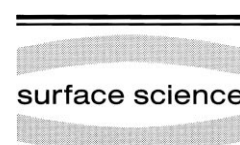




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Current-induced organic molecule–silicon bond breaking: consequences for molecular devices

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Abstract

The current carrying capacity of individual organic molecules covalently bound to silicon has been studied. Adsorbates consisting exclusively of saturated C–C bonds were found to be entirely stable whereas adsorbates containing π bonds could be controllably dislodged under modest conditions. The π bonds act as a chromophore, taking energy from a scattered electron, energy that can be selectively channeled into Si–C bond breaking. The class of adsorbates that are dislodged is closely related to unsaturated molecules widely investigated for enhanced molecular wire character. It is predicted that molecular devices containing such molecules will fail when operated. Measures to avoid current-induced bond breaking are described. New processes based upon the controlled bond breaking phenomenon are suggested. © 2000 Elsevier Science B.V. All rights reserved.

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Interest in molecular electronics has been sustained for over 25 years by steady advances in the theory of electrical transport in molecules [1–7] and in the practicalities of how and from what materials molecular devices might be built [8–13]. While many hurdles remain, the production of some form of molecular devices seems evermore likely. A particularly promising area, and one receiving much attention currently, aims at constructing hybrid organic molecule–silicon devices in an effort to enhance silicon technology [13]. An attractive aspect of the organic–silicon approach is that by combining molecular functional units with existing technology, many complex issues

such as physical support and connectivity may be simplified. It is also a great advantage that the scanning tunneling microscope, the key enabling tool in nanoscale science, is well suited to the study of silicon surfaces and adsorbates. 15 years ago very little was known about molecular adsorption on silicon but since the first application of scanning tunneling microscopy (STM) to monitor silicon surface chemistry [14] considerable progress has been made. In particular, understanding of alkene [15–21] and benzene [22] adsorption is well developed. Recent advances in the areas of adsorption dynamics and adsorbate manipulation have also moved the field forward [23–25].

A little explored, but crucial, issue in the area of molecular devices is the capability of organic molecules to sustain an electric current. Using a

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scanning tunneling microscope, we have studied the current carrying capacity of individual organic molecules covalently bound to silicon. The experiments were carried out in two separate UHV STM systems, one operating at room temperature, the other capable of variable sample temperature to as low as 20 K. Both chambers have base pressures below 5×10^{-11} Torr. The Si(100) samples were As doped, $0.005 \Omega \text{ cm}$. It has been found that structurally different molecules, though attached through very similar Si–C linkages, show different tendencies to suffer current-induced bond breaking. Two classes of molecules have been identified. Adsorbates consisting exclusively of saturated C–C bonds were found to be entirely stable. By contrast, adsorbed molecules which retain C–C π bonds upon adsorption could be controllably dislodged under modest conditions. The π bonds were found to act as a chromophore, taking energy from a scattered electron, energy that could then be selectively channelled into Si–C bond breaking.

The two classes of molecules identified are analogous to the two broad categories of molecular wires discussed by Ratner [2] and Datta [5]. They have described σ -bonded molecules that conduct coherently by superexchange, and, molecules which have low-lying states that intervene directly in an incoherent tunneling process. Molecules of the latter category generally have higher conductivity. The current-induced failure described here is therefore particularly significant. The same unsaturated molecular functions which might be added to increase molecular conductivity also enable a bond breaking mechanism. Though our results suggest a set-back for the molecule-on-silicon approach to devices, our message is one of caution, not condemnation. We expect that conditions and/or structures can be found that are immune to current-induced failure.

There is a second, more positive, message in this work. Controllable current-induced Si–C bond breaking may lead to useful processes – perhaps a form of lithography, or other applications as sketched below.

The adsorbed structures of the subject molecules shown in Fig. 1 have each previously been determined and are of interest as structures for the attachment of more complex molecules to silicon.

