

Organic Molecular Modification of Silicon Surfaces

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1. Introduction

Integration of organic molecules with existing microelectronics technology has the potential to greatly expand the capabilities of semiconductor devices. The wide range of functionality of organic molecules (molecular recognition, light emission/absorption, electron transfer, non-linear optical properties, *etc.*) is of interest for applications ranging from optoelectronic devices to biosensors. While light emitting diodes and thin film transistors based on organic molecules have existed for some time, these generally involve spin coated or evaporated films on metallic or oxide substrates. Recently there has been increasing interest in the direct modification of semiconductor surfaces via the covalent attachment of organic molecules. Novel approaches for formation of ordered molecular layers utilizing both vacuum deposition and wet chemical techniques are being developed.¹⁻¹⁰ As the chemical and physical properties of these films and nanostructures will be highly dependent on molecular structure and conformation, methods to control not only the position but also the bonding geometry of the adsorbed molecule will be required. Progress in this area requires a detailed understanding of how organic molecules interact with semiconductor surfaces including knowledge of bonding configurations as well as the dynamical processes (*i.e.* reactions, diffusion) involved in adsorption.

In this article we review some recent results from our scanning tunneling microscopy (STM) investigations of organic molecule adsorption on silicon surfaces. The examples presented here serve to summarize the current level of understanding of organic molecule adsorption on semiconductor surfaces and illustrate current capabilities for determining as well as controlling the position and bonding configuration of adsorbed molecules. Possible obstacles to progress in this area such as limited surface diffusion (hindering self-assembly, formation of ordered layers) and electron-induced Si-C bond breaking (a possible degradation mechanism in molecular devices) are also identified.

2. Imaging bonding geometries

The scanning tunneling microscope is a uniquely powerful tool with the ability to image and manipulate individual atoms and molecules. However, while STM

images can show approximately where molecular adsorption has occurred, it is in general difficult to extract details of the adsorbate bonding geometry. Interpretation of STM images is complicated as they involve a convolution of topography and electronic state information. Furthermore, covalent bonding with the dangling bonds of the semiconductor surface will drastically alter the geometry and electronic states of the adsorbed molecule. As a result, some form of theoretical modeling is necessary to understand the observed STM features. We have used a silicon cluster to model the surface, obtaining optimized bonding geometries and adsorption energies with a variety of quantum chemistry computational methods including the semi-empirical AM1 method,¹¹ as well as Hartree-Fock (HF) and density functional (B3LYP) methods.¹² This approach has previously been employed by Raghavachari *et al.* to successfully model the interaction of hydrogen and water with silicon surfaces.^{13,14} Charge density iso-surfaces, constructed from sums of all the energetically accessible molecular orbitals are also obtained. Within the Tersoff-Hamman approximation,¹⁵ these will simulate constant current STM images. Comparison of these synthesized images with those observed experimentally allows specific adsorbate bonding configurations to be identified.

The Si(100) surface consists of rows of silicon dimers, with each dimer having two dangling bonds. A clean surface can be prepared by heating to 1250 °C under ultrahigh vacuum conditions ($<10^{-10}$ torr) to desorb the native oxide layer. While saturated hydrocarbons do not react with this surface, unsaturated molecules such as alkenes and alkynes have been shown to react readily with the available dangling bonds.^{16,17} Figure 1 shows an STM image of trans-2-butene (C_4H_8) adsorbed onto Si(100) by controllably leaking the gaseous molecules into the vacuum chamber. The molecules are imaged as paired protrusions, centered along a dimer row. Comparison with the calculated bonding geometry (HF/3-21G*) shows that these protrusions arise from the two methyl groups on either end of the molecule. In this configuration, the two central carbons, sp^2 before adsorption, become rehybridized to sp^3 by forming covalent bonds with the dangling bonds of a silicon dimer. Similar bonding geometries are observed for other simple alkenes such as ethylene and propylene. The simulated STM image is seen to show good agreement with the experiment. The methyl groups were not expected to give rise to maxima in the images due to the large energy gap associated with saturated hydrocarbons. However, the calculations show that covalent bonding to the silicon modifies the orbitals associated with the molecule, inducing a small electronic density of states on the methyl groups for energies in the vicinity of the conduction band edge (with a bias voltage of +2 V, states within 1.5 eV of the band edge are accessible for tunneling). As the tunneling current is an exponential function of distance even a small density of states that is physically closer to the tip will contribute significantly to the image. We note that the measured "height" of the methyl groups relative to the clean Si dimers is only 0.6 Å at +2 V, much less than the actual distance above the surface of 2.5 Å.

