

LETTERS

Probing Repulsive Interactions on the Si(100)-2 × 1 Surface by Local Tip-Induced Excitation

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Received: January 11, 1999; In Final Form: March 22, 1999

The chemisorption of a series of diatomic molecules on the Si(100) surface was investigated using scanning tunneling microscopy, STM. For the molecules studied, dissociative chemisorption occurs and the adatoms produced are found at two types of surface sites. The stability of these sites is studied by exciting the adsorbate system via a tip voltage pulse. As a result of this excitation the adatoms undergo a rearrangement that depends both on the nature of the adspecies and on the site being stimulated. The directionality and spatial extent of these rearrangements are also site dependent. This behavior is attributed to the presence of anisotropic site-dependent repulsive interactions on the Si(100) surface.

Following its initial discovery,¹ scanning tunneling microscopy (STM) was primarily used to characterize the local structure and electronic properties of surfaces. In recent years, there has been considerable interest in developing STM as a tool to perturb or modify surfaces.² There is now evidence for a broad range of interactions between the STM probe tip and the surface, interactions that have been successfully exploited as a means of surface manipulation and modification.^{3–7} When combined, these perturbative and nonperturbative modes of STM operation provide a more complete picture of surface chemistry and physics. Here, we describe a new application in which STM is used to locally stimulate the surface and to observe and analyze the structural transformations that result.

In this letter, we investigate the presence of repulsive interactions on the Si(100) surface following the chemisorption of bromine, iodine, and sulfur molecules. These molecules dissociatively chemisorb on the surface and are found predominantly in two distinct configurations involving adjacent surface sites. After excitation by the STM probe, each type of adatom configuration undergoes a range of specific and systematic rearrangements. These rearrangements exhibit an excitation

threshold voltage that is dependent on the kind of adatom. Moreover, the spatial extent and direction of the rearrangements are site dependent. This behavior is shown to originate from a built-in repulsive interaction between adatoms at adjacent surface sites on the Si(100) surface.

The experiments described here were performed in a home-built ion-pumped ultrahigh vacuum chamber with a base pressure of 5×10^{-11} Torr. The clean Si(100) surface was prepared by annealing to temperatures of ~ 1400 K to remove the native oxide. All images were recorded in constant current mode at room temperature. The images shown are of empty states with an applied tip bias of -1 V. The halogen sources used in these studies are electrochemical cells with heated silver halide pellets.⁸ The sulfur source is a molybdenite, MoS₂, flake wrapped with a tungsten filament and produces S₂.⁹

Diatomic molecules frequently dissociate upon chemisorption on the Si(100)-2 × 1 surface. For halogens, evidence for dissociation is provided by the presence of a strong silicon–halogen loss peak in HREELS spectra.¹⁰ To our knowledge, the adsorption products in the case of molecular S₂ have not been previously reported. However, based on experiments

