higher than for "single hop" states.

When the experiment depicted in Figs. 1(a)–1(c) was repeated, it was found that 10% ± 3% of the time one of the other two center adatoms in the faulted half of the unit cell would be transferred rather than the one directly under the STM tip. One of these atoms could either move toward the atom under the tip or each other and were easily recognizable in the tunneling current data. It was further found that 15% ± 5% of the time, a center adatom in the faulted half of another unit cell would be transferred, indicating that excitations are not completely localized. As shown in Fig. 2(b), a dose of 3 V tunneling

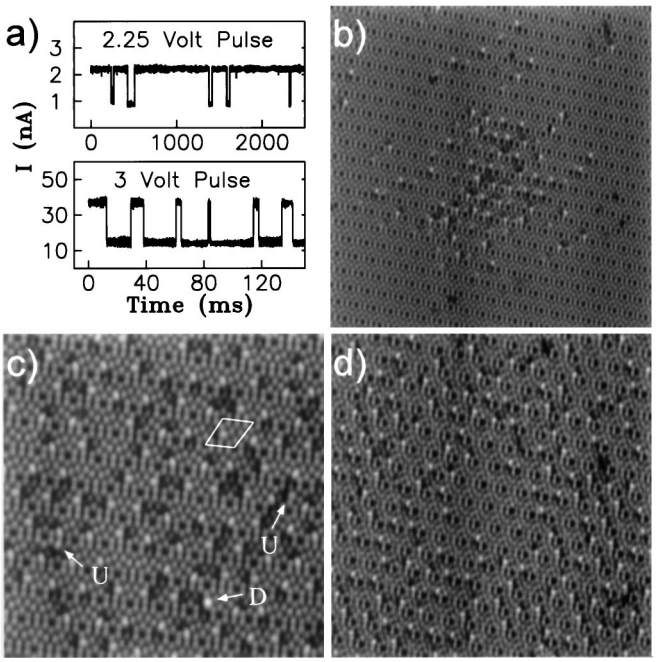

FIG. 2. (a) Current recorded at 2.25 and 3 V sample bias over a center adatom in the faulted half of a unit cell at 121 K. (b) STM image of the surface at 91 K after a very large electron dose at 3 V (10 nA, 100 s). (c) STM image of the saturated surface at 52 K after a previous scan at 10 V showing an outline of the unit cell, a large number of transferred adatoms in the faulted halves, a double hop (labeled *D*), and two hops in the unfaulted half of the unit cell (labeled *U*). (d) STM image of a saturated surface at 91 K after a very large electron dose at 2.25 V (40 nA, 300 s) near the middle of the imaged area.

electrons approximately 6000 times larger than that needed to induce a single hop leads to a large number of hops with some as much as 200 Å away.

An STM image of the surface after scanning at 10 V is shown in Fig. 2(c). For biases above the work function of the tungsten tip (4.5 V), field-emitted electrons bombard the surface over an area at least several nanometers across [15]. Because of the large tip-sample separation (about 25 Å at 10 V), it is not possible to detect changes in the current due to events on the surface. By scanning over the surface at high sample bias, it was not possible to induce the transfer of one center adatom in more than about 85% of the unit cells due to a balance between the transfer rate and return rate (saturation). We can conclude that the return rate for 10 V pulses is approximately 7 times lower than the transfer rate. Similar values were found for pulses in the range 4 to 10 V. A saturated surface would contain a small number of transferred atoms in the unfaulted half of the unit cell due to their low transfer rate and only about 3% double hops due to their high return rate. Since the return rate is higher than the transfer rate at 2.25 V for faulted-half single hops, it was possible to observe the return of atoms many unit cells away by applying a high dose of tunneling electrons confined to the atomic scale on a saturated surface as shown in Fig. 2(d).

The characteristic rates of return from the metastable site in the faulted half of the unit cell was studied as a function of temperature in the range 155 to 175 K. An example of data taken at 166 K is shown in Figs. 3(a) and 3(b). Typically, the surface was scanned at high voltage bias to induce a large number of hops. The same area was imaged at fixed time intervals to determine the decay rate. An Arrhenius plot of the return rates is shown in Fig. 3(c) and gives an activation energy of 0.49 ± 0.03 eV and preexponential of $10^{12.2\pm0.9}$ s^{-1}.