The ability to resolve the position of individual methyl groups allows the geometric configuration (cis or trans) of the adsorbed alkenes to be determined.¹⁰ For cis-2-butene, in which the methyl groups are on the same side of the molecule, the paired protrusions lie perpendicular to the dimer row direction, not at 30° as

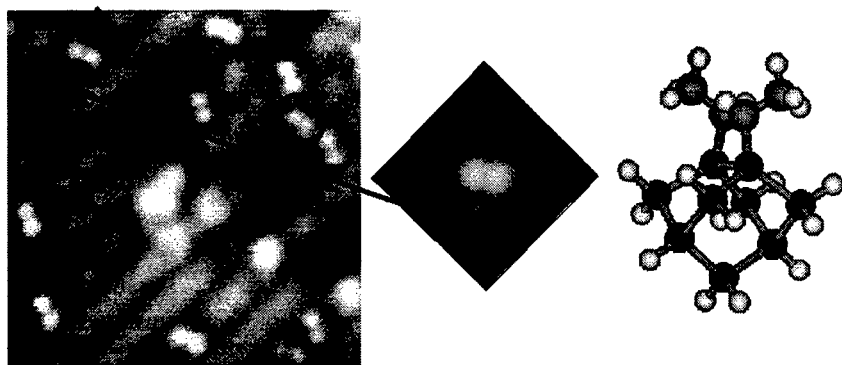


Figure 1. Unoccupied state STM image of trans-2-butene/Si(100) ($75 \times 75 \text{ \AA}$, $V_s = +2 \text{ V}$, $I = 40 \text{ pA}$), together with a simulated image for a five Si dimer cluster and optimized bonding geometry for a single dimer cluster. The circle denotes an adsorbed cis-2-butene molecule. The darkest and brightest features correspond to defects.

observed for the trans isomer. As a result the STM can be used to probe the degree to which adsorption of a given molecule is stereoselective (i.e. retains its geometric configuration). In Fig. 1 a single cis impurity is observed even though the trans isomer was introduced into the chamber (the level of cis impurity in the gas is $\leq 0.3\%$). Analysis of many adsorbed molecules indicates the concentration of the adsorbed cis configuration is $2.1 \pm 0.7\%$. This result indicates that while the reaction of 2-butenes with the Si(100) surface is stereoselective, in agreement with previous desorption studies,¹⁸ there is a small probability of isomerization upon adsorption.

The adsorption of alkenes is a rather simple case as the molecules are only observed to react in a single manner. Is the combination of the STM imaging together with cluster calculations useful for determining the bonding geometry of more complex molecules? To answer this question we have studied the adsorption of benzene, the prototypical aromatic molecule. As such it serves as a useful starting point for understanding the adsorption of larger conjugated molecules such as pentacene and anthracene which form organic semiconductors with high field-effect mobilities. Furthermore, the size of benzene is similar to the distance between Si dimers along a row, suggesting that bridging between these dimers may be possible. Previous experimental work has shown that benzene adsorbs molecularly, with significant rehybridization of some of the carbon atoms.¹⁹ Calculations using semi-empirical methods differ on whether bonding to a single dimer²⁰ or a bridging geometry²¹ yields the most stable adsorption site.

