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Formation of an Atomically Abrupt Interface between a Polycyclic Aromatic Molecule and the Silicon (001) Surface via Direct Si−C Linkage

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The reaction of acenaphthylene with the Si(001) surface has been investigated as a model system for understanding how complex π-systems interact with a π-bonded semiconductor surface. Scanning tunneling microscopy (STM) reveals that bonding occurs over a dimer row for more than 90% of the adsorbed molecules. Fourier transform infrared spectroscopy (FTIR), using isotopically labeled derivatives of acenaphthylene, shows that bonding occurs through the 1,2-alkene, leaving the aromatic portion of the molecule mostly unperturbed. The reaction between acenaphthylene and Si(001) represents a potential method for coupling extended π-electron systems with group IV semiconductor surfaces.

I. Introduction

The Si(001) surface consists of pairs of atoms that are formally linked together with a very weak Si=Si double bond.[1] Recent studies have shown that many aspects of the chemistry of the Si(001) surface are analogous to the chemistry of the π-bonds of organic alkenes and silenes, but with a significant amount of diradical and zwitterionic character introduced to the silicon dimer by the unusual geometry of the surface atoms and the very low strength of the surface π-bond.[2,3] Because of the importance of silicon in microelectronics, there is great interest in understanding how to control interfaces between silicon and organic compounds. Organic molecules that contain π-conjugated systems are of especially high interest because many of these molecules are organic semiconductors,[4] and may have the ability to function as active devices.[5,6] To successfully integrate organic materials with silicon-based technology, it is critical to be able to prepare very well-defined interfaces between silicon and a variety of organic materials. It is especially important to control how the interface formation affects the π-conjugation within the molecule, since loss of π-conjugation would significantly alter the electronic properties of the organic material.

Molecules in which the conjugated π-electron system extends through the entire molecule can directly link to the Si(001) surface, but the formation of covalent Si−C bonds at the interface is accompanied by loss of π-conjugation.[7] This problem can be avoided by using an external functional group such as an isothiocyanate,[8] vinyl,[9] amine,[10] or thiol[11] group. If the π-conjugated electron system is tethered to the surface through only one bond, however, there are still many degrees of freedom that are uncontrolled, generally leading to disordered molecular layers. Recent studies showed that 9,10-phenanthrenequinone could be linked to the Si(001) surface with two Si−O−C linkages per molecule, thereby forming a rigid layer of oriented π-conjugated molecules, as shown in Figure 1.[12,13] It is likely that Si−O−C linkages are comparatively insulating interfaces, in analogy to the well-known insulating properties of SiO_2. Since electron-donating and electron-withdrawing groups can strongly affect band alignment and conductivity at the interface, there is interest in designing other types of specific molecular structures that will yield predictable electronic properties at organic−inorganic interfaces.[14−16]

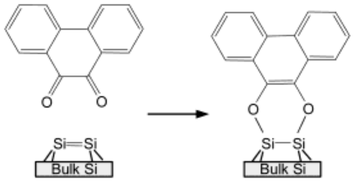

Figure 1. Previously reported [4+2]-cycloaddition reaction of 9,10-phenanthrenequinone with a Si dimer, from ref 12.

In this paper, we report the selective attachment of a pure π-conjugated hydrocarbon, acenaphthylene, to the Si(001) surface. Selective isotopic labeling studies show that acenaphthylene links to the surface in such a way as to preserve the aromaticity. This produces a layer of rigidly bonded molecules with intact, conjugated π-electron systems, linked to the surface via a direct Si−C bond.

II. Experimental Section

Experimental measurements were performed using scanning tunneling microscopy (STM) and Fourier transform infrared spectroscopy (FTIR). STM and FTIR experiments were performed in separate ultrahigh vacuum (UHV) chambers having base pressures $<10^{-10}$ Torr.

All STM and FTIR experiments used "on-axis" silicon samples that were oriented to (001) ± 0.5°. STM samples were highly doped (<0.1 ohm cm, As-doped), while FTIR samples were lightly doped (>5 ohm cm, B-doped). IR spectra reported here were obtained using nominally unpolarized light.

