

## Interfacial Chemistry of Pentacene on Clean and Chemically Modified Silicon (001) Surfaces

Kevin P. Weidkamp,<sup>†</sup> Christina A. Hacker,<sup>†</sup> Michael P. Schwartz,<sup>†</sup> Xiaoping Cao,<sup>†</sup> Rudolf M. Tromp,<sup>‡</sup> and Robert J. Hamers<sup>\*,†</sup>

Department of Chemistry, University of Wisconsin-Madison, 1101 University Avenue, Madison, Wisconsin 53706, and IBM Research Division, T.J. Watson Research Center, Yorktown Heights, New York 10598

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The interactions between pentacene and the Si(001)-(2 × 1) surface have been investigated using Fourier transform infrared spectroscopy (FTIR), ultraviolet photoelectron spectroscopy (UPS), and X-ray photoelectron spectroscopy (XPS). The pentacene molecules in the first layer react with the Si surface atoms through the C=C double bonds and via cleavage of C–H bonds. This chemisorption is accompanied by disruption of the conjugated  $\pi$  electron system. The disrupted interfacial layer is stable throughout deposition and evaporation of thicker pentacene films. Pentacene molecules in layers beyond the first layer adsorb molecularly and yield well-defined valence band features that are characteristic of a conjugated  $\pi$  electron system. Functionalization of the Si surface with a monolayer of cyclopentene inhibits dissociation of subsequently deposited pentacene molecules.

### Introduction

Organic monolayers and thin films on surfaces have been of significant interest in the effort to improve and expand existing microelectronics technology.<sup>1,2</sup> Thin films of semiconducting organic molecules in particular have been a focal point in order to develop electronic devices such as organic thin-film transistors (OTFTs).<sup>3,4</sup>

Metal and semiconductor substrates are a natural starting point for investigating organic thin-film deposition processes because these provide a means of integrating organic electronics with conventional silicon-based electronics. One of the most promising organic semiconducting materials is pentacene, which is a planar molecule consisting of five fused aromatic rings. This planar geometry enhances the ability to pack into a highly ordered crystal structure,<sup>5–8</sup> which in turn leads to high electrical mobility.<sup>9,10</sup> Recent experimental results have investigated the growth on metals and silicon.<sup>3,11–12</sup> On silicon, growth conditions were identified that lead to highly crystalline films.<sup>3</sup> However, the basic chemistry at the interface between the substrate and pentacene has not been well understood.

In the deposition of inorganic films it is widely recognized that the first interfacial layers play a particularly important role by controlling the “wetting” of one layer by another. For molecular systems the situation is complicated by the fact that molecules have lower symmetry. Thus, nucleation and subsequent growth of organic films involve a delicate balance of forces. A recent study showed that when pentacene is deposited directly on to the Si(001) surface, the initial molecular layer was not effective at nucleating a crystalline film.<sup>13</sup> This has been attributed to a strong interaction of the first layer with the surface dangling bonds,<sup>14</sup> disrupting the electronic and physical structure of the interface and inhibiting nucleation of pentacene crystals.

The chemical nature of the substrate also plays a role in the adsorption of the pentacene layer,<sup>15</sup> as pentacene crystal growth is improved when the substrate is less reactive.<sup>16</sup> Recent studies have shown how to form well-defined, ordered organic monolayers on the Si(001) surface.<sup>17–20</sup> When these molecules have only a single olefinic (C=C) group, the resulting film exposes only saturated organic groups that are very unreactive. A recent study showed that a monolayer film formed by reaction of cyclohexene significantly improved the nucleation and growth of pentacene crystals on the Si(001) surface.<sup>21</sup>

Here, we have used infrared spectroscopy (FTIR), valence band photoemission (UPS), and core-level photoemission (XPS) spectroscopies to investigate the changes in chemical and electronic structure that occur when pentacene is deposited onto clean and chemically modified Si(001) surfaces. Our results show that the initial layer of pentacene molecules involves some dissociation and involves strong Si–C bond formation that leads to a poorly defined interface, while pentacene deposition on organic-modified surfaces occurs without dissociation. More insight into these areas along with the aforementioned previous work provides a comprehensive view of the interactions of pentacene at the clean Si(001) surface.