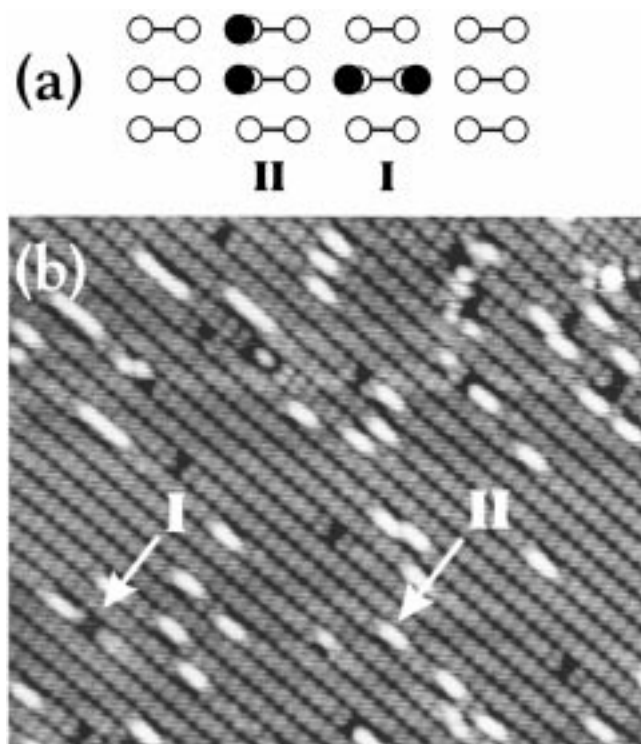


Figure 1. The chemisorption sites for diatomic molecules on the Si(100)- 2×1 surface. In schematic (a) the dimer rows are running vertically with the white and black balls representing the Si atoms and adsorbates, respectively. Both types of sites are illustrated in the schematic. The STM image ($22 \times 18 \text{ nm}^2$) in (b) shows iodine adsorption on Si(100) at the two types of sites. The image was obtained with a tip bias voltage of -1 V . The bright bean-shaped features are the dangling bonds at type II sites and the dark dimers are type I sites.

described here and elsewhere, S_2 dissociation on Si(100) is similar to that of a halogen molecule.¹¹ Dissociative chemisorption of these diatomic molecules occurs in two ways. At room temperature dissociation typically occurs at the same side of adjacent dimers of the same row, a configuration we shall

refer to as a type II site. Even though this configuration disrupts the π bonds on two dimers, it is favored at low temperature over adsorption on a single dimer, a type I site.¹² Figure 1(a) shows a ball-and-stick model of these two configurations. Both sites are evident in Figure 1(b), an image of dissociatively chemisorbed I_2 on Si(100), where the bright bean-shaped features are the dangling bonds at type II sites and the dark well-resolved dimers are type I sites.¹²

The stability of type I and type II sites was investigated using the STM probe tip as an excitation source. After applying a large negative voltage pulse to the tip, the bean-shaped type II features in Figure 2(a) are transformed into the doubletlike structures in Figure 2(b). This doublet structure is attributed to two adatoms, in this case bromine, on next nearest neighbor dimers. Close inspection shows that only one of the two adatoms actually moves and that both adatoms remain on the surface under the pulsing conditions described here. Figure 2(c) shows a ball-and-stick model of this process. Tip induced rearrangements of type II sites are specific at negative voltage pulses lower than -3.0 V ; not only are the two bromine adatoms always on the same side of the dimer row, they are always separated by just a single dimer unit, i.e., the excitation products are monodispersed. Larger negative voltage pulses produce separations that are greater than a single dimer. Additionally, the dimer rows in which the transformations occur become extensively buckled as this next nearest neighbor configuration pins and reinforces the anticorrelated dimer buckling that is intrinsic to the clean Si(100) surface.¹³

The behavior of type I sites is markedly different from that of type II sites. Figure 3(a) and (b) show an example of a typical probe-induced rearrangement of bromine adatoms at a type I site. After pulsing the tip, the initially paired configuration is now split into separate adatoms that are located on different dimer rows. This is schematically shown in Figure 3(c). In other cases, the separated adatoms are found in the same row, oftentimes on opposite sides of the row. Similar experiments were performed at type I and II sites containing iodine and sulfur adatoms, with identical results.