Wafers polished on both sides were used in all IR spectroscopy experiments. From these large wafers individual smaller samples (∼ 1 cm × 2 cm) were cut. The narrow edges (∼ 0.5 mm × 1 cm) were then polished at a 45° angle, making each Si sample a small prism. For all experiments, samples were degassed overnight at ∼840 K in UHV and then flash annealed

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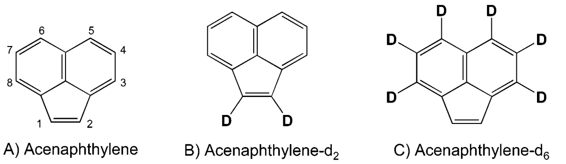

A) Acenaphthylene B) Acenaphthylene-d_2 C) Acenaphthylene-d_6

Figure 2. Molecular structures for (a) acenaphthylene, (b) acenaphthylene-d_2, and (c) acenaphthylene-d_6.

to ~1400 K until pressure stabilized at $<3 \times 10^{-10}$ Torr, producing a clean (2 × 1)-reconstructed surface.[17]

Infrared absorption spectra for adsorbed molecules were obtained using a Mattson RS-1 FTIR spectrometer coupled to a UHV system through two BaF_2 windows. The infrared light was focused into the narrow edge of the trapezoidal samples. After propagating down the ~2 cm length of the sample the light emerged from the narrow edge at the opposite end of the sample, where it was collected and focused onto a liquid nitrogen-cooled InSb detector. Spectra were acquired with 4 cm^{-1} resolution.

Direct observation of adsorbed molecules was achieved with a home-built UHV scanning tunneling microscope (STM). While a range of imaging conditions was explored, all images shown here were obtained using a sample bias of −2.3 V and a tunneling current of 80 pA.

Figure 2 shows molecular structures and atomic numbering for (a) acenaphthylene, (b) acenaphthylene-d_2, and (c) acenaphthylene-d_6. The carbon atoms in the 1 and 2 positions form a C=C bond that is conjugated to the aromatic portion of the molecule, and will be referred to as the 1,2-alkene. The aromatic portion of the acenaphthylene molecule is referred to as the naphthalene ring. Acenaphthylene (Figure 2a) was purchased from Fisher (99+% purity). Isotopically labeled samples (Figure 2b and 2c) were synthesized as explained in general synthetic methods (Part III).

In both vacuum chambers used for these studies, acenaphthylene was introduced using a leak valve and pressure was measured using an ionization gauge. Both the location of the leak valve and other geometric properties of the vacuum systems make the effective pressure at the sample higher than the background pressure rise detected by the ionization gauge. All pressures and doses reported here are based on the uncorrected background pressure measurement. Therefore, the true exposures at the sample are expected to be several times higher than the reported values. Due to the low vapor pressure of acenaphthylene, there was also significant time lag between achieving maximum dosing pressure and return to base pressure. Because of this lag in pressure, it is impossible to determine precise saturation exposure. On the basis of a maximum time lag, we can estimate the saturation exposure to be less than 1 langmuir (1 L = 10^{-6} Torr s). Larger exposures of acenaphthylene at room temperature did not change the spectra from those reported at lower coverage.

III. General Synthetic Methods

Me_2SO was distilled under vacuum, discarding the first 30% of the distillate. Me_2SO-d_6 and other compounds from commercial sources were used without further purification. ^1H and ^{13}C NMR spectra (Bruker AC-300 spectrometer) and ^2H NMR spectra (Bruker AC-250 spectrometer) were obtained in $CDCl_3$ or $CHCl_3$, respectively, with chemical shifts referenced to Me_4Si (^1H) or CD_2Cl_2 (^2H). Air-sensitive reactions were run under N_2 in oven-dried glassware.

[1,1,2,2-^{2}H]-Acenaphthene. The deuterated sample was prepared by base-catalyzed exchange in the protio starting material.[18] Acenaphthene (1.02 g, 6.61 mmol) was dissolved in 10 mL of Me_2SO-d_6 and heated slightly to speed up dissolution. After cooling to room temperature, NaH (60% dispersion, 52.2 mg, 1.31 mmol) was added and the reaction heated to 78 °C for 22 h. Water (5 mL) and HCl (1 M, 5 mL) were added and the acenaphthene precipitated from solution as a gray solid which was collected by vacuum filtration. Sublimation (0.02 Torr, 50−60 °C bath temp) gave acenaphthene-d_4 as white needles in 100% yield. Deuterium incorporation into the methylene positions was >98% by ^1H NMR and no deuterium incorporation into the ring was observed via ^2H NMR. ^1H NMR δ 7.58 (dd, J = 8.1, 0.6 Hz, 1H), 7.42 (m, 1H), 7.26 (m, 1H). ^2H NMR δ 3.44 (s). ^{13}C NMR δ 145.9, 139.4, 131.6, 127.7, 122.2, 119.2, 29.5 (m). MS (EI) m/z (relative intensity) 158 (M^+, 100), 129 (10), 78 (26). mp 92−93.5 °C.