STM images of benzene/Si(100) indicate the presence of multiple bonding configurations as three different types of features due to benzene molecules are observed. With the aid of the cluster calculations the geometry giving rise to each of these features can be identified as illustrated in Fig. 2. For all the calculated structures the molecule loses its aromatic character, becoming significantly

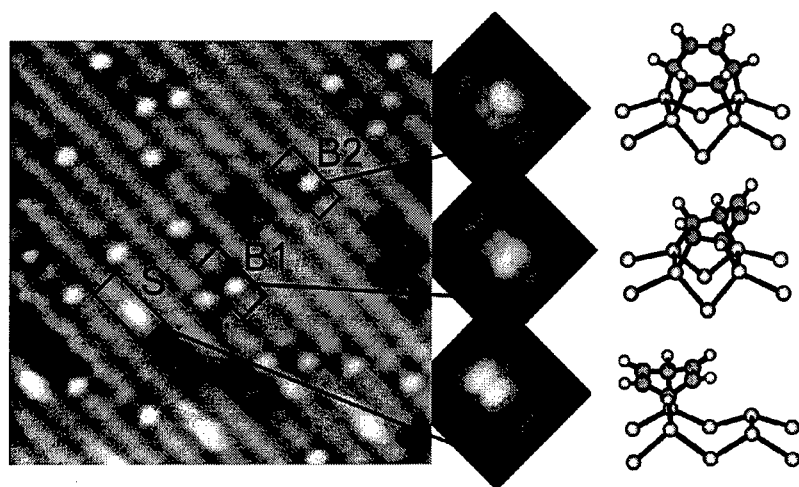


Figure 2. Occupied state image of benzene/Si(100) ($100 \times 100 \text{ \AA}$, $V_s = -1.5 \text{ V}$, $I = 40 \text{ pA}$) together with synthesized images (4 dimer cluster) and calculated structures (2 dimer cluster), from top to bottom; twisted bridge, tight bridge and single dimer.

distorted due to Si-C bond formation and rehybridization. The brightest protrusions (labeled S), centered over a single silicon dimer, are seen to arise from molecules bound to a single dimer in a butterfly configuration. The protrusion is due to the two double bonds that remain on the adsorbed molecule. The features labeled B1 and B2 both occupy two Si dimers and are assigned to two different bridging configurations. These geometries leave one double bonded unit remaining in the molecule, oriented parallel (B1) or perpendicular (B2) to the dimers, giving rise to the bright feature within the darkened area. Both of these bridging geometries require significant distortion of the Si lattice. The B1 feature requires a considerable shortening of the distance between dimers ("tight" bridge) while a twist of the dimers in the plane of the surface is required to accommodate the B2 configuration ("twisted" bridge). Adsorption energies, calculated at the B3LYP/6-31G* level, indicate the tight bridge to be considerably more stable (1.49 eV) than the twisted bridge (0.91 eV) or the single dimer geometry (0.88 eV). Infrared spectroscopy of the C-H stretch modes using the multiple internal reflection geometry indicates rehybridization of several of the carbons to sp^3 with some remaining sp^2 . Comparison of the measured spectrum with calculations yields evidence for all three of the configurations shown above.⁹

Consideration of the calculated adsorption energies suggests that the single dimer state should relax to the more stable tight bridge state. Furthermore, from the geometries depicted in Fig. 2 it is evident that such a relaxation would involve simply leaning over to one side and forming two additional Si-C bonds. In fact, while images taken shortly after dosing show most of the molecules in the single dimer state, time sequences of images over two hours reveal a slow conversion to

the tight bridge. The activation barrier for this conversion is determined to be 0.94 eV. As for the twisted bridge (B2), adsorption in this configuration is found to be a minority species occurring exclusively at a particular defect on the Si(100) surface known as type C. At these type C defects, thought to involve adjacent dimers buckled in the same direction as a result of a subsurface substitutional impurity, the dimers may be predistorted to accommodate the twisted bridge geometry. We note that, unlike the alkenes, which become completely saturated upon adsorption, all the observed benzene configurations have at least one double bond remaining on the molecule. This double bond presents an opportunity to carry out further chemistry such as a Diels-Alder addition, using the covalently attached benzene as a foothold on the surface.

In summary, these two examples indicate that the combination of STM and theoretical modeling using a cluster/quantum chemistry approach is quite effective in determining bonding geometries of organic molecules on silicon surfaces. This conclusion remains true even for more complex systems such as benzene/Si(100), for which adsorption leads to significant distortions of both the molecule and the substrate as well as the occurrence of multiple bonding geometries.

