Reversible Rotation of Antimony Dimers on the Silicon (001) Surface with a Scanning Tunneling Microscope

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The scanning tunneling microscope (STM) was used to control the configuration of antimony clusters on the (001) surface of silicon. In particular, the STM tip induced a reversible rotation between two orthogonal orientations of individual antimony dimers on the surface. This simple rotation can be explained by an atomic-scale torque exerted on the antimony dimers by the STM tip. The reversibility of this process could provide a basis for making atomic-scale memory cells.

The STM has been widely used to manipulate a variety of atomic or molecular adsorbates on solid surfaces. Examples of recent achievements include displacing atoms on the surface (*1*, *2*), transferring atoms between the tip and the surface (*3*–*5*), desorbing atoms (*6*, *7*), and fragmenting molecules (*8*). It is of particular interest to induce reversible transitions between different states of individual molecules without fragmentation or other damage because a reversible process could be used to make logic or memory devices with atomic or molecular dimensions. I report here STM tip–induced conversions between different configurations of Sb clusters on Si(001).

Four distinct types of precursors can be converted to the final state of chemisorption of Sb_4 on Si(001) with the STM tip. Although most conversions move irreversibly toward the lowest energy state, a reversible conversion can be induced between the final state and one of the precursor states. This reversible conversion is simply a rotation by 90° of individual Sb dimers on Si(001), which can be explained by an atomic-scale torque exerted on a single Sb dimer by the STM tip. The relative stability of Sb dimers in two orthogonal orientations can be determined.

I chose Sb_4 on Si(001) because of its relative simplicity as a model system. A study of the thermal stabilities of Sb_4 precursors on Si(001) has been reported (*9*) and the details of the experimental setup have been described (*10*). In a typical experiment, "observation" scans with low bias voltages were made before and after each "conversion" scan, which was taken with higher bias voltages to induce structural changes in the Sb clusters. Except for the bias voltages, all other parameters were the same for both types of scans. All scans were taken at room temperature.

Clean Si(001) forms a (2×1) reconstruction in which every two Si atoms in the top layer bond together to form a dimer (*11*). A linear chain of these dimers in the direction perpendicular to the dimer bonds is called a dimer row. In the STM images, the dimers appear as small rectangles with the dimer bonds parallel to their long sides. In some cases the tip was less sharp and individual dimers were not resolved; only dimer rows were seen.

Upon deposition of a small fraction, for example, ~2%, of a monolayer of Sb_4 on Si(001), five distinct types of Sb clusters were observed to coexist (Fig. 1). Because the optimal resolution was obtained with different bias voltages for different types of clusters, two images obtained with two different biases are shown in Fig. 1, together with schematic models illustrating their atomic configurations. The final state cluster (labeled E) consists of a pair of Sb dimers with the dimer bonds perpendicular to the Si dimer bonds (hence parallel to the dimer rows) in the substrate.

The four types of precursors have very different structures. Type B consists of two dimers, but, unlike the final state cluster, the dimer bond connecting the two atoms in each dimer is parallel to the Si dimer bonds (hence perpendicular to the dimer rows) in the substrate. They are called "rotated dimers." Type A, called "ball" clusters, has a round shape without any resolvable internal feature. It appears higher (brighter in the STM images) than the other clusters because it may have a more or less three-dimensional structure like the free tetrahedral Sb_4 molecule. The other two types of clusters look similar: each cluster has two pronounced peaks and two weak ones in between. I call the one with the long axis along the surface dimer rows a "dumbbell" (C) and the one with the long axis perpendicular to the surface dimer rows a "rotated dumbbell" (D).

At low bias voltages (~1.0 V), all the precursors were both structurally stable and spatially immobile. At higher bias voltages (~3.0 V, both polarities), however, all the types of precursor clusters could be induced to convert to the final state, sometimes going through one or two of the other states. The STM tip–induced conversions of three ball precursors (A) are shown in Fig. 2. Examples of the multistep conversion of the other three types of precursors (B, C, and D) are shown in Fig. 3.