The net total nonlocal transfer rate (not including the single atom under the STM tip) as a function of sample bias voltage at constant current (0.1 nA) is shown in Fig. 4(a). A sharp drop in rates can be seen below 4 V. These rates as a function of current for 10 and 3 V pulses are shown in Fig. 4(b). For 10 V pulses, the transfer rate was found to be linear over four decades in current. A fit to the data yields a rate proportional to I^N with $N = 1.03 \pm 0.03$, giving $(7.4 \pm 0.5) \times 10^{-9}$ transfers per electron. The exponent has begun to drop slightly at 3 V with $N = 0.89 \pm 0.05$. No statistically significant difference in transfers per electron was found over the temperature range of 30 to 155 K. The insensitivity of the transfers per electron at constant bias voltage in the range 3 to 10 V to both current and temperature strongly suggests that the events observed were caused by the electrons. Although room temperature adatom desorption experiments indicated a thermally activated field-evaporation process [10,11], the adatom displacement observed here is not thermally activated.

Displacement rates as a function of current for the single atom under the tip at 3 and 2.25 V biases are shown

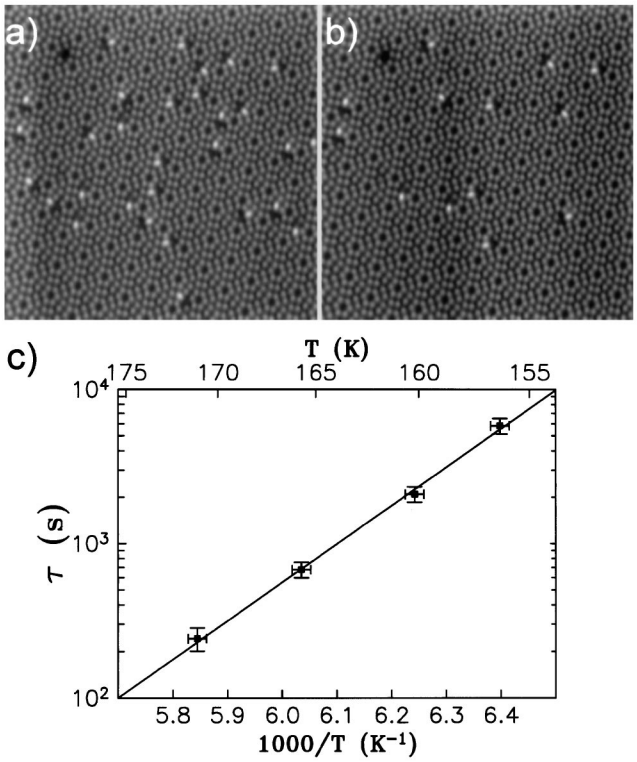

FIG. 3. (a), (b) STM images taken 10 min apart at 166 K after a previous 10 V scan. (c) Arrhenius plot of the characteristic return rate between 156 and 171 K.

in Fig. 4(b). For 3 V bias, $N = 0.72 \pm 0.05$, while for 2.25 V bias, the number of *transfers per electron* drops by about 2 orders of magnitude as the current is increased from 0.1 to 100 nA. The return rates were found to yield $N = 0.89 \pm 0.05$ and $N = 0.94 \pm 0.05$ for 3 V bias and 2.25 V bias, respectively. The deviations from constant transfers per electron at constant applied bias voltage are especially pronounced for the transfer rate at 2.25 V bias (but are also seen at 3 V). For this case the rate is a very sensitive function of voltage (which is not the case for the return rate at this voltage or for the transfer rates at higher voltages) and the loss in efficiency can be explained in terms of a decrease in tunneling voltage due to an increase in the voltage drop between the surface adatoms and the Si bulk as the tunneling current is increased. The data are consistent with a reduction in tunneling voltage of approximately 0.4 V as the current increases from 0.1 to 100 nA.