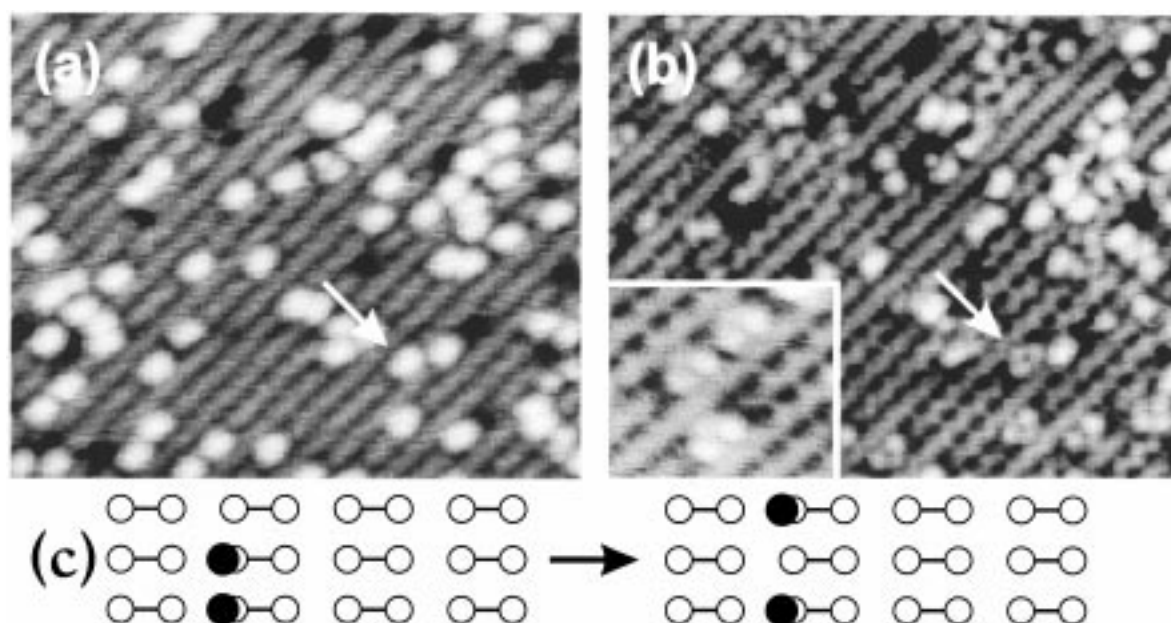


Figure 2. Dissociation and rearrangement of bromine at type II sites on the Si(100) surface. These $18 \times 15 \text{ nm}^2$ images were obtained using a bias voltage of -1 V applied to the probe tip. The bean-shaped type II site marked in (a) is changed into the doublet feature, Il_m , in (b) after an applied tip pulse of -3.3 V . This feature is produced when one of the atoms shifts over to the next dimer in the row (c). The inset is a magnified view of the type II separation and the dimer row buckling that it produces. The schematic drawing also shows the rearrangement of type II sites.

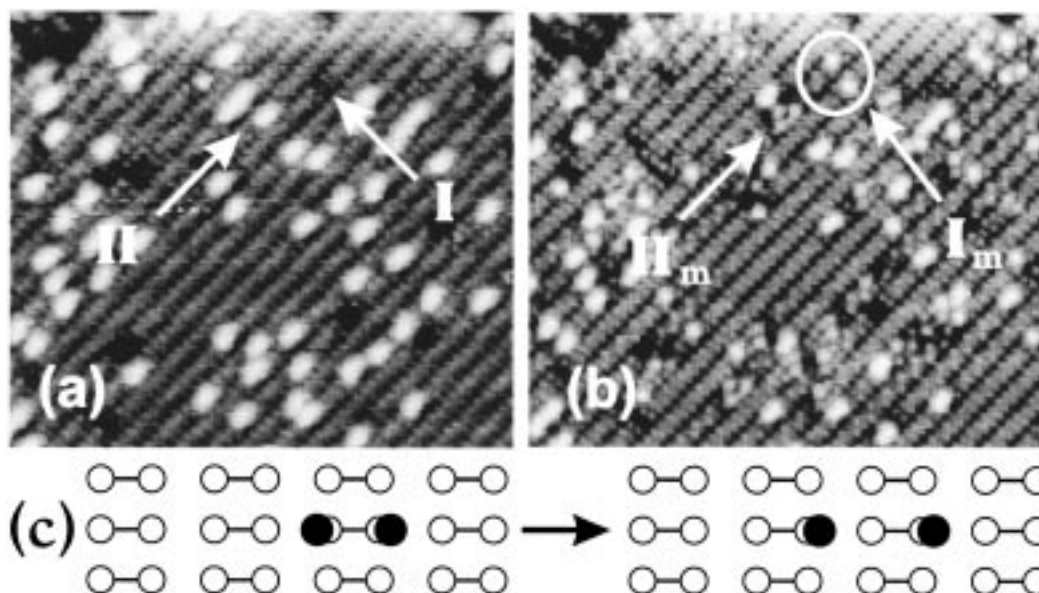


Figure 3. Dissociation and rearrangement of bromine at type I sites compared to type II sites. These $17 \times 15 \text{ nm}^2$ images were obtained with a tip bias voltage of -1 V . The dark dimer type I site identified in (a) is transformed into two separate individual adatoms identified in (b) following a tip pulse of -3.2 V . A rearrangement at a type II site is also labeled for comparison. This type I rearrangement is clearly seen in the schematic, (c), below the image.