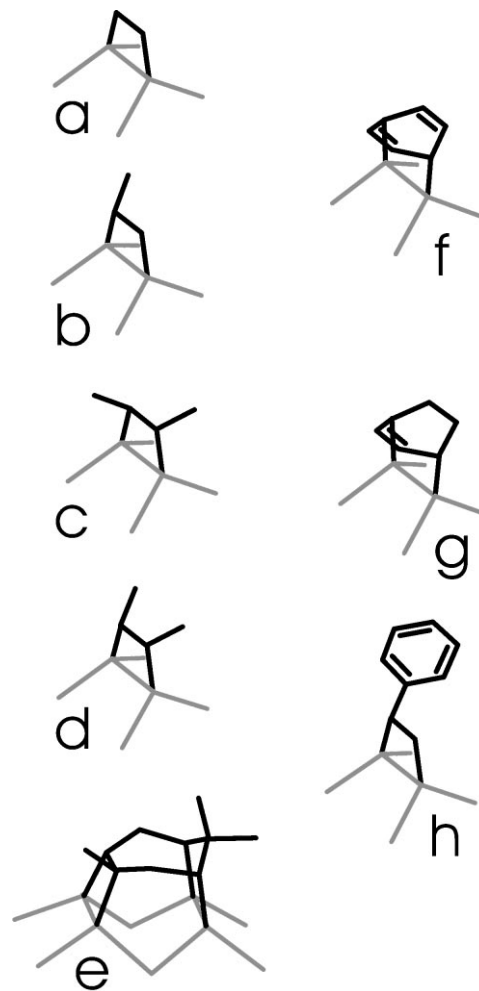


Fig. 1. Schematic diagrams of adsorbed (a) ethylene, (b) propylene, (c) *cis*-2-butene, (d) *trans*-2-butene, (e) carene, (f) benzene, (g) 1,3-cyclohexadiene, and (h) styrene on the Si(100) surface. Bonds between silicon atoms of the top two substrate layers are shown in grey.

Adsorbed ethylene, propylene, *cis*- and *trans*-2-butene, benzene, 1S(+)-3-carene (abbreviated carene), 1,3-cyclohexadiene and styrene were examined. All of these molecules adsorb by converting two sp^2 carbon atoms to sp^3 to form two Si–C bonds to one silicon dimer. (In the case of carene, further reaction occurs, resulting in two additional Si–C bonds thereby forming a bridging structure involving an adjacent dimer in the same row.) Upon adsorption, benzene, 1,3-cyclohexadiene and styrene retain C–C π bonds. The

other molecules become alkane like once adsorbed, and no double bond character remains. The following discussion focuses primarily on the mechanism by which covalently adsorbed benzene is dislodged.

The chemical bonding configurations and electronic structure of benzene on Si(100) are well understood [22,26–30]. We study the single dimer-bound configuration shown in Fig. 1f. The molecule is highly distorted relative to the free molecule, it is symmetrically placed and bound through carbon atoms 1 and 4. On crossing a 0.94 eV activation barrier the single-dimer configuration converts to a two-dimer bridging structure. At low temperatures the one-dimer species can be stabilized. Here we focus only on the one-dimer species. Benzene can be dislodged at positive sample voltages by a process that we believe is similar to that acting at negative biases. The negative sample process is most facile and we study it exclusively here. The remaining two pairs of carbon atoms are double bonded. Structural calculations show that the doubly bonded C atoms are displaced approximately 3 Å from the surface [22]. In STM images the single-dimer bound benzene molecules appear as bright featureless protrusions centered on an Si dimer, with an apparent height of 1.3 Å at -2.3 V sample bias relative to adsorbate free dimers, as shown in Fig. 2. The protrusions are closely associated with the π bonds of the carbon double bonds [22]. The adsorption energy is 1.1 eV [22]. In this work interactions between molecules were minimized by working at low surface coverages, on the order of 6%.

The two consecutive STM images recorded at 21 K and a sample bias of -2.3 V shown in Fig. 2 illustrate tip-induced breaking of Si–benzene bonds. On comparing the two images it is apparent that several of the benzene molecules have been displaced. Unaffected molecules in Fig. 2 are circled. About 80% of the time a displacement event is accompanied by an abrupt truncation of the molecule-derived protrusion indicating that the tip-induced bond breaking interaction is localized over approximately the same lateral scale as the image of the molecule. Obvious examples of truncated molecule images in Fig. 1 are labeled with a T. Some of the affected molecules are displaced