### Experimental Section

The adsorption of pentacene at the Si(001) interface was studied using three techniques: Fourier transform infrared spectroscopy (FTIR), ultraviolet photoelectron spectroscopy (UPS), and X-ray photoelectron spectroscopy (XPS). All experiments were carried out in ultrahigh vacuum (UHV) chambers with base pressures  $<3 \times 10^{-10}$  Torr. Lightly doped p-type Si(001) (B-doped, 15  $\Omega\cdot\text{cm}$ ), polished on both sides, was used for all IR measurements. N-type Si(001) (As-doped, 0.005  $\Omega\cdot\text{cm}$ , Virginia Semiconductor) was used for all XPS and UPS experiments. Before introduction to vacuum, samples were sonicated in acetone, then in methanol, and residual carbon contamination was removed by exposure to ozone for 15 min.

\* Corresponding author. Telephone: 608-262-6371. Fax: 608-262-0453. E-mail: rjhamers@facstaff.wise.edu.

<sup>†</sup> University of Wisconsin-Madison.

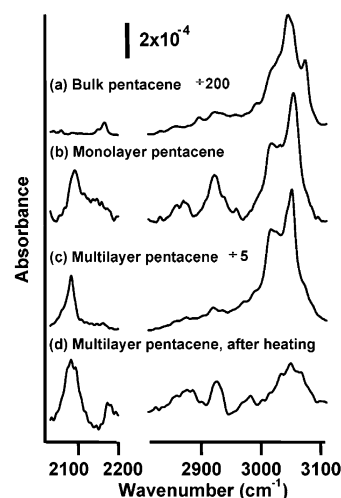
<sup>‡</sup> IBM Research Division, T.J. Watson Research Center.

Once in a vacuum, samples were degassed overnight at 850 K and annealed to 1400 K to remove the oxide layer. This process has been shown to produce a clean, reconstructed Si(001)-(2 × 1) surface.<sup>22</sup>

Pentacene (98%, Fluka) was dosed in a vacuum by sublimation from a boron nitride crucible. A tungsten wire was used to resistively heat the crucible, and the temperature was monitored by an internal thermocouple. The crucible and its contents were outgassed overnight at 380 K prior to evaporation in order to remove any higher vapor pressure contaminants. Pentacene was evaporated normal to the sample at a horizontal distance of ~3 cm to ensure relatively uniform coverage of the surface. Exposures were determined from the background chamber pressure and are reported in Langmuir (1 L = 1 × 10<sup>-6</sup> Torr·s). Because of the chamber geometry and the directed dosing, exposures at the surface are higher than those reported. In multiple-dose experiments, exposures are given as a sum of individual doses. Heating of the samples after dosing was done resistively, with the temperature determined by comparison to a previously obtained calibration curve relating power dissipated across the sample to its temperature as measured by a thermocouple.

FTIR spectra were measured using a Mattson RS-1 spectrometer with a liquid nitrogen-cooled InSb detector. Infrared light passed in and out of the UHV chamber through BaF<sub>2</sub> windows. Samples were 0.8 cm × 2.0 cm × 0.5 mm in size with the small ends polished at 45° to act as a prism in a multiple internal reflection geometry. Spectra shown were obtained with 4 cm<sup>-1</sup> resolution. The geometry of the chamber prohibited measuring a background spectrum before the sample was dosed with pentacene; therefore, background spectra were measured at the end of each experiment, after annealing the dosed sample to >800 K to dissociate the surface species. Cyclopentene-*d*<sub>8</sub> (98%, CDN Isotopes) was dosed through a variable leak valve, and adsorption to the surface was confirmed prior to dosing pentacene. Diffuse reflectance IR measurements were performed on a Bruker Vector 33 system with a liquid nitrogen-cooled InSb detector and at 4 cm<sup>-1</sup> resolution.