From both the above and the thermal annealing experiments (*9*), I conclude that the type E cluster is the final state for the dissociative chemisorption of Sb_4 on Si(001) and that the order of relative stabilities of the five cluster types, from the least to the most stable, is as follows: ball (A), dumbbell (C) or rotated dumbbell (D)

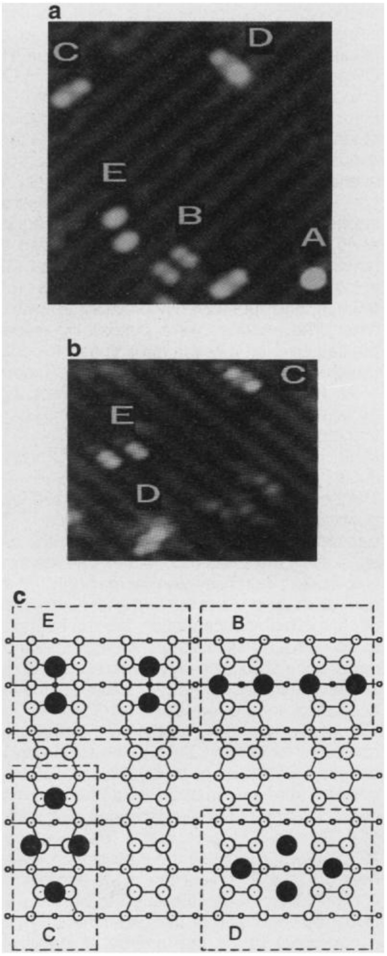

Fig. 1. STM images of Sb_4 clusters on Si(001) deposited at room temperature. The images in (a) and (b) were taken with a tunneling current of 0.2 nA. (**a**) Five types of clusters: one ball (A), one set of rotated dimers (B), one dumbbell (C), one rotated dumbbell (D), and one final state cluster (E). The image area is 70 Å by 80 Å. The dimer rows in the substrate run diagonally across the image. For a tip bias of +1.0 V, four atoms are clearly resolvable in B clusters. (**b**) With a bias of +0.7 V, four atoms in each of the three types (C, D, and E) of clusters can be seen. The image area is 70 Å by 60 Å. (**c**) Schematic models of four types of clusters. Filled circles are Sb atoms, and the largest open circles are the top-layer Si atoms.

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(*12*), rotated dimer (B), and the final state (E). Between any two states there is an energy barrier that prevents a conversion at room temperature in the absence of the STM tip.

Interestingly, a dimer can be converted back and forth between the rotated state (B) and the final state (E), even though all other conversions are irreversibly toward the more stable states. The conversion of a dimer from the final state (E) to a rotated state (B) and then back to E again is shown in Fig. 4. It was more difficult to convert a final state dimer to a rotated dimer than vice versa. I estimate that, at 3.0-V bias, the "reverse" conversion from E to B is less frequent by a factor of 1 in 5 than the "forward" conversion from B to E. It typically takes one high bias scan to convert a rotated dimer to the final state, but it takes an average of five scans with the same parameters to reverse it.

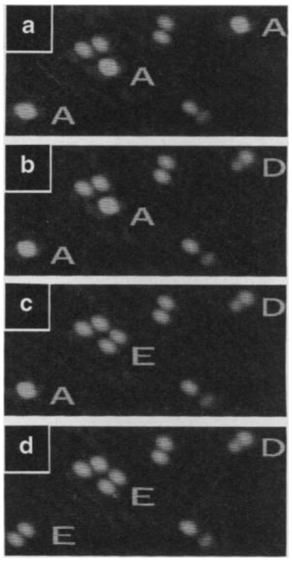

Fig. 2. The STM tip–activated conversions of three ball precursors. All four panels are observation scans (+1.0 V) sandwiched by three conversion scans (+3.0 V), which are not shown. At the end, two balls (A) convert to the final state cluster (E), while the other ball is converted to a rotated dumbbell (D). The tunneling current is 0.4 nA.

The conversion between B and E states is simply a rotation of an Sb dimer between two orthogonal orientations (see Fig. 1c), with the Sb dimer bond either parallel or perpendicular to the Si dimer bonds in the substrate. When the STM tip comes close to a dimer, it exerts a torque on the dimer if the forces on the two atoms are not equal. If this torque is large enough, the dimer can overcome an energy barrier and rotate to another orientation. Because a dimer in the final state (E) has lower energy than a dimer in the B state, the energy barrier for the forward conversion from B to E is smaller than that for the reverse conversion from E to B. This explains why it is relatively easier to convert B to E than vice versa. After a reverse conversion from E to B, the rotated dimer is trapped by the energy barrier that it cannot overcome at room temperature.

The equilibrium configuration of dimers formed by group III or group V atoms on Si(001) might have the dimer bond parallel to that of the Si substrate (B state) (*13*). This result indicates that, although such is not the case for Sb dimers on Si(001), the energy difference between the two dimer orientations is nevertheless not very large so that the reversible conversion can occur.