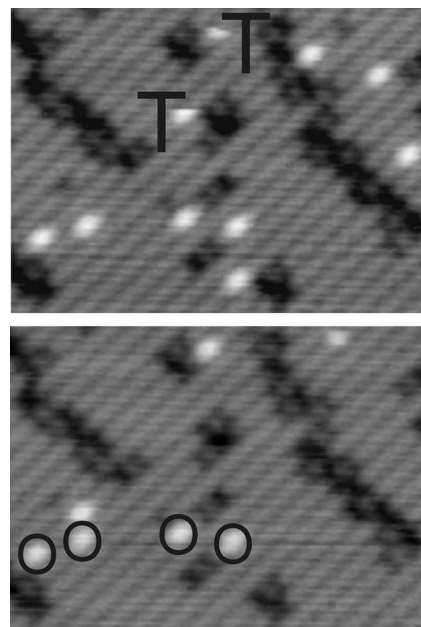


Fig. 2. Two successive STM images of the same area showing tip-induced motion of single-dimer benzene molecules on an Si(100) surface cooled to 22 K. Silicon dimer rows run across the images diagonally. Benzene molecules bound to single dimers are imaged as bright protrusions. Surface defects are imaged as depressions. The letter 'T' marks a truncated molecule image, that is, a molecule that was dislodged while being imaged. Molecules which have not moved are circled. The images are 15 nm across. Tunneling conditions are -2.3 V sample bias and 42 pA with a scan rate of 300 nm s^{-1} . Individual scan lines were taken from left to right as the raster scan proceeded from the bottom to the top of the image.

laterally and re-adsorb in the single-dimer configuration while others evidently desorb. No evidence of C–H or C–C bond breaking has been observed. No correlation between scan direction and the direction of adsorbate jumps has been found. This, together with the observation that at a given current setting the likelihood of bond breaking increases in inverse proportion to the scan rate (i.e. slower scanning breaks more bonds) leads us to discount near-tip bond breaking mechanisms such as 'sliding' and 'pushing' [8].

A number of STM 'tip-induced' bond breaking processes have been documented. In each case, excitation of adsorbate–substrate bonds to a dissociative level occurs. That can be achieved in single or multiple steps via inelastic electron tunnel-

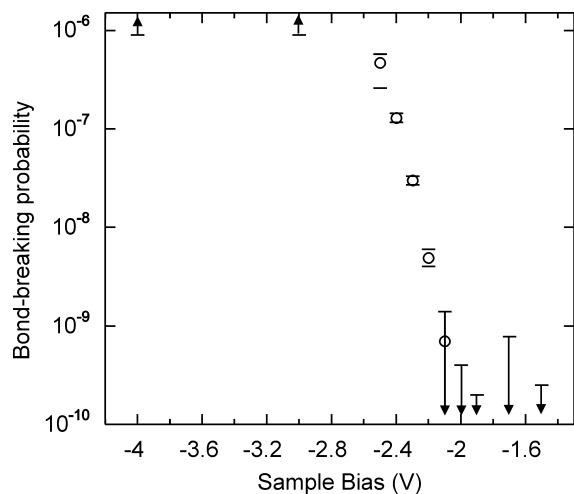


Fig. 3. Bond breaking probability as a function of STM sample bias at 22 K. The open circles are data points. Upper and lower error bars are indicated. For the lowest negative voltages studied no bond breaking was observed allowing only upper bounds to be determined, as indicated by bars and downward pointing arrows. At the highest negative voltages studied all molecules moved allowing only a lower limit on bond breaking probability to be determined.

ing. In some cases excitation to an upper electronic state is involved, in others only the ground electronic state plays a role. Furthermore, an upper state, when involved, may lead directly to dissociation, or alternately, can serve as an intermediate state that leads to vibrational excitation on return to the ground electronic state. Single-step excitations have been treated theoretically [31,32] and are likely behind the displacement of Si adatoms [33] on Si(111)-(7×7), the displacement of CO from the Cu(111) surface to the STM tip [34]. Si–H bonds can be broken either by driving a $\sigma \rightarrow \sigma^*$ transition at high bias (>6 V), or at low bias by multiple vibration excitation [25]. In all of these cases it appears that bond breaking involves a resonant scattering process. Fortunately, each of these processes has idiosyncrasies that allow its identification. We assess the relevance of each of these processes to the case of benzene/Si(100).

In Fig. 3, the bond breaking probability (BBP) for single-dimer bonded benzene is plotted versus sample bias at 22 K. Bond breaking yields have been measured in the following way. After imaging a fresh area at a bias for which the benzene–Si

bonds are stable (typically -1.5 V), the same area is then rescanned at a bias that induces bond breaking, giving each molecule a measured dose of electrons. If p denotes the probability of a tunneling electron to break a benzene–Si bond, then the probability of a benzene–Si bond surviving a dose of N electrons is $\exp(-pN)$. After re-scanning at the benign bias and comparing with the initial image, a BBP can be deduced using the measured adsorbed benzene area of 0.5 nm^2 . It has been found that at bias values more positive than -1.6 V no measurable bond breaking occurred even for electron doses as high as 10^9 per molecule. In between -1.6 and -2.7 V there is a sharp threshold over which the bond breaking yield rises as sharply as an order of magnitude per 0.1 V change in sample bias. After the steep initial rise, the curve appears to saturate at more negative bias. For bias values more negative than -2.7 V virtually all the benzene molecules in an image would disappear or move to new sites. Studies between room temperature and 20 K show that the BBP does not decrease with decreasing temperature (the BBP actually increases with decreasing temperature). We expect that this reflects a change (a decrease) in coupling of the adsorbate excited state to the bulk silicon levels with lower temperature. This rules out any thermally activated bond breaking mechanisms (including field-driven processes wherein the adsorbate is effectively pulled over a barrier to move laterally or vertically) and points to dissociation via an electronic excitation.