UPS was carried out using a differentially pumped He I source that produced photons at 21.2 eV. Emitted photoelectrons were detected by a Physical Electronics hemispherical analyzer coupled to a 16-channel detector. Binding energies are reported with respect to the Fermi energy of the system, which was determined by fitting the low binding energy cutoff from the Ta clips on the sample holder to a Fermi-Dirac distribution function. All other spectra were shifted by this energy, which was typically 0.4 eV. The pass energy for all spectra was 5.85 eV, yielding a resolution of 0.09 eV, and electrons were collected at 10° from the surface normal. Peak energies are reported from direct measurements of the spectra and are not based upon any fitting algorithm. XPS spectra were measured immediately before the UPS spectra at each level of exposure. XPS was performed using a Physical Electronics setup with monochromatized Al K<sub>α</sub> radiation at 1486.6 eV. This source is mounted on the same chamber as the ultraviolet source and uses the same detection scheme for determining core level binding energies as was described above. Si(2p) spectra were recorded and used as an internal standard by correcting each spectrum to binding energies of 99.4 and 100.0 eV for the 2p<sub>3/2</sub> and 2p<sub>1/2</sub> lines, respectively. C(1s) spectra were then corrected by the same value as the corresponding Si(2p) spectrum. The takeoff angle of all measured photoelectrons was 37° (53° from normal). A pass energy of 11.75 eV was used for the hemispherical analyzer, yielding an instrumental resolution of 0.18 eV. Spectra



**Figure 1.** FTIR spectra of (a) bulk pentacene (by diffuse reflectance in KBr) and the Si(001)-(2 × 1) surface after exposure to (b) 0.008 L pentacene and (c) multilayer coverage of pentacene. Spectrum (d) is the result of heating the sample from (c) to >380 K to desorb pentacene multilayers.

were fit using IGOR, a commercial software package (Wave-metrics) where peaks were fit to a mixed Gaussian–Lorentzian shape with the goodness of fit determined by achieving a reduced  $\chi^2$  value close to 1.<sup>23</sup> The number of peaks was increased until no significant improvement in the reduced  $\chi^2$  was evident upon addition of another peak.

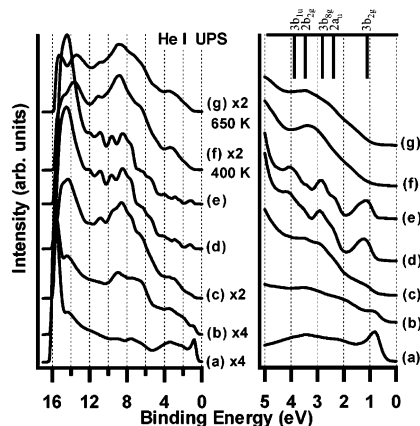
AFM images were obtained using a Digital Instruments NanoScope IV microscope in tapping mode with a silicon cantilever. Samples were prepared in UHV and removed for analysis in air.

## Results

**1. FTIR Data.** Figure 1a shows the FTIR spectrum of pentacene crystals at low concentration in KBr, measured using diffuse reflectance infrared spectroscopy. Peaks are observed at 3045 and 3074 cm<sup>-1</sup> with a shoulder near 3022 cm<sup>-1</sup>. The region above 3000 cm<sup>-1</sup> is a region often associated with C–H stretching vibrations of *sp*<sup>2</sup>-hybridized carbon atoms, and the strong absorption bands in this region are consistent with the fact that all carbon atoms in pentacene are *sp*<sup>2</sup>-hybridized. There is also a small amount of absorption between 2800 and 3000 cm<sup>-1</sup>, but this is very weak in intensity compared to the peaks above 3000 cm<sup>-1</sup>.

Figure 1b shows an FTIR spectrum of a silicon sample after exposure to a small dose (0.005 L) of pentacene. In addition to large peaks at 3019 and 3054 cm<sup>-1</sup>, the spectrum shows significant peaks at 2870 and 2922 cm<sup>-1</sup>, and the appearance of an absorption feature at 2091 cm<sup>-1</sup>. The region from 2800 to 3000 cm<sup>-1</sup> is characteristic of *sp*<sup>3</sup>-hybridized C–H stretching vibrations, and the presence of new peaks in this region suggests that when pentacene molecules interact with Si(001) at least some of the C atoms undergo a change from *sp*<sup>2</sup> to *sp*<sup>3</sup> hybridization. The 2091 cm<sup>-1</sup> peak matches the frequency of Si–H vibrations. The presence of this peak demonstrates that at least some of the pentacene C–H bonds are cleaved upon adsorption.

