Tunneling Electron Induced Bromine Hopping on Si(100)-(2 × 1)

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Tunneling electrons from the tip of a scanning tunneling microscope can be used to induce adatom hopping on Br-terminated Si(100)-(2 × 1) at low current and without voltage pulses. Hopping does not occur when electrons tunnel from a sample to a tip. The threshold energy is +0.8 V, and tunneling spectroscopy shows antibonding Si-Br states 0.8 eV above the Fermi level. Electron capture in these states is a necessary condition for hopping, but repulsive adsorbate interactions that lower the activation barrier are also required. Such interactions are strong near saturation for Br but are insufficient when the coverage is low or when Br is replaced by Cl.

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Scanning tunneling microscopy (STM) offers a way to visualize individual atoms and molecules on surfaces. Recently, attention has focused on STM-based manipulation of surface moieties and on their electronic properties in metal junctions [1]. For example, single Xe atoms can be transferred reversibly between an STM tip and a Ni (110) surface [2], high tunneling currents can induce hopping of CO on Cu (111) [3], and CO_2 can be produced by manipulation of CO onto O adsorbed on Ag (110) [4]. These studies emphasized metal surfaces, and all of them required activation by short voltage pulses or high tunneling currents [2–5]. Little attention has been paid to manipulation on semiconductor surfaces [6,7] and, though it has been clear that the local electronic properties must play a key role in excitation processes, there has been no clear indication that low-current, low-energy tunneling electrons might contribute to semiconductor surface modification.

In this paper, we show that electrons tunneling *into* the surface under normal scanning conditions induce migration of covalently bonded Br atoms on Si(100)-(2 × 1). The threshold for manipulation is +0.8 V, corresponding to electron capture in Si-Br antibonding $\sigma*$ levels lying 0.8 eV above the Fermi level. We show that manipulation does not occur when electrons tunnel out of the surface. Moreover, manipulation does not occur if the Br concentration is low or if Cl is substituted for Br. Thus, capture in the antibonding resonance is necessary, but it is not sufficient, and we argue that a second needed component is a strong repulsive interaction between adatoms. To our knowledge, these are the first studies that achieve manipulation without short pulses or high current in the tunneling junction.

The experiments were performed in an ultrahigh vacuum system with a base pressure of 4×10^{-11} Torr [8]. The sample was a boron-doped Si(100) wafer with resistivity 0.01 Ω cm. Clean Si(100) surfaces having initial defect densities below 1% were prepared following procedures reported by Hata *et al.* [9] Thereafter, these surfaces were exposed at room temperature to a flux of Br_2 from an electrochemical cell to accumulate surface concentrations of 0.18, 0.93, and 0.99 monolayer (ML). We also prepared Cl-covered Si(100) surfaces to compare adatom interactions for different halogens. After exposure the samples were heated at 750 K for 10 min to enhance ordering. Filled-state images were then obtained with a very low tunneling current of 30 pA. Under these conditions, the surface structures were stable. Subsequently, manipulation occurred when samples were scanned *once* under positive sample bias so that electrons were emitted from the tip (empty-state imaging) as it moved at 83 nm/s diagonal to the dimer rows. We stress that this is a standard tunneling condition with the feedback loop engaged and no voltage pulse applied to the tunnel junction. After this positive-bias scan, the same surface area was scanned again to obtain a filled-state image so that migration could be quantified. The normalized tunneling conductance, $(dI/dV)/(I/V)$, was obtained for individual sites from measured I-V data. The latter were established with a set point of −2.0 V at 30 pA.

Figure 1 summarizes the key features for Br-Si(100)-(2 × 1). Figure 1(a) is a filled-state image of a nearly saturated surface where one surface dimer with one Br adatom, denoted SiSiBr, appears dark against a background of dimers with two Br adatoms, 2SiBr (sample bias −0.65 V). Si dimer vacancies, DVs, are also dark. In contrast, bare dimers, BD, are manifest as three bright features. This triplet reflects the interaction of the widely expanded π bonding states with Br $4p_y$ orbitals of adjacent Br-occupied dimers [10]. Their characteristic brightness makes it easy to identify bare dimers and to deduce the coverage. Figure 1(b) depicts representatives of surface features. The bias dependence of bare dimer sites is evident in Figs. 1(c) and 1(d) where they are bright at −0.65 V but dark when the tip probes the Br $4p_z$ states at −2.0 V. The appearance of DVs and SiSiBr species [not present in 1(c) and 1(d)] does not change between −0.65 and −2.0 V.