In order to determine whether the excitation of Si–C bonds to a dissociative level occurs by single or multiple steps the bond-breaking yield as a function of tunneling current at a fixed sample bias was measured. A linear relationship indicates a single-electron process whereas the definitive signature of a multiple-excitation process is a strong power-law increase of the BBP with STM current [33–36]. The observed (approximately) linear BBP to electron dose reveals that Si–C bond breaking is a single-electron driven process.

It is necessary to determine next the nature of the excitation that underlies the inelastic single-electron scattering process. One candidate for electronic excitation involves a tunneling electron exciting a $\pi \rightarrow \pi^*$ transition associated with the

adsorbate C–C double bond. This is rejected, however, because the large $\pi \rightarrow \pi^*$ energy gap of about 4.5 eV [30] for adsorbed benzene cannot be reconciled with the observed saturation in the BBP at just -2.5 V bias. At -2.5 V we would at best be on the tail of such a resonance – saturation at 2.5 V indicates that we have reached the peak of a much lower energy resonance.

One clear candidate for excitation remains. That is a positive ion resonance, existing transiently as the electron leaves the molecule and extinguished when an electron hops from the substrate to the adsorbate. Significantly, a photoemission study identifies a C–C π bonding state approximately 2.3 eV below the Fermi level [30]. The sharpness and position of the BBP threshold at -2.5 V is thus consistent with a bond breaking mechanism involving resonant electronic excitation of this state. (Further evidence that resonant excitation of a surface state mediates the bond breaking mechanism will be offered in a subsequent paper. Briefly, pinning centers are deactivated to cause a Fermi level shift. The onset in the BBP curve shifts in unison demonstrating the central role of the molecular-derived resonance.)

Excitation of vibrations by resonant inelastic tunneling events has been previously described [31,32,37]. Such a process is depicted schematically in Fig. 4. Bond breaking requires that the tunneling electron lose energy matching or exceeding the bonding energy. Theoretically the inelastic tunneling channel should have a peak at an energy coinciding with the energy level of the resonant state on the adsorbed molecule [37]. Upon removal of an electron, creating a temporary positive ion, the adsorbate begins to distort to conform to its new potential energy surface. When neutralization occurs, the adsorbate may be found highly extended or contracted with respect to its various vibrational modes of motion, the degree of distortion increasing with the lifetime of the temporary ion. The distorted neutralized adsorbate will evolve as a vibrationally excited species. With some significant probability, a mode selecting focusing of internal energy evidently then occurs leading to dissociation of the Si–C bonds. There is a partial analogy to unsuccessful efforts to achieve selective bond breaking in molecules by pumping one mode

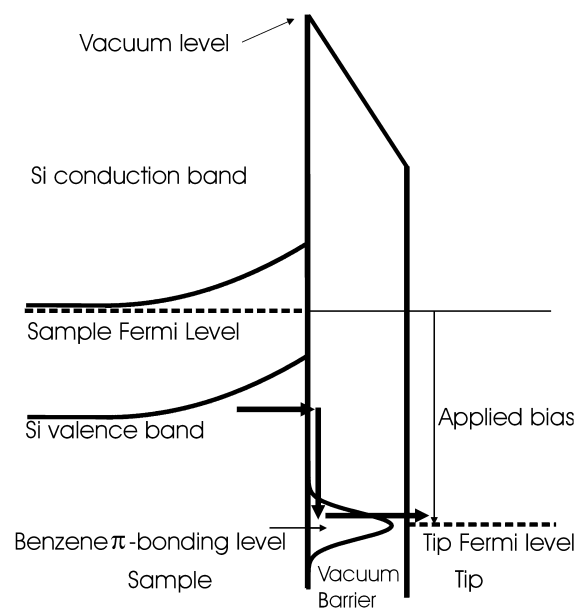


Fig. 4. Schematic energy-level diagram of STM Si/benzene/vacuum/tip tunneling junction under negative sample bias. Bulk band edges, with band bending are shown with heavy curves to depict Fermi level pinning by surface states. Inelastic tunneling of an electron when close to resonance from the sample to the tip via the benzene π resonance is depicted by three arrows.

with infrared photons – generally, rapid energy redistribution leads to dissociation of a bond other than the one intended. While the end result is vibrational excitation to dissociation – the route there is a single electronic excitation.

