

Imaging and Manipulation of Benzene Molecules on Si Surfaces Using a Variable-low Temperature Scanning Tunneling Microscope

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A variable-low temperature scanning tunneling microscope (VT-STM), which operates from 77 to 350 K in ultrahigh vacuum, was built and used to study imaging and manipulation of benzene molecules on Si surfaces. Four types of benzene adsorption structures were first imaged on the Si(5 5 12)-2x1 surface. Desorption process of benzene molecules by tunneling electrons was studied on the Si(001)-2x1 surface.

Key Words : Scanning tunneling microscope, Surface dynamics, Silicon, Surface science, Single molecules

Introduction

The scanning tunneling microscope (STM)¹ provides a spatially localized electron beam, capable of delivering a high current density. This property has been exploited in the characterization of surface and surface adsorbate topologies, the study of surface dynamic processes, including diffusion, desorption, dissociation, chemical reactions, growth, and phase transformations. Since temperature strongly influences the kinetics of such dynamic processes, controlling the STM temperature may be an avenue for adjusting the rate of these processes to a time scale that allows monitoring by STM. Furthermore, the STM has been used to move and position single molecules.² Electrons tunneling through the electronic states of a molecule adsorbed on a surface also couple to intrinsic molecular motions such as rotation and vibration, leading to the possibility of inducing chemical transformation in the molecule.^{3,4} Dissociation of single molecules has also been accomplished on both metal⁵ and semiconductor surfaces.⁶

Adsorption of benzene on the Si surface is a topic of great interest both because it represents a model system for the study of molecular adsorption (and desorption) of hydrocarbon on semiconductor surfaces, and because it is considered a promising precursor for the technologically relevant processes, such as the growth of Si-C and chemical vapor deposition diamond thin films on silicon surfaces. Many experimental and theoretical investigations,⁷⁻¹³ have been reported on the adsorption mechanism of benzene on low-index silicon surfaces. Although details of the electronic structures are still under debate, the dominant bonding mechanism and the adsorption geometries seem to be understood on the low index Si surfaces. Organic molecules adsorbed on the high index Si surface, which may act as a template for fabricating one-dimensional molecular nanowires,^{14,15} however, has not been studied.

In this paper, we briefly described the construction of a variable-low temperature STM (VT-STM) that is capable of single-molecule resolution on silicon surfaces in the temperature range of 77-350 K. We used our VT-STM to image and manipulate benzene molecules on the Si(5 5 12)-2x1 and the Si(001)-2x1 surfaces.

STM Design and Experimental

Figure 1 shows a schematic diagram of our VT-STM design.¹⁶ The STM base plate is suspended inside two radiation shields with stainless steel springs to provide vibrational isolation from the cold tip of the cryostat. Eddy current damping of the low frequency resonance is provided by three magnets (Sm-Co) attached to a copper cross-piece bolted under the base plate. The STM scanner is of the Besocke-type¹⁷ and consists of four piezoelectric tubes. Molybdenum was used as the sample holder material because the entire sample holder is heated along with the sample during sample cleaning. The inner and outer shields are equipped with three clearance holes (directed from the

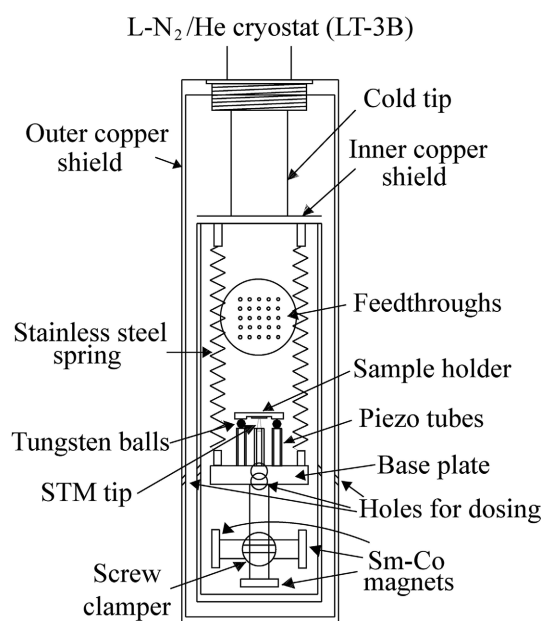


Figure 1. The variable-low temperature scanning tunneling microscope (VT-STM). The STM base plate and the sample are suspended from three metal springs for vibrational isolation. The holes on the two shields allow *in situ* dosing of atomic or molecular species. A wobble stick manipulator is used to manipulate the samples and tips. See the text for details.