3. Tip-induced Si-C bond breaking

Fabrication of devices based on organic molecules will require patterning of these layers. The STM tip can be used for atomic resolution lithography as demonstrated by desorption of hydrogen atoms from the H-terminated Si(100) surface.²² Two distinct mechanisms of tip induced hydrogen desorption have been identified:²²⁻²⁴ electron-induced electronic excitation and vibrational heating. As the H-terminated surface is not reactive towards organic molecules under vacuum conditions, adsorption will only occur where hydrogen has been removed to create Si dangling bonds. Spatially selective adsorption of organic molecules using this approach has been used to create 250 X 150 Å regions of norbornadiene/Si(100).²¹

We have demonstrated that it is also possible to break Si-C bonds with a tip induced process, offering a strategy for the direct patterning of organic films. In particular, by imaging benzene/Si(100) at slightly elevated tip voltages, electrons from the STM can locally induce desorption, diffusion, and conversion between two different chemisorbed states. Figure 3 shows two images of the same area of a Si(100) surface with a low coverage of adsorbed benzene before and after scanning at a sample bias of -3 V. Immediately apparent is the larger fraction of bright protrusions, characteristic of the single dimer state, in the image on the right. Further comparison of the images reveals that all the molecules have moved except for the circled ones. At these locations, tight bridge features have converted directly to single dimer protrusions at the same position. This conversion is the reverse of the thermally induced binding state conversion discussed in the previous section. Inspection of the geometries accompanying Fig. 3 indicates that conversion from the tight bridge to single dimer state involves breaking two Si-C bonds. The observation of considerable diffusion is also surprising as imaging at lower bias voltages has shown that there is no thermally induced diffusion at room

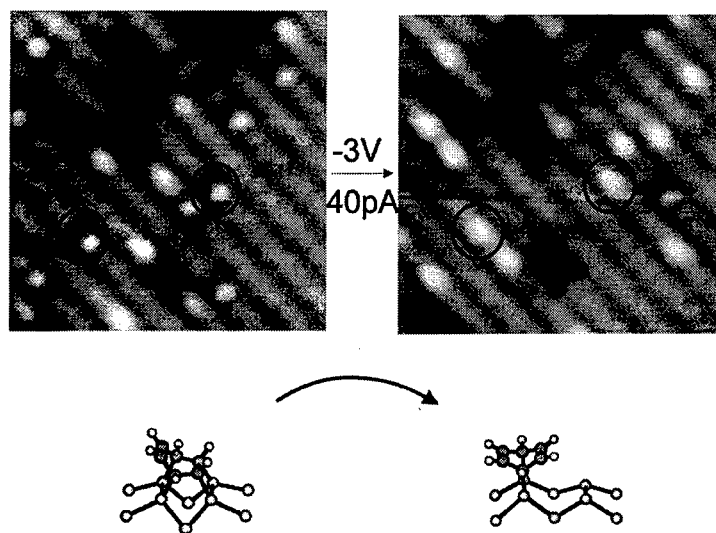


Figure 3. STM images of benzene/Si(100) ($75 \times 75 \text{ \AA}$, $V_s = -1.5 \text{ V}$, $I = 40 \text{ pA}$) showing the effects of scanning at elevated bias voltage (-3 V). The circled regions indicate two induced sites where the tip has induced conversion from the tight bridge to single dimer configurations as shown schematically below the image.

temperature. Analysis of the tip-induced diffusion events indicates that the average jump length is $10 \pm 5 \text{ \AA}$, approximately 2.5 dimer units, with no apparent preference for diffusion along or perpendicular to a dimer row. Comparison of the images also indicates there are two fewer molecules in the right hand image. While these could have simply diffused out of the image, larger area scans confirm that the tip is inducing desorption. Both desorption and diffusion require breaking of all four Si-C bonds. Diffusion, however, requires that the molecule remains bound to the surface, suggesting the existence of a mobile, metastable state. A molecule excited into this weakly bound state by the tip can diffuse along the surface and either desorb or return to the more stable covalently bound state. In the present case benzene molecules re-bonding with the surface will have to pass through the single dimer state before being able to bridge, accounting for the increased number of single dimer molecules observed after tip-induced diffusion. As discussed in the next section, a weakly bound metastable state has in fact been observed directly for benzene/Si(111) using low temperature STM.