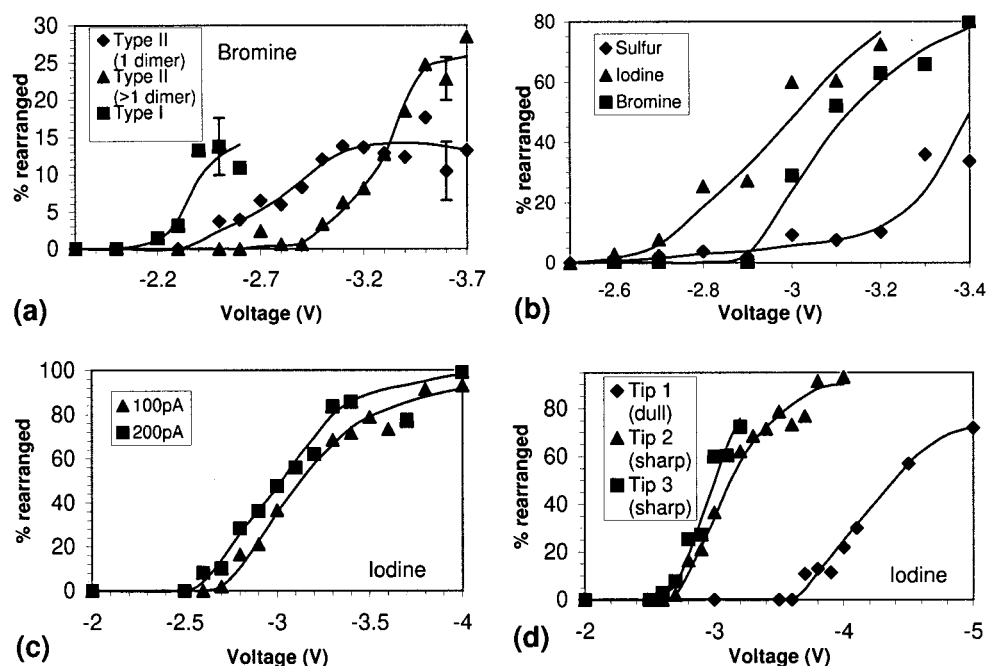


Figure 4. The efficiency of rearrangement as a function of tip pulse voltage. (a) compares different types of sites. Type I sites have the lowest excitation threshold voltage, while type II sites exhibit two higher thresholds, each at higher voltages. The lower threshold corresponds to separations for which the adatoms are one dimer apart. The second threshold is for larger separations. (b) shows the dependence of the threshold voltage on the type of adatom. Iodine exhibits the lowest threshold and sulfur the highest. (c) reveals how the threshold varies as the set point current is changed for a given tip. (d) shows how the threshold for I_2 rearrangement at type II sites can vary from tip to tip. The lines in (a)–(d) were drawn solely as guides to the eye. Typical error bars are also shown.

To further investigate this phenomenon, we studied the behavior of populations of type I and II sites that were subject to excitation by the STM probe tip. These experiments were conducted by freezing the probe tip's position using a sample-and-hold circuit and then pulsing the voltage applied to the tip from the scanning value of -1 V to a larger negative value. Rather than pursuing individual sites, voltage pulses (3) were applied in a grid every 1.2 nm over a $24 \times 24 \text{ nm}^2$ area on the surface.¹⁴ Each pulse was 2 ms in duration with a rise and fall time of $115 \mu\text{s}$. This method reduced problems associated with drift and piezo creep and produced a large population of excited

sites yielding improved counting statistics. A drawback of the method is that the position of the tip is not precisely controlled, so there is some error in the critical excitation voltage or field required for rearrangement.