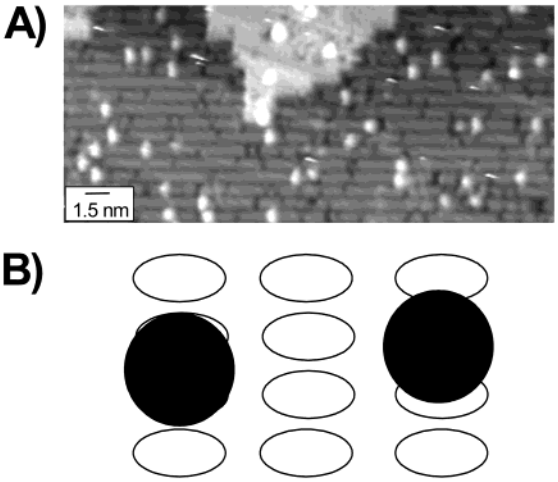

Figure 3. (a) STM image of subsaturation coverage acenaphthylene on the Si(001) surface. Image was acquired at −2.3 V bias and 8 pA tunneling current. Each of the species present is centered over a dimer row. (b) Schematic representation of the position of acenaphthylene molecules relative to the underlying dimer row.

[1,2-^{2}H]-Acenaphthylene (referred to as acenaphthylene-d_2). The bromination/debromination procedure of Anderson et al.[19] was followed to give acenaphthylene-d_2 from [1,1,2,2-^{2}H]-acenaphthene in 37% overall yield after purification by sublimation (0.02 Torr). ^1H NMR δ 7.80 (d, J = 8.1 Hz, 1H), 7.68 (d, J = 6.6 Hz, 1H), 7.54 (t, J = 7.2 Hz, 1H). ^2H NMR δ 7.17 (s). ^{13}C NMR δ 139.6, 129.0 (t, J = 26.1 Hz), 128.2, 128.1, 127.6, 127.2, 124.1. MS (EI) m/z (relative intensity) 154 (M^+, 100), 128 (24), 77 (75). HRMS calcd for $C_{12}H_6D_2$ 154.0752, found 154.0752. mp 87−89 °C.

[3,4,5,6,7,8-^{2}H]-Acenaphthylene (referred to as acenaphthylene-d_6). [3,4,5,6,7,8-^{2}H]-Acenaphthene was synthesized in an identical manner as [1,1,2,2-^{2}H]-acenaphthene above, starting from perdeuterioacenaphthene and protio Me_2SO. ^1H NMR δ 3.40 (s). ^2H NMR δ 7.66 (s, 1D), 7.47 (s, 1D), 7.30 (s, 1D). MS (EI) m/z 160 (M^+, 100), 131 (11). Bromination/debromination then provided [3,4,5,6,7,8-^{2}H]-acenaphthylene: ^1H NMR δ 7.08 (s). ^2H NMR δ 7.93 (s, 1D), 7.80 (s, 1D), 7.65 (s, 1D). MS (EI) m/z (relative intensity) 158 (M^+, 100), 130 (8).

IV. Results

Figure 3a shows an STM image of a Si(001) surface with a very low coverage of adsorbed acenaphthylene molecules. At low coverage, STM images provide information about the spatial location of the adsorbed molecules relative to the underlying Si(001) crystal lattice, as well as the number of inequivalent binding sites. Analysis of STM images like that shown in Figure