On the basis of the above speculative scenario, one can imagine that if the forces exerted by the STM tip on the two atoms of a dimer are equal, the dimer will tend to move without rotation. Indeed, displacements of both E and B dimers are frequently induced by the STM tip. A series of displacement events is shown in Fig. 5, in which the two rotated dimers are dragged closer by one lattice site after each high bias scan and eventually become nearest neighbors.

On the basis of these observations, let us examine the possible origin of the force between the STM tip and the Sb atoms. Because both positive and negative biases of the same magnitude can induce conversions, neither a net charge nor an initial dipole on the Sb clusters is responsible. I believe that the most likely cause is the polarizability (*2*) of the Sb clusters. An external electric field can polarize a cluster by driving its positive and negative charges apart to produce a dipole moment. This dipole moment in turn interacts with the field to lower the energy by an amount E, given by (*14, 15*)

$$E = -\frac{1}{2}\alpha F^2$$

where F is the strength of the electric field and α is the polarizability of the molecule. In the STM, the electric field is localized in the tunneling junction with a lateral di-

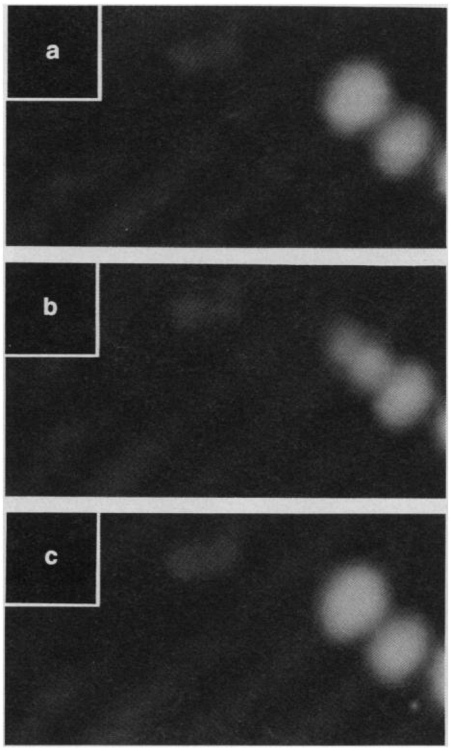

Fig. 4. Reversible rotations (in the sequence **a** through **c**) of a dimer between two orthogonal orientations, B and E. The bias voltage is 1.0 V and the tunneling current is 0.4 nA. The conversion scans are taken at 3.0 V.

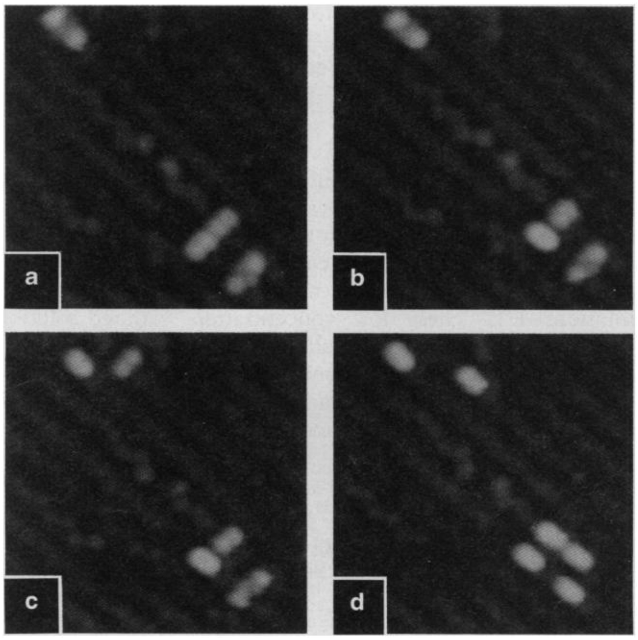

Fig. 3. STM tip–activated conversion of three types (B, C, and D) of Sb_4 precursors to the final state. All four panels are observation scans taken with a tip bias of +1.0 V, which does not cause any structural changes. The conversion scans are taken between observations scans at +3.0 V. The tunneling current is 0.4 nA. The time sequence of the scans is (**a**) to (**d**).

mension that is about the same as the tip-to-surface distance. The strong lateral gradient in the electric field tends to pull the atoms to the area under the tip (*2*). This is the origin of the force between the STM tip and the Sb atoms.