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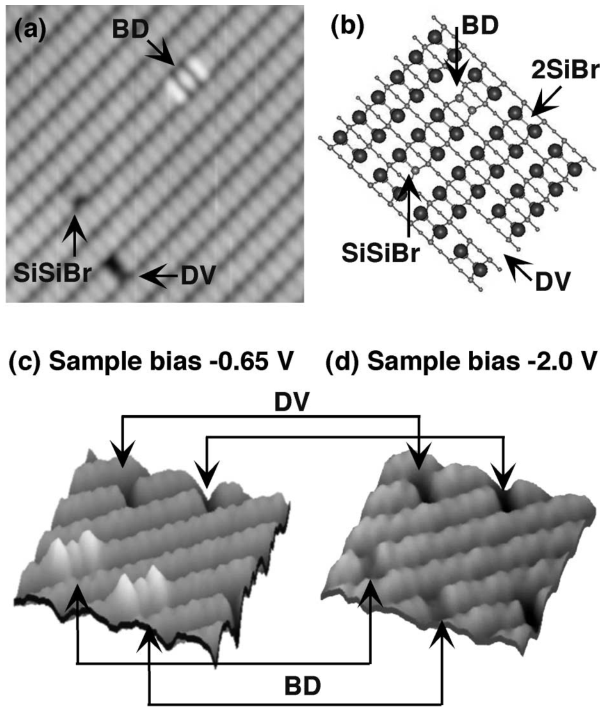

FIG. 1. (a) Filled state image of nearly saturated Br-Si(100)-(2×1) showing a bare dimer, BD, a dimer with one Br adatom, SiSiBr, and a dimer vacancy that appear dark against a background from dimers with two Br adatoms (sample bias -0.65 V, tunneling current 30 pA, 80×80 Å^2). (b) Schematic of a bare dimer, a dimer with one Br adatom, a dimer vacancy, and dimers with two Br adatoms. (c) and (d) are empty-states images with sample biases of -0.65 and -2.0 V. The bare dimer appears as a bright triplet when imaged at -0.65 V; it becomes darker at -2.0 V. The appearance of the dimer vacancy does not change. The image size is 60×60 Å^2.

Figures 2(a)–2(f) make it possible to visualize the effect of tunneling electrons [sample bias -1.0 V for 2(a) and 2(d) and -0.65 V otherwise; current 30 pA; Br coverage 0.99 ML]. At -1.0 V, the triplet features are slightly darker than when imaged at -0.65 V. Images 2(d)–2(f) were obtained on the same areas as 2(a)–2(c) after scanning *once* at a sample bias of $+1.5$ V (current 30 pA). Comparison demonstrates that the bare dimers in 2(a) moved along the dimer row. Arrow I indicates movement by three units (at least six Br hopping events), as depicted in 2(g), and arrow II points to a site that moved by eight units [11]. Whereas electrons from the tip induced tandem Br migration in most cases, they could also induce single atom migration. This is evident in 2(e) and 2(f) where the bare dimers in 2(b) and 2(c) were replaced by SiSiBr features that were imaged as single dark spots. Arrows identify places where this occurred, and the initial and final configurations are illustrated in 2(g) for events III and IV. At least three Br hops would be necessary to account for the changes in features III, and four must occur for feature IV. Conversion of feature V would require displacement of at least ten Br atoms as the Br vacancy moved along the dimer row. Br adatoms moved randomly along the row whereas hopping across dimer rows was not observed [12].

Herrmann and Boland [13] recently reported STM images obtained at 725 K where some dimer-sized features appeared to be bright on one half and dark on the other, like the dark half-dimers produced in Figs. 2(e) and 2(f) by electron tunneling. Their STM images were taken with a tip bias of -1.7 V, where electrons tunneled into the surface. They argued that dark half-dimers reflected units with a missing Si *atom* and two Br adatoms on the unpaired Si atom, $SiBr_2$. Thus, the final configuration of III in Fig. 2(g) would have two Si vacancies and two $SiBr_2$ units instead two SiSiBr units. To confirm that the features were indeed Br adatom vacancies on a dimer, we imaged surfaces as a function of Br concentration, finding that the density of dark half-dimers decreased with Br_2 exposure [14]. We conclude that they are not Si vacancies [15].

The probability that a Br atom would hop can be determined by comparing images such as Fig. 2 obtained before and after electron exposure (positive-bias tunneling). Figure 3(a) summarizes the dependence of the hop probability on applied voltage, obtained by analyzing about 200 bare dimer sites for each point. The probability indicates a steady increase with sample voltage. This suggests that there is only one process for Br hopping. The yield can be determined from the total number of events and the total number of incident electrons [16]. It increased monotonically from 3.5×10^{-11} to 4.2×10^{-10} atom/electron from $V = 1.0$ to 1.6 V for a surface with 0.93 ML of Br. This hopping yield is similar to the yield of H desorption induced by high tunneling currents from H-terminated Si(100) [6].