To test whether this initial interfacial layer is stable, the sample was heated to 400 K for two minutes. No changes in frequency or intensity were observed. Because under these same conditions pentacene multilayers will desorb from the surface (vide infra), the results of this experiment indicate that the 0.005



**Figure 2.** UPS spectra of the Si(001) surface after exposure to different amounts of pentacene: (a) 0 L, clean Si(001)-(2 × 1), (b) 0.008 L, (c) 0.04 L, (d) 0.07 L, and (e) 0.2 L. Spectrum (f) was obtained after heating to 400 K and spectrum (g) after heating to 650 K to desorb pentacene multilayers. On the right is a blow-up of the 0–5 eV range. Above the spectra are the five lowest energy pentacene  $\pi$  orbitals, shifted down by 5.4 eV from the gas-phase values reported in ref 26.

L nominal exposure does not produce multiple pentacene layers and yields a thermally stable interfacial layer.

Figure 1c shows an FTIR spectrum of a multilayer thin film of pentacene deposited on the clean Si(001) surface (nominal exposure 0.009 L). This spectrum has peaks at 3019 and 3054  $\text{cm}^{-1}$  and a smaller peak at 2919  $\text{cm}^{-1}$  that all arise from C–H species, and a peak at 2087  $\text{cm}^{-1}$  that is attributed to Si–H species. A comparison of the multilayer (Figure 1c) and monolayer (Figure 1b) spectra shows that most of the C–H modes have approximately the same frequency, but there are large changes in the relative intensities of the peaks. In the spectrum of the multilayer film (Figure 1c), the intensity of the peaks in the  $sp^2$ -hybridized region ( $>3000 \text{ cm}^{-1}$ ) is much more intense than those in the  $sp^3$ -hybridized region ( $<3000 \text{ cm}^{-1}$ ), while in the monolayer film (Figure 1b) these peaks are closer in relative intensity. The large intensity of peaks  $>3000 \text{ cm}^{-1}$  relative to those  $<3000 \text{ cm}^{-1}$  in Figure 1c indicates the formation of a multilayer pentacene film. To confirm the formation of a multilayer film, samples were analyzed by ex situ atomic force microscopy (AFM) (see below).

The multilayer sample in Figure 1c was heated to 350 K for 5 min. Although our estimated temperature is slightly lower than the value of 380 K reported as the peak desorption temperature from thick multilayer films,<sup>12</sup> our data and existing vapor pressure data<sup>24</sup> indicate that thin multilayer films desorb within 5 min at the temperature of  $\sim 350 \text{ K}$  used in our experiments. After heating, the FTIR spectrum (Figure 1d) shows that the large peaks above  $3000 \text{ cm}^{-1}$  are much smaller and three peaks are now visible at 2880, 2919, and 2978  $\text{cm}^{-1}$ . A peak centered at 2880  $\text{cm}^{-1}$  is also present, slightly broader and slightly shifted from that in Figure 1b. The decrease in the intensity of the 3019 and 3054  $\text{cm}^{-1}$  peaks indicates that most of the pentacene desorbs during heating. However, the residual presence of the three peaks below  $3000 \text{ cm}^{-1}$  indicates the presence of a chemisorbed layer that is spectroscopically similar to that prepared by submonolayer deposition onto the clean surface, as in Figure 1b.

**2. UPS Data.** Ultraviolet photoemission was used for examining the valence band characteristics of pentacene adsorbed on Si(001). UPS spectra as a function of pentacene exposure and temperature are shown in Figure 2. The clean silicon surface (Figure 2a) exhibits few features other than a sharp peak at 0.8 eV, which is attributed to the Si=Si dimer

bond that forms upon surface reconstruction.<sup>25</sup> After limited exposure (0.008 L, Figure 2b) to pentacene, the intensity of the 0.8 eV peak decreases notably, but is still recognizable as a slight bump in the spectrum. This implies that some of the surface dimers have reacted with the adsorbed pentacene, but that some of them remain unreacted. The appearance of peaks at 6.6 and 8.9 eV indicates that pentacene molecules have adsorbed on the surface, as this region has been shown to be characteristic of carbon  $\sigma$  bonds.<sup>26</sup>