As a further test of the above explanation, let us estimate the energies involved. By assuming a typical polarizability of the order of 10 Å^3 for the Sb atoms (*16*) and a strength for the electric field of 0.5 V/Å, we obtain an energy decrease of the order of ~0.1 eV due to the STM tip. This value is of the same order of magnitude as typical energy barriers for atomic motion on a solid surface, in support of the above explanation based on the field polarization effect (*17*).

The reversible rotation of the Sb dimers by the STM tip exhibits the features of a memory cell, in which the two orientations of each dimer represent "0" and "1," respectively. With improved control and stability of the STM tip position, it may be possible to move the Sb dimers to form, for instance, a linear chain of "bits" and to "switch" any of them by voltage pulses. The value stored in these nonvolatile memory cells can be read out by the same STM tip. Because the speed of read-write access is determined by the slow scanning speed of the STM, this type of memory device may be limited to archival memory. The density of this memory device is significantly higher than that of the current devices, because the size of each bit is only several angstroms.

Compared to other possible ways of making atomic-scale memories, dimer rotation offers an advantage in terms of reliability because the rotation process is gentle and the chance for damaging either the tip or the surface is low. The fact that the dimer orientations are stable at room temperature provides a practical advantage in operation.

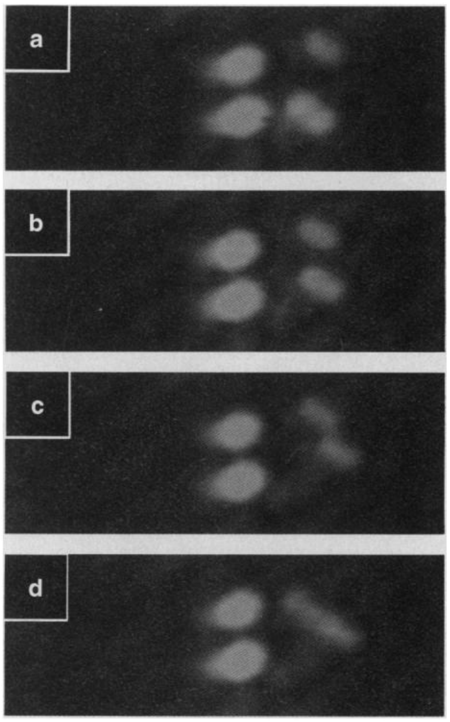

Fig. 5. The STM tip–induced displacements of two rotated dimers (in the sequence **a** through **d**). The two rotated dimers on the right move toward each other step by step until they become nearest neighbors. The two final state dimers on the left do not move.

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17. To convert the other three types of precursors (A, C, and D), the tip first needs to break them into dimers by exerting unequal forces on the four atoms in each cluster and then must rotate type B dimers into the final state.
18. I thank R. Walkup, J. Demuth, P. Avouris, D. Newns, and T. Jung for valuable discussion and assistance.

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Multiple Ion Association in Supercritical Aqueous Solutions of Single Electrolytes

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Solute speciation in supercritical aqueous alkali metal halide solutions plays an important role in various industrial and natural processes, for example, corrosion of metals, solvent extraction, crystal growth, metamorphism, and the formation of hydrothermal ore deposits. To better characterize such speciation, degrees of formation of polyatomic clusters of sodium and chlorine ions have been computed with the aid of dissociation constants generated from Monte Carlo calculations which are consistent with both supercritical conductance measurements and electrostatic theory. The calculations indicate that the solute in alkali-halide solutions is successively dominated by increasingly complex polyatomic clusters as the solute molality increases at pressures and temperatures where the dielectric constant of water is ≤15.

Much of what is known about solute speciation in supercritical aqueous electrolyte solutions comes from high-temperature measurements of the specific conductances of dilute (<0.1 molal) alkali metal halide solutions (*1*). These low concentration conductance data were originally interpreted by assuming that monatomic ions and diatomic neutral ion pairs are the only solute species in solution and that the activity coefficients of neutral ion pairs can be regarded as unity in dilute solutions. Although valid at molalities <0.1, these assumptions have, due to a lack of experimental data, been applied to more concentrated solutions (*2*). However, recent advances in high-temperature solution chemistry indicate that this practice is inconsistent with reality and that serious error may result from failure to take into account formation of polyatomic clusters in concentrated supercritical electrolyte solutions.

The dielectric constant of the solvent controls to a large extent the degree to which solute species associate in aqueous electrolyte solutions (*3*). The dielectric constant (ϵ) of H_2O at 25°C and 1 bar is

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