front, right and left sides) for *in situ* dosing, as well as an access door. The VT-STM system was on a solid foundation; the laboratory floor where the VT-STM table was located was made of 3 meter deep concrete. No special measures were taken to shield the STM laboratory from electromagnetic or acoustic noise. Electromagnetic pick-up noise was minimized by grounding the ultrahigh vacuum (UHV) chamber with thick ground cable and eliminating all ground loops. To control the temperature of the VT-STM, the continuous flow liquid nitrogen cryostat is supplied by a flexible transfer line connected from the liquid nitrogen dewar.

The silicon samples employed in this work, Si(5 5 12) and Si(001) (Virginia Semiconductor), were ultrasonicated with ethyl alcohol. After degassing overnight at ~ 700 °C in a UHV system with a pressure lower than 1×10^{-10} Torr, clean Si samples were prepared by repeated cycles of 500 eV Ne⁺ ion sputtering and flashing at 1450 K to ensure surface cleaning. We found that, during flashing at 1450 K, excessive surface roughening occurred if the vacuum pressure exceeded 3×10^{-9} Torr. To maintain the pressure below 3×10^{-9} Torr during flashing, the e-beam heater must be heavily degassed before flashing. After flashing, the sample was rapidly cooled to 1200 K, and then to room temperature at a rate of 2 K/s for surface reconstruction. The cleanliness of the samples was confirmed with the VT-STM. A base pressure of the vacuum chamber is below 2×10^{-11} Torr. Benzene molecules (Aldrich) were further purified through several cycles of freeze-pump-thaw before being dosed onto the clean Si surface. Dosing was carried out through a leak valve equipped with a microcapillary-array filled tube for uniform adsorption on the surface. The use of a microcapillary-array doser also minimized the increase of chamber background pressure during dosing. An optical pyrometer was used to measure the sample temperature while the sample was in the heater. Electrochemically etched tungsten tips were prepared in the e-beam heater using repeated cycles of self-sputtering by field emission in a Ne atmosphere and by heating in a strong electric field.

Results and Discussion

Figure 2a shows an STM topographical image (filled states) of low coverage benzene molecules adsorbed on the Si(5 5 12)-2x1 surface, and Figures 2b and 2c show schematic diagrams of the top and cross-sectional views of the Si(5 5 12)-2x1 structure, respectively. The Si(5 5 12) surface is an energetically stable high-index surface 30.5° miscut from the [001] to the [111] orientations. When this bulk-terminated Si(5 5 12) surface is reconstructed to reduce its surface free energy, the periodicity along the $\bar{1}10$ direction becomes doubled with a unit cell of size 7.73×53.5 Å². Although the precise atomic arrangement of the reconstructed Si(5 5 12) surface is still under debate, one finds that the long side of the unit cell along the $[6\bar{6}5]$ direction,¹⁴ perpendicular to the long Si chains in the $\bar{1}10$ direction, consists of two unit cells of the (337) surface (**D1**