Regarding the mechanism for the observed Si-C bond breaking, the threshold for this process is around 2.3 eV and the probability is roughly linear in the applied current. No tip-induced desorption or diffusion has been observed for the alkenes, which become totally saturated upon chemisorption, suggesting that the π electrons remaining on the rehybridized benzene play a crucial role. The tip breaking occurs during tunneling of occupied states (i.e. electrons moving from sample to tip). While assignment of a mechanism is somewhat still speculative,

the facts suggest desorption via a positive ion resonance created by removal of an electron from a π state of the molecule. This case differs from the one of tip-induced hydrogen desorption, which is typically observed at positive sample bias (electron flow to the sample). However, H-desorption at negative bias via a hole resonance was reported recently.²⁶ Besides being of interest for patterning, these tip-induced reactions can model electron stimulated effects in devices. The low voltage, low current electron induced Si-C bond breaking observed here suggests a possible degradation problem for devices based on unsaturated molecules.

4. Precursor -mediated diffusion

Schemes for making molecular devices based on the concept of self-assembly require substantial diffusion of adsorbed molecules. However, for organic molecules covalently bound to semiconductor surfaces, diffusion barriers are found to be rather large. For several different alkenes and benzene on Si(100) we found no evidence of diffusion at room temperature. This finding is in agreement with previous studies of benzene/Si(111) in which diffusion was observed only for temperatures close to the desorption temperature.²⁷ When diffusion did occur, the average jump length corresponded to several lattice sites, similar to the tip-induced diffusion for benzene/Si(100), which also involved multiple site hops. These observations are in contrast to the usual situation for adsorbates on metal surfaces where the diffusion barrier is generally much smaller (~10% of the desorption energy) and usually takes place via single site hopping. The present observations can be explained if diffusion occurs via a weakly bound, mobile "precursor" state, as suggested in the previous section.

Consider the potential energy diagram in Fig. 4(a) for an adsorbate approaching a surface. The system passes through a weakly bound (physisorbed) state on its way to the covalently bound (chemisorbed) state. While in the chemisorbed state there is a high barrier to lateral motion as this involves breaking of covalent bonds, in the physisorbed state the molecule is expected to be highly mobile. Thus diffusion can occur by first surmounting the barrier from chemisorbed to physisorbed states. As can be seen from Fig. 4, this model implies the barrier to diffusion is similar to that for desorption. In this model the diffusion length will be determined by the diffusion barrier in the physisorbed state as well as the time-scale for rechemisorption. If the diffusion barrier is significantly smaller than the barrier for rechemisorption, multiple site hopping will result.

Using a variable temperature STM has made it possible to trap molecules in this precursor state, providing the first direct observation of this evasive yet probably common entity.²⁸ Figure 4 shows benzene adsorbed on the Si(111) surface at two different temperatures. For adsorption in the 100–300K range, benzene appears as a darkening of the Si adatoms of the (7X7) reconstruction, as in Fig. 4(b). The appearance of benzene as "missing" adatoms is understood in terms of covalent bonding quenching the adatom dangling bonds, which dominate the clean surface image. For adsorption at 78 K, the image is dramatically different, the honeycomb pattern. These protrusions can be associated with

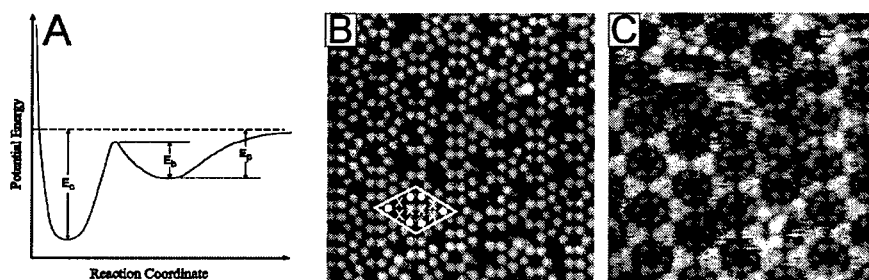


Figure 4. A) Schematic potential energy diagram describing precursor mediated adsorption. B) STM image of benzene/Si(111) at 120 K. The white diamond marks the unit cell of the (7X7) reconstruction with the six corner and six center adatoms denoted by white circles and X's, respectively. C) STM image of benzene/Si(111) at 78 K. Both images are 140 x 140 Å areas ($V_s = +1.5$ V, $I = 100$ pA).