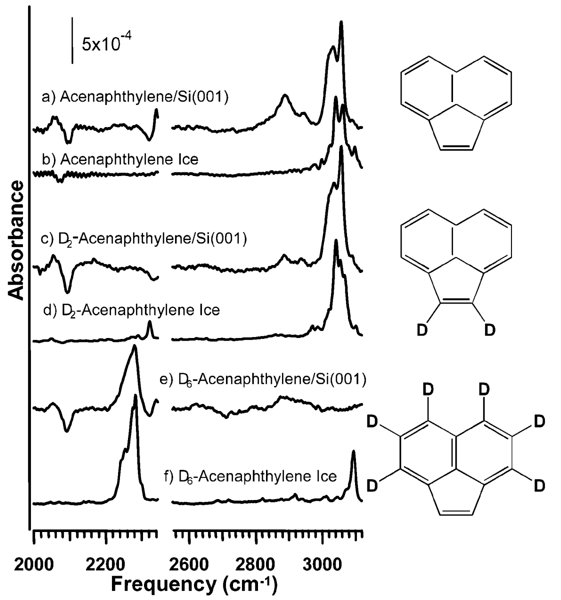

Figure 4. FTIR spectra for (a) Si(001) surface exposed to saturation coverage acenaphthylene at 300 K, (b) multilayer of acenaphthylene, (c) Si(001) surface exposed to saturation coverage acenaphthylene-d_2 at 300 K, (d) multilayer of acenaphthylene-d_2, (e) Si(001) surface exposed to saturation coverage acenaphthylene-d_6 at 300 K and (f) multilayer of acenaphthylene-d_6 at 110 K.

3a indicates that more than 90% of the molecules give rise to a bright protrusion centered on top of a dimer row, as schematically represented in Figure 3b. The presence of a dominant feature in the STM images that represents more than 90% of the adsorbed molecules indicates that there is one preferred bonding configuration. The remaining 10% of the molecules appear to be bonded in other alternative configurations and may be associated with defects of the underlying surface.

To gain further information about the bonding geometry, FTIR spectroscopy was used to determine how chemical bonds in acenaphthylene change upon adsorption onto the Si(001) surface. Because all carbon atoms in acenaphthylene are sp^2 hybridized (unsaturated), evaluation of the C−H stretching region provides clues about how attachment to the Si(001) surface occurs.

Figure 4 shows FTIR spectra of a Si(001) surface exposed to (a) saturation coverage of acenaphthylene at 300 K, (b) a multilayer of acenaphthylene, (c) saturation coverage of acenaphthylene-d_2 at 300 K, (d) a multilayer of acenaphthylene-d_2, (e) saturation coverage of acenaphthylene-d_6 at 300 K, and (f) a multilayer of acenaphthylene-d_6. Multilayer spectra were acquired by lowering the sample temperature to ∼110 K followed by further exposure to over 10 L acenaphthylene, using the acenaphthylene monolayer-terminated surface as a background.

Figure 4a shows the FTIR spectrum of a Si(001) surface exposed to 0.6 L (3×10^{-8} Torr, 20 s) acenaphthylene. Further exposure did not result in any changes in the FTIR spectrum, indicating that the Si(001) surface is saturated after exposure to 0.6 L acenaphthylene. The FTIR spectrum of acenaphthylene adsorbed on Si(001) is characterized by several peaks between 2800 and 3200 cm^{-1}. The peaks at 2888 and 2944 cm^{-1} are in the region typically associated with C−H stretching vibrations of sp^3 hybridized carbon atoms, such as in alkanes. The higher-lying peaks at 3034 and 3059 cm^{-1} are in the region typically associated with sp^2 hybridized carbon, such as in alkenes.

For comparison, Figure 4b shows the FTIR spectrum of a multilayer of acenaphthylene formed by deposition on a Si(001) surface held at 110 K. This spectrum is characterized by peaks at 2954, 2977, 2999, 3025, 3041, 3062, and 3099 cm^{-1}, as well as shoulders at 3079 and 3110 cm^{-1}. With the exception of the small peak at 2977 cm^{-1} and the shoulder at 3110 cm^{-1}, this spectrum is in excellent agreement with a literature spectrum of acenaphthylene solid.[20]

A comparison between acenaphthylene/Si(001) and solid acenaphthylene reveals that attachment results in the appearance of new peaks in the alkane C−H stretching region that were not present for the parent molecule. The increase in intensity of the C−H stretching peaks below 3000 cm^{-1} suggests that a significant fraction of carbon atoms undergo a change from sp^2 to sp^3 hybridization when acenaphthylene bonds to the Si(001) surface.