The results obtained using this procedure are summarized in Figure 4, which shows the fraction of rearranged sites as a function of tip-pulse voltage for a variety of conditions. Each curve shows a low voltage region where the additional energy provided by the tip pulse has no effect on the surface sites. With increasingly higher negative voltage, there is a threshold region where the rearrangement efficiency begins to increase until

finally a saturation value is achieved. Figure 4(a) shows that the excitation threshold for rearrangement of type I sites is significantly less than that of type II sites. Moreover, the rearrangement of type II sites shows two distinct thresholds. The lower voltage threshold corresponds to rearrangements involving a separation of a single dimer unit. Larger separations require a higher negative voltage pulse applied to the tip.

Each adsorbate studied exhibited a different excitation threshold voltage for rearrangement. Figure 4(b) shows the results for a series of pulse experiments conducted at type II sites using iodine, bromine, and sulfur adatoms. The same probe tip and tunneling current (100 pA) were used throughout. Iodine required the lowest voltage pulse to separate (~ -2.7 V) while bromine had a threshold voltage of ~ -2.9 V. Sulfur required the highest voltage (~ -3.2 V) and exhibited a slower "turn on". This trend can be attributed to the strength of the bond between the adatom and the surface Si atom. Even though complete bond cleavage (i.e., desorption) does not occur, it is well established that the energy required for diffusion scales with the bond energy.¹⁵

Although it is unclear how the voltage pulse perturbs the adsorbate system, there are several possible mechanisms that might explain these observations. The most obvious is the possible role of tip-induced heating in which electrons locally heat the surface after being accelerated through the voltage drop across the tunneling gap. This mechanism is consistent with the observation that positive voltage pulses up to +5 V fail to induce rearrangements of any kind. To investigate this heating mechanism, we varied the tunneling current while maintaining the same set point voltage. Figure 4(c) shows a series of iodine type II rearrangements obtained using set point tunneling currents of 100 pA and 200 pA. Although, there is a slight shift in the threshold to smaller negative voltages at higher current, there is little discernible change in the saturation value. These experiments are not consistent with tip-induced heating. Doubling the set point current automatically doubles the power input but does not produce the shift in the threshold to half the original voltage value that would be expected of a simple Joule heating mechanism. Moreover, at higher set point currents the tip is closer to the surface so that the current density and heating effects should be disproportionately larger, which again is inconsistent with Figure 4(c).

Other possibilities include electron attachment and field-induced effects. The former involves a process whereby the bound surface–adatom system interacts with an electron and is excited into a repulsive antibonding excited state.¹⁶ The threshold for this process is determined by the vertical excitation energy (E_1) from bound ground state with a maximally extended bond length to the repulsive excited state. The threshold is thus expected to be significantly larger than the binding energy (see Figure 5). However, the thresholds observed in the present study are rather low (2.5–3.0 eV) compared to the binding energies (about 3 eV for the silicon–iodine system), suggesting that vertical excitation to a repulsive excited state does not occur in this case.

Another possible electron attachment mechanism involves excitation to a bound, low-lying ionic excited state, followed by a curve-cross to the ground-state surface. In this case, the excitation energy, labeled E_2 in Figure 5, is lower than the binding energy. This mechanism does not induce bond cleavage (desorption) but rather leaves the silicon–adatom bond vibrationally excited. Although the absence of desorption and the requirement for electron injection from the tip are both consistent