This model suggests that other adsorbates containing π bonds should exhibit bond breaking under similar conditions. Two other candidates have so far been examined and both were found to undergo Si–C bond breaking. Adsorbed 1,3-cyclohexadiene, Fig 1g, has only one C–C double bond where benzene has two. The Si–C bonds are very similar in the two species but benzene is bound by 1.1 eV while the adsorption energy for 1,3-cyclohexadiene is calculated to be 2.3 eV [38]. The difference is due primarily to the extra stability of free benzene which is aromatic. We calculate the π resonance of adsorbed 1,3-cyclohexadiene to be very similar to that of benzene, ~ 2.5 eV below the Fermi level. This is in accord with STM images which show the mole-

cule to be much more prominent on changing the bias voltage from -2.0 to -2.5 V. Consistent with its greater adsorbed stability, 1,3-cyclohexadiene Si–C bond breaking is approximately $500 \times$ less probable than that for benzene. Styrene, Fig. 1h, is also calculated to be bound by 2.3 eV, and exhibits BBPs similar to those for 1,3-cyclohexadiene, $\sim 2 \times 10^{-9}$ for tip biases in the 2.4–3 V range. At a bias of 1.5 V, the BBP decreases to less than 3×10^{-11} . Styrene shows the most striking example of the chromophore effect – energy initially goes to aryl ring excitation, but ultimately leads to breaking of the rather distant Si–C bonds.

In contrast to the adsorbed molecules containing π bonds, the molecules that became saturated upon adsorption were found to be stable when subjected to similar conditions. No tip-induced desorption or movements were observed for adsorbed ethylene, propylene, *cis*- or *trans*-2-butene or carene. The σ -bonded adsorbates studied possess C–H, C–C and Si–C bonds similar to those in adsorbed benzene but lack any π bonding. Carene is comparable in size with benzene, 1,3-cyclohexadiene and styrene, but, has no π function and was found to be stable.

In summary, we have studied two classes of adsorbates; those that are exclusively sigma bonded, and adsorbates that contain π bonds. The former are entirely stable while the latter suffer current-induced Si–C bond breaking. It has emerged that bond breaking arises from a single inelastic electron tunneling event and that a low-lying, poorly coupled π state localized on the adsorbate is centrally important in the bond breaking mechanism.

Substituted benzenes (alkyl or other chains attached) will have bonding and electronic character very little altered from that of benzene. We predict, therefore, that bonds of such molecules to Si(100) will soon fail when negatively biased at or above 2 V and carrying modest currents. Since the inelastic scattering resonance is very sharp, the same structure biased below 1.5 V will be relatively long lived, at least $5000 \times$ longer. The available data allow only an upper bound on the BBP at low voltage to be determined; further study is required to establish the actual value. The present

results suggest that it would be prudent to bear in mind the possibility of current-induced bond breaking when designing an organic–silicon molecular device. One way to avoid the problem identified here is to use σ -bonded systems. The enhanced stability of 1,3-cyclohexadiene and styrene suggests that π -containing molecules with yet stronger attachment to Si might be sufficiently robust in some applications. Further study is required to determine if placing the chromophore function farther from the surface will reduce Si–C bond breaking.

Before closing we note that applications may emerge from the phenomena described here. In this work isolated adsorbates have been studied, but the consequences of bond failure will be environment (device) dependent, possibly ranging from complete loss of the molecule at one extreme to immediate repair in a constrained environment. For example, a current susceptible molecule surrounded by simple alkanes might suffer Si–C bond breaking but be held in place and encouraged to rapidly re-bond to the surface. By adjusting the character of the surroundings, one can imagine forming a switch or a memory device using the fact that in the broken state the conductivity of the device will be lower.

Another enticing aspect of controlled current-induced Si–C bond breaking is the potential to create a form of lithography. Preliminary work shows that areas of silicon can be freed of covalently bound benzene at will using an STM tip. An electron beam may also be used. An attractive feature of this process is that only clean silicon exists in the affected area, and no carbonaceous or other residue remains. Moreover, useful variants may be envisaged that take advantage of the energy and chemical-specific nature of the effect.

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