To determine which specific carbon atoms form bonds between the acenaphthylene molecule and the Si(001) surface, we collected and analyzed FTIR spectra in which selected H atoms within the acenaphthylene molecule were replaced with deuterium. Figure 4c shows an FTIR spectrum of a Si(001) surface exposed to 8 L (4×10^{-8} Torr, 200 s) acenaphthylene-d_2, while Figure 4d shows the corresponding spectrum of a multilayer film deposited onto a cold sample. In the spectrum for the monolayer chemisorbed onto Si(001), high-frequency C−H peaks (typical of sp^2 hybridized carbon) are observed at 3036 and 3059 cm^{-1}, with a shoulder at ∼3021 cm^{-1}. Lower-frequency peaks (typical of sp^3 hybridized carbon) are observed at 2885 and 2938 cm^{-1}, but these peaks have a very low intensity.

The corresponding spectrum of the multilayer film (Figure 4d) shows several peaks in the C−D and C−H stretching regions. While we were unable to find previous assignment of the FTIR peaks for acenaphthylene-d_2, a comparison to acenaphthylene combined with the fact that substitution of H atoms with D atoms shifts FTIR peaks to a lower frequency allows us to make reasonable assignments. A peak at 2323 cm^{-1} (in the C−D stretching region) is attributed to the C−D stretch of the 1,2-alkene since this is the only portion of the molecule that contains C−D bonds. Several weak−strong peaks are observed in the C−H stretching region from 2971 to 3110 cm^{-1}. These peaks are attributed primarily to C−H stretching of the naphthalene portion of the acenaphthylene-d_2 molecule.

While we can conclude that the majority of the observed absorbance in the C−H stretching region is due to C−H stretches of the naphthalene portion of the acenaphthylene-d_2 molecule, it is also possible that there is some contribution from combination bands. Styrene-d_3, a molecule that is similar to acenaphthylene-d_2 in that it is fully conjugated and contains only sp^2 hypridized carbon atoms, exhibits several combination bands in the 2800−3100 cm^{-1} region.[21] Therefore, it is possible that some small peaks in the FTIR spectrum for acenaphthylene-d_2 may also be due to combination bands. However, combination bands for styrene-d_3 were observed to be quite weak,[21] and it is expected that the same would be true for acenaphthylene-d_2.

Although there are some differences in relative intensity, the C−H vibrational frequencies of acenaphthylene-d_2 chemisorbed onto the Si(001) surface (Figure 4c) are nearly identical to those of the multilayer film (Figure 4d). This similarity suggests that adsorption onto the Si(001) surface leaves the naphthalene portion of the molecule relatively unperturbed. Unfortunately, frequency-dependent changes in detector response, combined with the low number of D atoms in each molecule, make it difficult to detect the C−D vibrations of the acenaphthylene-d_2 monolayer. Consequently, we also investigated the adsorption of acenaphthylene-d_6, in which all H atoms on the naphthalene ring are substituted by D, leaving only H atoms that are part of the 1,2-alkene group.

Figure 4e shows the FTIR spectrum for a Si(001) surface that has been exposed to 10 L (5 × 10^{-8} Torr, 200 s) acenaphthylene-d_6. This spectrum is characterized by a strong C−D stretch at 2275 cm^{-1} and a very weak but broad feature extending from 2825 to 3000 cm^{-1}. Notably, no significant absorbance is observed above 3000 cm^{-1}, even though the spectrum in this region appears quite flat and with good signal-to-noise.

For comparison, Figure 4f shows the FTIR spectrum of a multilayer of acenaphthylene-d_6. The multilayer shows peaks at 2253, 2275, and 2282 cm^{-1} and a shoulder at ∼2243 cm^{-1}, each within the C−D stretching region, and a sharp C−H vibration at 3094 cm^{-1} along with several other weak vibrations between 2800 and 3150 cm^{-1}. Once again, it is possible that some of these peaks may be due to combination bands.[21]

Comparing the spectrum of the chemisorbed molecule (Figure 4e) to the multilayer film (Figure 4f) shows that upon interacting with the surface, the vibration at 3094 cm^{-1}, which is due to sp^2 hybridized C−H stretching of the parent molecule (Figure 4f), disappears and is replaced by a new feature at much lower frequency (2800−3000 cm^{-1}) (Figure 4e), characteristic of sp^3 hybridized carbon. In contrast, the C−D vibrations between 2200 and 2300 cm^{-1} (Figure 4f) are almost completely unaffected by bonding to the surface (cf. Figure 4e). This comparison strongly suggests that bonding of acenaphthylene-d_6 to the Si(001) surface occurs almost exclusively via the 1,2-alkene group, leaving the naphthalene ring nearly unperturbed.