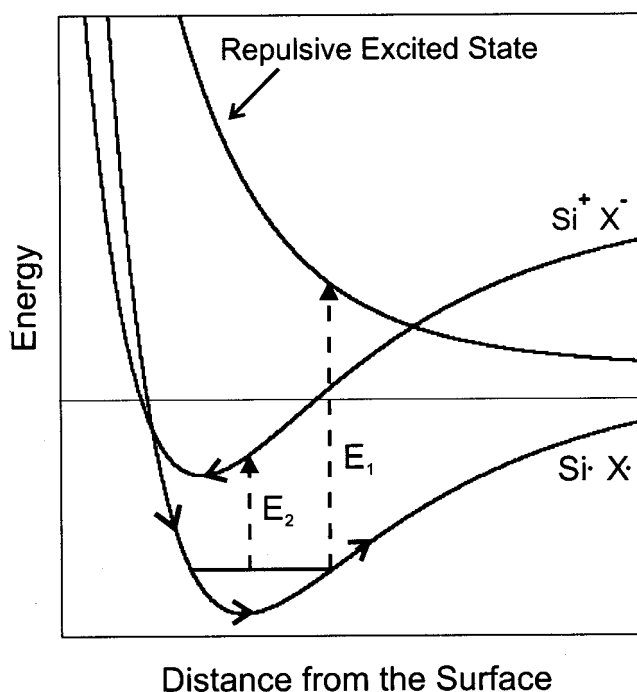


Figure 5. Schematic potential energy surfaces of the ground and excited states for a generic adsorbate–surface system. The excited states include a total repulsive antibonding state and a bound ionic state. Note the relative differences between the threshold energies, E_1 and E_2 , for electron attachment to the excited states and the binding energy. The threshold energy is determined by the maximally extended bond length on the ground-state potential energy surface.

with experiment, we have no direct evidence for the existence of such bound, low-lying ionic excited states.

Additional insight into this excitation mechanism can be gained from a study of how the rearrangement probability is influenced by the field between the probe tip and the surface. Evidence for the possible role of the electric field is seen in Figure 4(d), where three distinct curves are obtained for iodine rearrangement at type II sites using three different probe tips. Whereas it is well established that large fields can induce desorption, the role of the electric field is not clear in the present case. For instance, we cannot rule out the presence of adsorbates or contaminants on the probe tips that cause the actual voltage drop across the gap to be less than the applied voltage. The direction of the applied field is such that the surface–adatom bond is actually *strengthened* during the voltage pulse.¹⁷ This is a consequence of the fact that, under zero-field conditions, the valence levels of the adatoms in this study are lower in energy than those of the surface silicon atoms. For these reasons STM field-induced desorption has been reported only when a positive voltage is applied to the probe tip,^{18,19} a condition which does *not* induce any adatom rearrangement in the present system.

Whatever the exact origin of the excitation mechanism, the present data are consistent with the following picture. During an excitation pulse the adatom binding interaction with the surface is reduced so that the adatom becomes more sensitive to its immediate local environment and, in particular, to local interactions that are present at different surface sites. In the absence of such local forces the adatom relaxes back to the surface, consistent with our observation that single, isolated adatoms are unaffected by a voltage pulse. Since there is no evidence for adatom removal, bond weakening rather than complete desorption occurs. This is consistent with an indirect electron attachment mechanism via a low-lying ionic excited state. Under appropriate tip-pulse conditions, bond weakening

occurs to such an extent that these local interactions overcome the remaining binding interaction with the surface, leading to the observed rearrangements.

In this picture, tip-induced adatom rearrangements provide insight into local interactions present at different surface sites. In particular, for the Si(100) surface there would appear to be an intrinsic repulsive interaction between adatoms at type I and II sites. Based on the different behaviors of adatoms at these sites, these interactions have different strengths. Since the adatoms studied here are each more electronegative than Si, this interaction may be due to an electrostatic repulsion between local bond dipoles. As a result of this repulsion, type I and II sites are both under compressive stress. This stress is uniaxially directed along the line between the adatoms and is then responsible for the directionality of the separation following excitation. Since adatoms are closer at type I sites, the electrostatic repulsions are greater²⁰ and, in agreement with our data, exhibit a lower threshold. We note that this occurs despite the fact that type I rearrangements involve motion between dimer rows and involve a larger barrier to diffusion compared to separations in the same row, i.e., at type II sites.²¹ Other possible interactions exist, such as chemisorption-induced pinning of the local $c(4 \times 2)$ surface structure of the clean Si(100) surface, but this is unlikely to reproduce the directionality reported here.

In this letter we have demonstrated that the STM tip can be used to excite and probe local interactions between adatoms on the Si(100) surface. Initial excitation may occur via an electron attachment mechanism, but the specific details of the subsequent rearrangement are controlled by local adatom interactions on the surface. In particular, we have shown that adatoms at different binding sites exhibit different thresholds for rearrangement, each with its own specific directional dependence. Moreover, different types of adatoms exhibit different thresh-

olds. Given these results, this may represent a useful technique to study interactions on surfaces, particularly if it proves possible to better control the local field of the STM probe.

Acknowledgment. The authors acknowledge the National Science Foundation for their financial support under contracts DMR9509790 and DMR9413999.

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