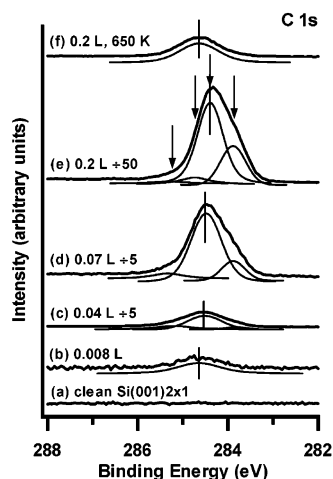
After further pentacene exposure (Figure 2c), the Si=Si dimer peak at 0.8 eV disappears. It is clear that other changes have taken place in the region below 5 eV as the originally featureless spectrum exhibits small peaks at 2.9 and 3.4 eV. After 0.07 L exposure (Figure 2d), peaks at 1.2, 2.4, 2.9, 3.5, and 4.0 eV appear in the spectrum and then grow in further, but do not change in position or relative intensity by 0.2 L exposure (Figure 2e). These low binding energy peaks correlate well with the relative energies of the  $3b_{2g}$ ,  $2a_u$ ,  $3b_{8g}$ ,  $2b_{2g}$ , and  $3b_{1u}$  orbitals of pentacene<sup>27,28</sup> when a static shift of 5.4 eV is included to account for the difference between the ionization potential of gas-phase and surface-bound molecules. This strong correlation suggests that intact pentacene molecules are present at the surface of the multilayer film. The absence of any further change after a nominal exposure of 0.07 L implies that the electronic structure has reached a bulklike state where further deposition of pentacene does not cause the spectrum to change. The electronic structure at this point is much different than that of the low coverage spectrum, suggesting that the initial layer of molecules is significantly different electronically than a thicker film.

The valence band character of the sample after heating is given in Figures 2f and 2g. The sample was heated for 10 intervals of two minutes each. Temperature was increased for each successive interval, with a complete range from 300 to 650 K. After each interval the sample was allowed to cool to room temperature. Two representative spectra are shown in Figure 2. Figure 2f was obtained after the sample had been heated to 400 K and Figure 2g was taken after the final heating period (650 K). A broad peak at 3.3 eV appears in both of these spectra and is the only feature below 5 eV. This peak has been seen in other work and has been attributed to the silicon substrate.<sup>14,29</sup> None of the other peaks below 5 eV that existed prior to heating (Figure 2e) show up after heating (Figure 2f or 2g). Broad peaks at 6.6 and 8.8 eV are seen in both spectra, making them appear similar to Figures 2b and 2c. With mild heating, the general shape of the spectrum changes from that of a bulk film (Figure 2e) to resemble a low coverage spectrum (Figure 2c). With further heating, the shape changes to look more like that of the submonolayer film (Figure 2b). These changes show that desorbing pentacene from a multilayer interface results in an electronic structure very similar to that observed at submonolayer coverage on the clean Si surface.

**3. XPS Data.** Figure 3 shows the C(1s) XPS spectra of the same Si(001) sample and the same pentacene exposures as the UPS spectra in Figure 2. At low exposure, a single carbon peak appears at 284.6 eV (Figure 3b). The spectrum evolves from this single peak at 0.008 L to four peaks at 283.9, 284.4, 284.7, and 285.3 eV at 0.2 L exposure (Figure 3e). The appearance of new peaks as the pentacene layer grows thicker shows that the chemical environment of the molecules in the thicker film is different from that of the interfacial molecules.

The C(1s) XPS spectrum after heating the same sample to 650 K is shown in Figure 3f and it is fit to a single peak with a binding energy of 284.6 eV. The comparatively low binding





**Figure 3.** XPS spectra of the Si(001) surface after exposure to different amounts of pentacene: (a) 0 L, clean Si(001)-(2 × 1), (b) 0.008 L, (c) 0.04 L, (d) 0.07 L, (e) 0.2 L. Spectrum (f) came after heating the sample to 650 K to desorb pentacene multilayers.

**TABLE 1: C/Si Ratios and C Surface Densities for Various Pentacene Exposures**

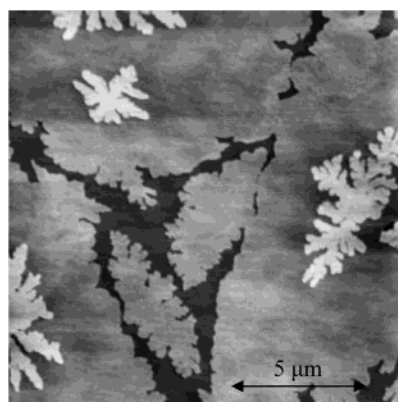
exposure (L)	$A_C/A_{Si}$	$\sigma$ (C atoms/cm <sup>2</sup> )	$\sigma/22$ (molecules/cm <sup>2</sup> )
0.008	0.061	$6.1 \times 10^{14}$	$2.8 \times 10^{13}$
0.04	0.38	$3.8 \times 10^{15}$	$1.7 \times 10^{14}$
0.07	1.6		
0.2	21		
0.2 + heating	0.23	$2.3 \times 10^{15}$	$1.1 \times 10^{14}$

energy of this peak is identical to that observed at the lowest coverage of pentacene on the clean surface and the area is slightly larger.