In summary, STM shows that more than 90% of the acenaphthylene molecules are adsorbed to Si(001) through a single bonding configuration. FTIR spectra show that (1) acenaphthylene reacts with the Si(001) surface in such a way as to give rise to unsaturated C−C bonds within the molecules, (2) the C═C bond of the 1,2-alkene group is saturated to form a C−C bond, and (3) the naphthalene ring portion of acenaphthylene is mostly unperturbed.

V. Discussion

Evaluation of the experimental data for attachment of acenaphthylene to the Si(001) surface reveals several pieces of information that help to establish the bonding geometry. First, there is a unique STM feature that accounts for more than 90% of the adsorbed molecules (Figure 3a). Even though the STM images cannot definitively determine the bonding configuration, they do show that there is a predominant species, thereby establishing that the FTIR spectra can be treated as arising from molecules in a single configuration instead of a mixture of configurations.

Analysis of the bonding configuration from FTIR hinges upon several points. The first is that the C−H stretching vibrations of sp^2 hybridized carbon (as in alkenes) virtually always occur at frequencies >3000 cm^{-1}, while C−H stretching vibrations of sp^3 hybridized carbon (as in saturated alkanes) are nearly always <3000 cm^{-1}. Previous studies with a variety of alkenes and more complex organic molecules show that this trend is also true for molecules bonded to Si surfaces.[7,9,22−25] When unsaturated molecules such as styrene bond to the Si(001) surface, the high-lying vibrational modes are shifted to lower frequency due to the transition from sp^2 to sp^3 hybridization and by the donation of electron density from silicon to the carbon atom.[9]

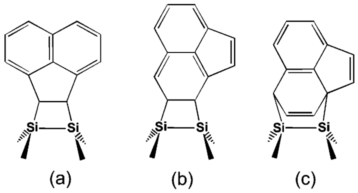

Figure 5. Three possible bonding configurations for acenaphthylene adsorbed on the Si(001) surface. (a) Adsorption through the 1,2-alkene group to form a four-membered Si_2C_2 ring. (b) Adsorption through the naphthalene portion of the ring to form a four-membered Si_2C_2 ring. (c) Adsorption through the naphthalene portion of the ring resulting in a [4+2] product.

Shifts in vibrational frequency upon chemisorption give important information about the bonding configuration(s) for acenaphthylene/Si(001). For the parent acenaphthylene molecule, the changes in the FTIR spectrum upon adsorption indicate that some C atoms change from sp^2 to sp^3 hybridization, resulting in the appearance of new C−H features at 2888 and 2944 cm^{-1} (Figure 4a). A comparison of the spectra for acenaphthylene-d_2 (Figure 4c) and acenaphthylene (Figure 4a) shows that both molecules have similar spectral features in the 3000−3100 cm^{-1} region. Since acenaphthylene-d_2 has only H atoms on the naphthalene portion of the molecule, the FTIR peaks at 3036 and 3059 cm^{-1} can be attributed to C−H stretching of the naphthalene ring. These FTIR peaks are identical (within the resolution of the experiment) to the acenaphthylene FTIR peaks at 3034 and 3059 cm^{-1}. Therefore, we can conclude that the FTIR peaks at 3034 and 3059 cm^{-1} for acenaphthylene are due to naphthalene ring C−H absorption. Also, the presence of intense vibrational features >3000 cm^{-1} for chemisorbed acenaphthylene-d_2 (Figure 4c) along with the absence of these features for acenaphthylene-d_6 (Figure 4e) strongly suggests that chemisorption of acenaphthylene occurs primarily through the 1,2-alkene portion of the molecule.