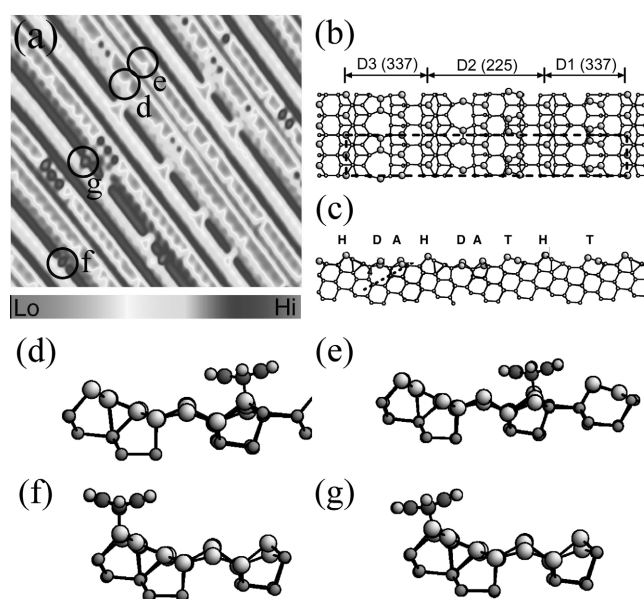


Figure 2. Illustration of single benzene molecule imaging. (a) STM topographical image of low coverage benzene molecules adsorbed on the Si(5 5 12)-2x1 surfaces. The images were obtained at a tunneling current of 0.5 nA and a sample bias voltage of -1.8 V. Four types of protrusions for the molecules are observed in the images. (b) and (c) Schematic drawings of top and cross-section for the Si(5 5 12)-2x1 structure, respectively. 'H', 'D', 'A', and 'T' indicate a honeycomb chain, dimer row, adatom row, and tetramer row, respectively. The scan area for the image (a) is $125 \text{ \AA} \times 125 \text{ \AA}$. (d)-(g) Schematic drawings of cross-section for the possible adsorption structures on benzene *d*, *e*, *f*, *g* shown in Figure 2(a), respectively.

and **D3**) plus one unit cell of the (225) unit (**D2**) surface. The boundary (honeycomb structure, H) is a chain structure. One (337) unit has a dimer-facing-adatom (D/A) geometry and the other (337) has only a tetramer (T) structure. The (225) unit consists of D/A and T structures.

Adsorbed benzene molecules appear as protrusions in the STM image. Four types of adsorption structures are observed for the benzene (indicated by circles): two types (higher protrusions) are observed on the H chain between **D1** and **D2**, and another two types (lower protrusions) are observed on the D/A structure. The latter are the most abundant ($\sim 96\%$), which were counted by sampling 350 protrusions, and stable under up to 3 V bias voltage at 0.5 nA tunneling current. This suggests that the latter are more stable energetically than the former. Benzene may be adsorbed in butterfly-type geometry, similar to on the dimer of Si(001) surface.⁷⁻¹³ Figures 2d-2g show the possible adsorption geometries for the benzene. Protrusions [*d*, *e*, and *g* in Figure 2(a)] on the **D3** and **D2** unit appear as asymmetric protrusions along the $[1\bar{1}0]$ direction. They appear slightly lower than the H chains in the topographical images, but are higher than D and A. The asymmetric feature is due to a tilted adsorbed benzene structure [Figures 2(d), 2(e), 2(g)]. Other protrusion, *f* is the symmetric highest protrusion and is observed on H chains separating **D1** and **D2** units. This may be due to the symmetric butterfly-type

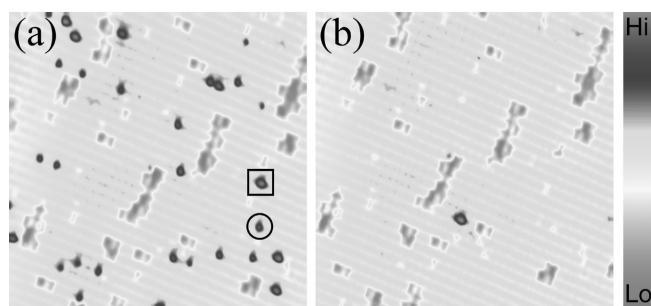


Figure 3. Illustration of benzene molecule manipulation on the Si(001)-2x1 surface. (a) STM image of benzene molecules adsorbed on the Si(001)-2x1 surface at 110 K. Scanning at a sample bias voltage of -2.5 V and a tunneling current of 1.0 nA causes the desorption of most benzene molecules (b). The same location is marked in both images. The images were obtained at a sample bias voltage of -1.5 V, a tunneling current of 0.5 nA, and a sample temperature of 110 K.

geometry [Figure 2(f)].

Low coverage adsorption of benzene molecule on the Si(001)-2x1 structure was studied at 110 K (Figure 3a). The Si(001)-2x1 structure is formed when Si(001), contaminated with Ni, undergoes reconstruction.¹⁸ Although the vacuum cleaning process for the contaminated one is the same as for the noncontaminated Si samples, the 2x1 reconstruction is reproducibly observed. This is explained by that Ni is added to the Si(001) even by slight contact of the bare sample with stainless steel, which would be expected to impart Fe, Cr, and Ni metals as the major contaminants. Fe and Cr metals can be easily removed by heating the sample in vacuum; however, Ni cannot be eliminated because of its high diffusion coefficient.¹⁹ Several works have been reported the effects of Ni contaminations on silicon,^{19,20} but the fundamental mechanism for the 2x1 reconstruction has yet to be explained. Very small amounts of Ni (<1%) are sufficient to induce the Si(001)-2x1 reconstruction.