XPS data were also analyzed quantitatively to determine actual coverage of the pentacene layer at each step in the dosing procedure and thereby to determine at which point a complete monolayer had formed. Peak areas in XPS spectra are proportional to the number of carbon and silicon atoms in the area of the analysis, so the C/Si area ratio can be used to approximate the number of pentacene molecules in a given area. The ratio of the carbon ( $A_C$ ) and silicon ( $A_{Si}$ ) areas,  $A_C/A_{Si}$ , the number density of silicon,  $\rho_{Si}$ , the electron escape depth,  $t_{esc}$ , the atomic sensitivity factors,  $S_{Si}$  and  $S_C$ , and the surface density of carbon atoms,  $\sigma$ , are related by the equation:

$$\frac{A_C}{A_{Si}} = \frac{\sigma \cdot S_{Si}}{\rho_{Si} \cdot t_{esc} \cdot S_C} \quad (1)$$

This equation assumes that the pentacene film is thin enough that it does not attenuate the signal from the underlying bulk Si. Direct measurements in our XPS system of the attenuation of the Si signal induced by pentacene overlayers shows that an exposure of 0.2 L yields an average thickness of  $\sim 56$  Å. On the basis of this result, we estimate that at pentacene exposures of  $<0.07$  L there is no significant attenuation effects and eq 1 should be valid. For the higher exposures (0.07 and 0.2 L), this simple model for surface density breaks down, as evidenced by attenuation of the Si(2p) signal and the plateauing of the C(1s) signal. While in principle the attenuation effects can be corrected for if the layers are planar, the presence of local height variations due to island formation makes this difficult in practice. These electron attenuation effects make analysis of high exposure data complicated, but they do not affect analysis of the first monolayer of adsorbed pentacene molecules, which is the focus of this paper.



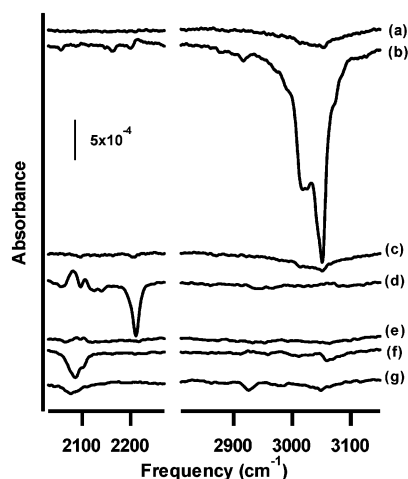
**Figure 4.**  $15 \mu\text{m} \times 15 \mu\text{m}$  AFM image of pentacene multilayers on clean Si(001). The height difference between features is between 1 and 1.5 nm, suggesting that each represents a single molecular layer step.

Measured C/Si area ratios for each exposure level are given in Table 1. An approximate value for the escape depth was calculated from the inelastic mean free path for an electron with kinetic energy of 1400 eV<sup>30</sup> emerging at an angle of  $53^\circ$  from the surface normal. The number of pentacene molecules per square centimeter for each exposure level was then calculated from eq 1. As shown in Table 1, the C/Si ratio increases with increasing exposure and then upon heating returns to 0.23, a value between those measured at 0.008 and 0.04 L exposure (0.061 and 0.38, respectively). These experiments indicate that the strongly bonded organic layer produced by depositing a multilayer film and then desorbing the thermally labile component is similar in number density of molecules to that for which the UPS data show a transition from a “disrupted” to a pentacene-like electronic structure.

**4. Atomic Force Microscopy Data.** Figure 4 is an AFM image after a nominal exposure of 0.04 L pentacene on clean Si. Three layers are visible, indicating the formation of a multilayer film, and the height of each layer is between 1 and 1.5 nm, roughly the molecular height of pentacene. Some crystals are as large as a few microns in length, which makes them comparable to those seen in past studies.<sup>21</sup> This image suggests that the manner of deposition employed in this study produces multilayer pentacene films consistent with those seen in previous work.