The small peaks at 2885 and 2938 cm^{-1} (sp^3 hybridized C−H stretching region) for acenaphthylene-d_2/Si(001) appear similar to the 2888 and 2944 cm^{-1} peaks observed for acenaphthylene/Si(001). The appearance of low-frequency FTIR peaks for acenaphthylene-d_2/Si(001) suggests that either a small amount of acenaphthylene-d_2 bonds to the surface through the naphthalene ring or that the deuteration may be less than 100% complete. However, a comparison of the intensity of these peaks shows that the 2885 and 2938 cm^{-1} peaks of acenaphthylene-d_2/Si(001) (Figure 4c) are much lower in intensity than the 2888 and 2944 cm^{-1} peaks of acenaphthylene/Si(001) (Figure 4a), while the C−H peaks at higher frequency have similar intensity. This suggests that most (but not all) acenaphthylene-d_2 molecules bond through the 1,2-alkene group, with some smaller fraction (<10% based on STM images) possibly bonding through the naphthalene ring.

There are several possible bonding configurations that could be formed when acenaphthylene adsorbs to the Si(001) surface. Three of these are shown in Figure 5. The absence of significant IR absorbance in the Si−H stretching region (2000−2100 cm^{-1}) suggests that the majority of the adsorbed species bond without dissociation. On the basis of the IR data, we can rule out several configurations. Since the naphthalene ring remains unperturbed after adsorption, bonding configurations of the type shown in Figure 5b and 5c and other similar or more complex schemes involving the naphthalene portion of the molecule can be ruled out. Coupling the lack of naphthalene ring interaction with evidence for the side group changing from an alkene (sp^2) to an alkane (sp^3) species shows that the only reasonable bonding configuration is the one shown in Figure 5a. Therefore, we conclude that acenaphthylene adsorbs to the Si(001) surface through the side group in a manner similar to a [2+2]-

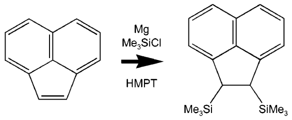

Figure 6. Reductive silylation of acenaphthylene to form 1,2-bis-(trimethylsilyl)acenaphthene, from ref 30.

cycloaddition reaction and the naphthalene portion of the molecule remains relatively unperturbed.

Selective chemistry of acenaphthylene has previously been observed for reactions with several substituted ethylene species. The 1,2-alkene group of acenaphthylene preferably reacts through a [2+2] cycloaddition with acrylonitrile,[26] tetracyanoethylene (TCNE),[27] and several more complex substituted ethylene species (each under irradiation).[28] Reactions under irradiation between TCNE and acenaphthylene resulted in several products (in addition to the [2+2] product), all involving the 1,2-alkene portion of the molecule.[29] Reductive silylation of acenaphthylene also proceeded through the 1,2-alkene group to form 1,2-bis-(trimethylsilyl)acenaphthene, as shown in Figure 6.[30] In each case, even under very reactive conditions, reaction of acenaphthylene occurred through the 1,2-alkene portion of the molecule, leaving the naphthalene ring unperturbed.

Several Si(001) surface reactions with C=C containing molecules, in which the C=C portion of the molecule reacts with a Si=Si dimer to form a four-member C_2Si_2 ring, have also been observed.[2,9,23,31−41] In particular, styrene, a molecule containing an aromatic ring species with a conjugated vinyl side group, attaches selectively through the vinyl side group, resulting in an intact aromatic species tethered to the Si(001) surface.[9] Selectivity for styrene originates in the fact that the interaction between the π electrons of the vinyl group and the end of a Si=Si dimer is attractive at relatively large separations, whereas interaction with the ring involves an energy barrier. This leads to selective bonding of styrene to the Si(001) surface through the vinyl group into a [2+2] adduct via a low-symmetry pathway.[9] While computational work has not been done for this study, it is likely that a similar explanation can account for the reaction of acenaphthylene with the Si(001) surface. A reaction barrier that is larger for attachment through the naphthalene portion of the molecule than for the 1,2-alkene side group would result in a kinetically mediated pathway that leads to the product shown in Figure 5a.

VI. Conclusion

π-Conjugation is responsible for most of the interesting electronic characteristics of organic molecules. Therefore, simple schemes that lead to selective attachment of large π-systems to semiconductor surfaces are highly desirable. We have developed a simple, selective attachment scheme in which the 1,2-alkene group of acenaphthylene is used to couple an extended π-system to the Si(001) surface. The chemistry of acenaphthylene on Si(001) may be a model system for developing ways to couple more complex π-systems to semiconductor surfaces.

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