Benzene molecules adsorb molecularly both at room and lower temperatures. Two types of benzene adsorption structures were observed as protrusions in STM image (Figure 3a). The higher protrusions are observed on a single dimer (indicated by a square in Figure 3a) and the lower protrusions on a bridge site (indicated by a circle). We found that the adsorption probability depends on the adsorption site, but is independent of temperature. No preferential adsorption on the defects of si(001)-2x1 was observed.

Benzene is known from previous experiments to adsorb exclusively on top of the Si(100) surface dimer rows, thus avoiding energetically disfavored structures with unsaturated, isolated Si dangling bonds. Even so, since the size of the benzene molecule is comparable to the spacing between two adjacent dimers on the same row, many different bonding configurations are possible. Among the structures proposed up to now as the lowest-energy configurations, a tetra- σ -bonded configuration where benzene is bonded to two adjacent surface dimers,^{8,12} is supported by semi-empirical calculations, STM, and IR spectroscopy experiments. Instead,

other experiments suggest either the 1,3-cyclohexadiene-like (tilted structure)¹⁰ or the 1,4-cyclohexadiene-like (butterfly) configuration,¹¹ in which the benzene molecule is di- σ -bonded to the two dangling bonds of the same Si surface dimer, is supported by thermal desorption and angle-resolved photoelectron spectroscopy, STM, vibrational infrared (IR) spectroscopy, and near-edge x-ray absorption fine-structure techniques, and first-principles cluster calculations.

According to the previous reports,^{8,12} the lower protrusions in Figure 3a can be assigned to the tetra- σ -bonded configuration. The higher protrusions are assigned to 1,4-cyclohexadiene-like configuration. Both structures are observed at room temperature STM study,¹² however only the former was observed at 22 K surface temperature.⁹ Room temperature STM and IR spectroscopy results support the hypothesis that benzene is initially chemisorbed in a butterfly-like state (metastable), and then slowly converts (within minutes) to a lower-energy final state, which is a tetra- σ -bonded one.¹² Moreover, recent IR experiments suggest that,¹³ at room temperature, benzene is predominantly adsorbed in the butterfly configuration, while the existence of a less stable structure, consistent with a tetra- σ -bonded configuration, is proposed. Room temperature STM study¹² reports that the conversion from the butterfly-like state to the tetra- σ -bonded configuration is activated either by thermal energy or tip-induced energy. We found that both states are interchangeable at 110 K by tip-sample voltages (not by thermally). This suggests that the barrier energy for the conformational change is higher than 110 K.

Control of benzene molecules on the surface is achieved with tunneling electrons. Tunneling electrons cause the benzene molecules to be desorbed. Figure 3b shows the surface shown in Figure 3a after scanning at high bias voltage. Comparison of the two images shows that application of a high bias voltage causes the desorption of almost all benzene molecules. In some cases, benzene does not desorb, but rather moves across the silicon surface (diffusion). Desorption yields (probabilities per electron) was measured by counting the fraction of molecules that are desorbed after scanning at a various bias voltages. The fraction is used to extract a yield using the measured area of a single benzene adsorbate and the known tunneling current going through the tip. We found that the rate of desorption depended strongly on the bias voltage but was less sensitive to the tunneling current (0.1-10 nA).²¹ The desorption yield increases to 10^{-6} (from 10^{-9} at -2.0 V sample bias at 1 nA tunneling current) at the sample bias voltage of -2.5 V and the tunneling current of 1 nA. This suggests that the desorption mechanism may involve a field-induced lowering of the relevant activation barriers. This is similar to the case of H adsorption on Si,²² where the Si-H bond dissociation energy for a Si₁₀H cluster showed a weakening of the bond under fields of ~ 0.5 V/Å, comparable to those in this work. The desorption rate is similar to that of 22 K experiment,⁹ which indicates thermal activation for bond-breaking is not much involved in the benzene desorption. This suggests that the desorption process may occur via an electronic

excitation. According to the theoretical model based upon first principles electronic structure calculations and quantum mechanical wave packet dynamics,⁹ the desorption process occurs via transient ionization of a π state of the adsorbed molecule.

Conclusions

We constructed the VT-STM which operates from 77 to 350 K and used it to study benzene molecules adsorbed on two types of silicon surfaces. We first imaged four types of adsorption structures on the Si(5 5 12)-2x1 surface at a molecular scale. Desorption process of benzene molecules from the Si(001)-2xn surface by tunneling electrons was demonstrated.

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