For the Si(111)-(7×7) surface, surface states derived from the dangling bonds of the Si adatoms lie at and pin the Fermi level to the middle of the band gap at the surface [16]. Unlike the case for unpinned or weakly pinned surfaces, the position and voltage of the STM tip does not have an effect on the depletion layer in the absence of current [17]. With current flow, however, the potential of the surface must adjust itself relative to the bulk to support the demanded current. In order to estimate this voltage drop we have measured the I-V characteristic for atomic scale tip-sample point contacts in the temperature range

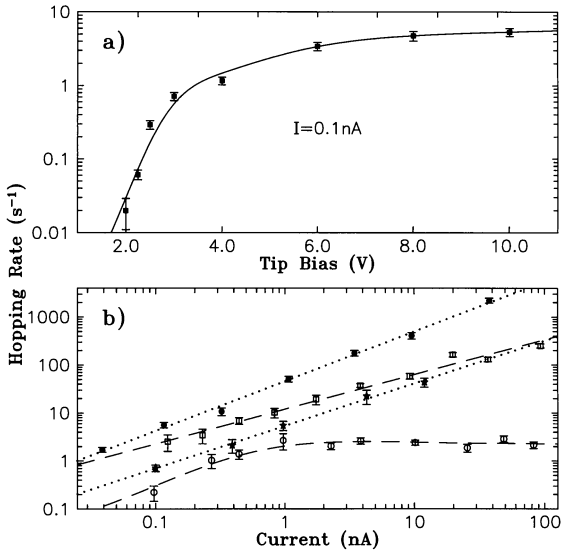

FIG. 4. (a) Nonlocal transfer rate as a function of pulse voltage (pulse current = 0.1 nA, $T = 101$ K). (b) Nonlocal and single atom transfer rates as a function of pulse current. Curves shown are for 10 V nonlocal (solid circles), 3 V nonlocal (solid stars), 3 V single atom (open squares), and 2.25 V single atom (open circles). Nonlocal data taken at 101 K and single atom data taken at 121 K.

of the above experiments in a manner similar to previous experiments performed at room temperature [18]. This assumes there is no significant change in the depletion layer when the atomic scale point contact is formed. We find that between 0.1 and 100 nA, the voltage change is approximately 0.3 V, in good agreement with the estimate based on the loss in efficiency in the atomic displacement rates shown in Fig. 4.

In the work of Schlüter and Cohen [19], the conduction-band surface resonances were computed for the bare as well as for the H and Cl terminated Si(111) surfaces. A band with essentially the same structure in all cases was found in the range 3 to 8 eV above the Fermi level due to *s*-like Si adatom orbitals. In the case of H and Cl termination, the resonance may be viewed as due to the $\sigma^\star$ Si-adsorbate antibonding states. The mechanism proposed for H desorption from Si(100)-(2 × 1) induced by field-emitted electrons involved a σ to $\sigma^\star$ electronic transition [5]. The similarity of this experimental data with various other H and Cl desorption experiments on Si(111) surfaces [6–9] as well as the data given here suggests the same mechanism in all cases: the temporary occupation of the surface resonance by electrons from the STM tip. The nonlocal events observed in our experiments are attributed to propagation of energetic electrons along the surface through this surface resonance. Multiple vibrational excitations involving more than one electron do not occur due to the very short vibrational lifetime of the Si adatom. The top of the bulk phonon band for silicon is 63 meV [20]. Since the coordination of the adatom is less than a bulk atom, one can expect an adatom vibration to lie within the bulk band. If one assumes the localized vibrational mode couples to the entire band, the vibrational lifetime can be estimated as $\hbar/63$ meV $\sim$ 10 fs. Since this vibrational lifetime is much shorter than the time between electron tunneling events, $e/I \sim 600$ fs at 100 nA, the excitation process involves only one electron and adatom displacement is linear in current.

Tunneling electrons from the STM provide a well-defined initial excitation source of atomic dimensions which allows the investigation of local and nonlocal effects. We find dramatically different behavior for the different adatoms that make up the Si(111)-(7 × 7) unit cell under the influence of either electron bombardment or tunneling. Although the phenomenon shown here is short lived at higher temperatures, these metastable states may play a significant role in systems or processes involving this surface and the use of an electron beam—even at room temperature. These experiments suggest the need to consider spatially resolved electronic properties which underlie the stability and dynamics of adatom motion and surface chemistry.

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