The dependence of hopping on bias voltage can reflect either an energy dependence of the excitation cross section or the changing electric field as the moving tip couples with the dipole moment induced by the adatom [17]. The electric field increases as the separation between the tip and sample decreases. In contrast, the field does not vary significantly with tunneling current because the separation depends logarithmically on current. Therefore, if the field effect is negligible, then the number of events should be proportional to the number of electrons. To determine whether this were true, we varied the current while maintaining a fixed bias voltage. Figure 3(b) shows that the hopping probability increased linearly with tunneling current. We conclude that the hopping mechanism is related to the excitation cross section.

The question remains as to the physical origin of atom hopping. In principle, energetic electrons can either be captured in a surface resonance or they can induce electronic excitations. Though neither had been connected with atom manipulation, either can cause atom displacement via a Frank-Condon process. To determine whether Br migration on Si(100) is related to a specific electronic state, we performed local conductance measurements. Figure 4 shows normalized dI/dV spectra for

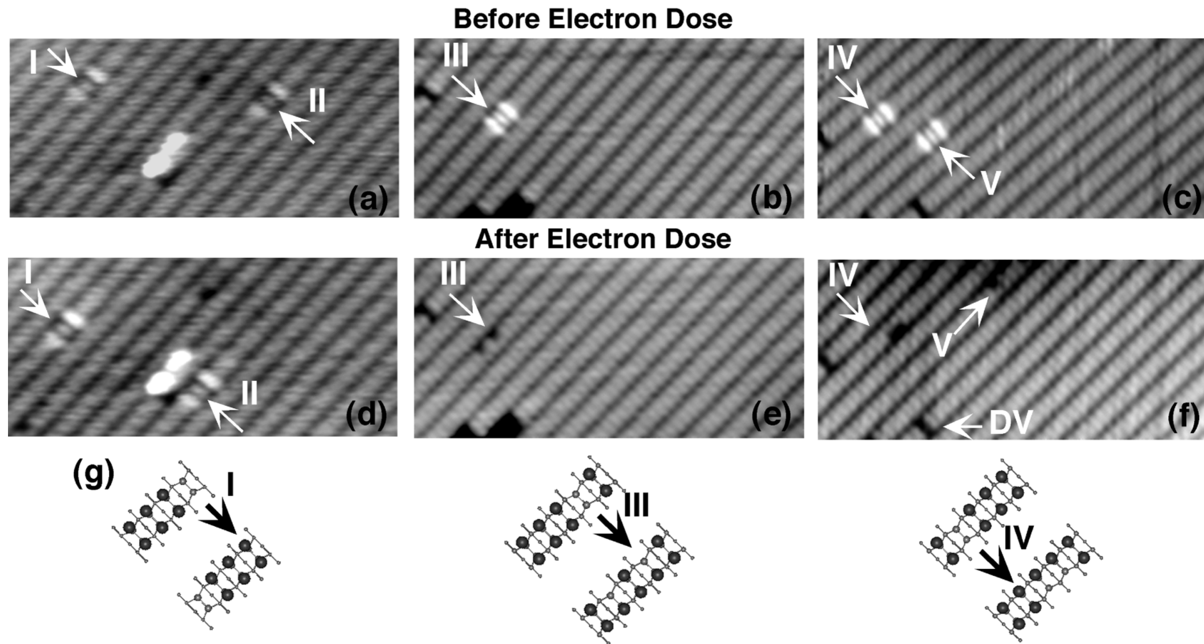

FIG. 2. Filled state images for Br-Si(100) with a coverage of 0.99 ML. Images (a)–(c) were obtained before an electron irradiation event that involved a single scan with positive sample bias; (d)–(f) show the same areas after irradiation. Sample bias −0.65 V except (a) and (d) where it was −1.0 V, tunneling current 30 pA, size 130×60 Å^2. (g) Schematic of the initial and final Br configurations.