physisorbed benzene; the "fuzziness" of the image is associated with motion of the molecule on the time scale of scanning. The honeycomb pattern indicates that the molecules are not completely delocalized across the surface but prefer to spend time over certain sites, in particular the center adatoms. In images at 95 K, this pattern becomes more noisy and less distinct. Above 110 K, the precursor is too mobile to be observed. From these observations the diffusion barrier in the precursor state can be estimated to be ~ 0.2 eV. While observation of physisorbed molecules is not in itself remarkable, the precursor state is unique in that it occurs over a site where chemisorption can and will occur. In fact, sequences of images reveal decay of some of the molecules from the precursor to chemisorbed states. By monitoring the rate of this process the barrier to chemisorption, E_B , can be estimated to be 0.3 eV. Using the measured barriers for diffusion and re-chemisorption the expected diffusion length at room temperature can be calculated to be 27 Å, close to the experimental value of 23 ± 1 Å.

Although the precursor state observed in Fig. 4(c) was observed directly upon dosing at 78 K, the STM tip can also be used to prepare this state at will, starting from the chemisorbed benzene. Conditions for dislodging molecules from the chemisorbed into the physisorbed state occur under similar conditions (-3 V, 100 pA) as required for the Si-C bond breaking observed for benzene/Si(100), suggesting a similar mechanism may be operative. Both these observations indicate that tip-induced population of the physisorbed precursor state offers a possible route for facilitating surface diffusion.

5. Wet chemical modification

While UHV offers a well-controlled environment for studying organic adsorption and making ordered films, it is ultimately desirable to do modifications via wet-

chemical methods in order to simplify processing and lower cost. In order to form well-ordered, covalently bound layers of organic molecules it is necessary to start from an atomically flat, oxide free surface. Chabal and Higashi showed that it is possible to form monohydride terminated Si(111) surfaces by etching with ammonium fluoride.²⁹ Chidsey has used this surface as a starting point for further chemistry, producing densely packed alkyl monolayers from alkenes using a radical initiated reaction.^{1,2} Lewis has prepared alkyl terminated Si surfaces via a two step process involving replacement of the hydrogen with chlorine followed by reaction with alkyl-Li or alkyl-Grignard.³ Electrochemical characterization indicates that these alkyl terminated surfaces have a rather low density of surface recombination sites (comparable to that of the H-terminated surface), corresponding to one electrically active defect every 10^5 atoms.³ While these insulating alkyl chains are of interest as passivating layers, molecular devices will also involve conducting molecules. Oligothiophenes are conjugated molecules that are among the organic semiconductors of choice for thin film transistors and may be interesting candidates for building efficient organic-based lasers.³⁰ Covalent attachment of thiophene and terthiophene molecules on Si(111) has recently been demonstrated by bromination followed by reaction with thienyllithium.⁸ We are currently working towards STM imaging and characterizing the electronic properties of these modified surfaces.

6. Concluding remarks

Covalent bonding of organic molecules to semiconductor surfaces has the potential to lead to novel hybrid devices with expanded functionality. The understanding of organic chemistry on silicon surfaces, necessary for further progress in this area, is still being developed. We have shown that the combination of STM and quantum chemistry calculations, using a cluster model for the surface, is a useful approach for determining the bonding geometry of adsorbed organic molecules. The interaction of small molecules such as alkenes and benzene with the Si(100) surface is now fairly well understood, and can be used as the starting point for attachment of more complex molecules with interesting molecular recognition or optoelectronic properties. Methods for control of the adsorbate bonding geometry via tip-induced modifications are also being explored. Tip-induced processes could prove useful for inducing diffusion of the adsorbed molecules. The developing wet chemical approaches for organic modification appear promising. Results obtained thus far indicate that these methods have tremendous potential for producing well-ordered layers with good electrical characteristics via relatively simple processing.

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