Si(100)-(2×1) over bare dimers and over dimers with Br adatoms. For comparison, the distribution of electronic states over dimers with Cl is also shown. From Fig. 4, halogen adsorption eliminates the clean surface π and $\pi*$ states at −0.5 and +0.5 eV, consistent with previous results [19–21], and introduces σ states at −1.6 eV and $\sigma*$ states at 0.8 eV for Si-Br, and $\sigma*$ states at 1.6 eV for Si-Cl. From Fig. 3, the separation between bonding and antibonding states of Si-Br is 2.4 eV and σ-$\sigma*$ transitions cannot be excited by our low-energy tunneling electrons. However, the hopping threshold from Fig. 3(a) is 0.8 V for Si-Br, and Fig. 4 confirms that electron capture in the Si-Br antibonding states is a necessary condition for atom migration. Capture results in a repulsive potential that

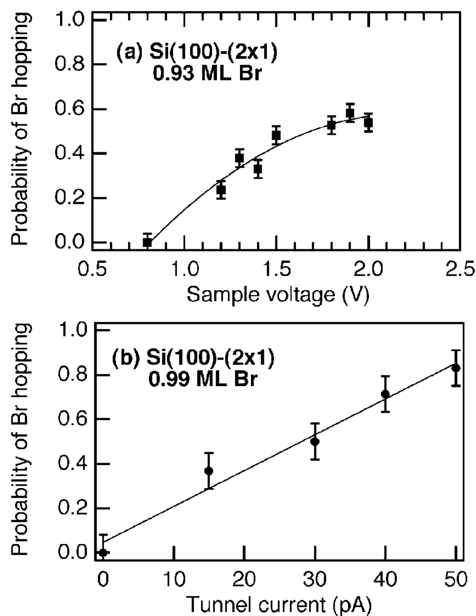

FIG. 3. (a) Probability of Br hopping as a function of sample bias with a tunneling current of 30 pA showing an onset when tunneling into the $\sigma*$ states becomes possible. (b) Br hopping yield as a function of tunneling current with 1.0 V sample bias demonstrating that hopping is related to the excitation cross section rather than a field effect.

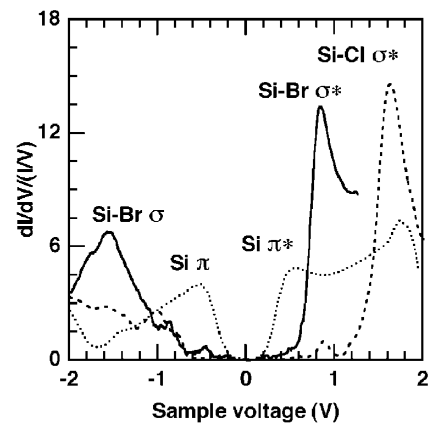

FIG. 4. Averaged tunneling spectra on a Si dimer and on dimers with Br and Cl adatoms. The tip was established with a set point of −2.0 V at 30 pA. The π and $\pi*$ surface states of Si are replaced by Si-Br σ and $\sigma*$ states at −1.6 and 0.8 eV. The Si-Cl $\sigma*$ states appeared at 1.6 eV, but the σ states are calculated to lie at ~ -2.5 eV [18].

lowers the hopping barrier for the halogen atom. Electrons injected at energies above the $\sigma*$ resonance can scatter inelastically in unoccupied Si bulk states near the surface and still can be captured. As the tunneling current increases, the number of electrons that can reach these states increases linearly, as observed in Fig. 3(b). This linear dependence on current suggests that capture involves one event rather than multiple excitations. Low-energy tunneling electrons not only induce local excitation of an individual adatom but also scatter in an extended area because the mean free path of $\sim$2 eV electrons is more than 100 Å. This is evident in Fig. 2 where multiple hopping occurs instead of single hopping.

Our images show that tunneling induced hopping occurs for Br but not for Cl, even though capture by $\sigma*$ levels should occur for both. The difference can be rationalized by a bond strength [22] and a combination of electrostatic and steric repulsion effects [23]. Recently, Herrmann *et al.* [24] calculated the steric repulsive energy of Br for intra- and interdimer rows. Further, calculations by Aizawa *et al.* [18] showed that the effects of surface stress due to these repulsive interactions are greater for Br than for Cl. To gauge the importance of these repulsive contributions, we prepared a Br-Si(100) surface with only 0.18 ML coverage. No adatom hopping was observed when the surface was scanned with a sample bias up to 2.0 V at tunneling current of 60 pA. This indicates that repulsion at high Br coverage serves to lower the activation energy and electron capture in the $\sigma*$ level is sufficient to active efficient hopping.

In this paper, we have demonstrated that atomic manipulation can be accomplished through a combination of electron capture in long-lived resonance levels and inherent adsorbate repulsive interactions. Although we cannot control the direction and the length of diffusion, these results shed new light on the essence of atomic scale manipulation.

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