**5. Pentacene on an Organic-Functionalized Si Surface.** To determine how organic functionalization of the Si(001) surface affects the formation of subsequent interfaces to pentacene, we performed experiments on Si(001) surfaces that were first functionalized using cyclopentene molecules and then exposed to pentacene. Previous studies have shown that cyclopentene forms an ordered, self-terminating monolayer on the Si(001) surface via reaction of the C=C double bond with the dangling bonds of the Si(001) surface, thereby leaving the surface terminated with a saturated hydrocarbon monolayer.<sup>17</sup> To distinguish the initial organic layer from the subsequent pentacene layers in infrared spectroscopy, we used cyclopentene- $d_8$ , where all hydrogen atoms were replaced with deuterium. Isotopic labeling yields clearly separated spectra for the interfacial monolayer and the subsequent pentacene layers.

Figure 5 shows IR spectra from a Si(001) surface that was exposed to saturation coverage (10 L) of cyclopentene- $d_8$  followed by deposition of pentacene (nominal exposure 0.2 L) on top. Previous experiments showed that the 0.2 L exposure is sufficient to form a multilayer thin film. Because our experimental apparatus does not allow pentacene to be evaporated onto the sample when in position for obtaining FTIR



**Figure 5.** FTIR spectra of the desorption of species from a Si(001)/cyclopentene- $d_8$ /pentacene interface after heating to temperatures of (a) 375 K for 5 min, (b) 415 K for 5 min, (c) 415 K, additional 10 min, (d) 625 K for 10 min, (e) 700 K for 10 min, (f) 750 K for 5 min, and (g) flash to 1000 K.

spectra, the pentacene-covered sample was prepared first and then transferred within the ultrahigh vacuum chamber to the FTIR stage. A set of FTIR spectra was then recorded in which the sample was annealed to an elevated temperature for  $\sim 5$  min, cooled back to room temperature, and another FTIR spectrum was measured. While these data can be presented in several ways, in Figure 5 the spectra show the results in which the previous FTIR spectrum in this set was used as a background. Each spectrum therefore represents the change in the spectrum resulting from the specific heating cycle of interest, with positive peaks indicating an increase in vibrational intensity after heating, and negative peaks indicating a decrease in intensity.

After heating the sample to  $\sim 375$  K (Figure 5a), there is a small, broad negative feature between 3013 and 3054  $\text{cm}^{-1}$ . Heating to 415 K yields two very large negative peaks at 3019 and 3052  $\text{cm}^{-1}$  (Figure 5b); because there is no corresponding increase in intensity of any other features, we associate these changes with desorption of the pentacene molecules from the multilayer film. Ten additional minutes of heating at that same temperature (415 K) results in only a small change in absorption at frequencies  $> 3000$   $\text{cm}^{-1}$  (Figure 5c), but there is also a small negative peak at 2203  $\text{cm}^{-1}$ . This peak does not appear in any prior spectra and it is in the frequency region characteristic of C–D species.<sup>31–34</sup> After heating the sample to  $\sim 700$  K (Figure 5d), the negative peak attributed to desorption of C–D species is much larger and is located at 2211  $\text{cm}^{-1}$ . In addition, two positive peaks appear at 2082 and 2106  $\text{cm}^{-1}$ , in the region characteristic of Si–H absorption, indicating possible dissociation of pentacene and attachment of H atoms to the surface. Heating to 800 K does not produce any changes in the C–D stretching region, but leads to a slight increase in intensity for peaks in the Si–H stretching region (Figure 5e). At 850 K (Figure 5f), the Si–H peak is negative, suggesting that this temperature is hot enough to remove H atoms bound to the surface. Flash annealing the sample up to  $\sim 1000$  K (Figure 5g) shows a slight negative peak in the Si–H region; however, the small intensity of the peak suggests most of the adsorbed H atoms had already been removed during the previous heating cycle.

These data show that under the conditions employed here, pentacene multilayers are removed at temperatures between 375 and 415 K; more extensive heating leads to partial removal or dissociation of the cyclopentene- $d_8$  layer. The small Si–H peak

visible after heating to 700 K suggests that some pentacene molecules did not desorb with the rest of the pentacene molecules at 415 K; these remaining molecules undergo C–H bond cleavage when heated to 700 K, leading to Si–H species on the surface.

## Discussion

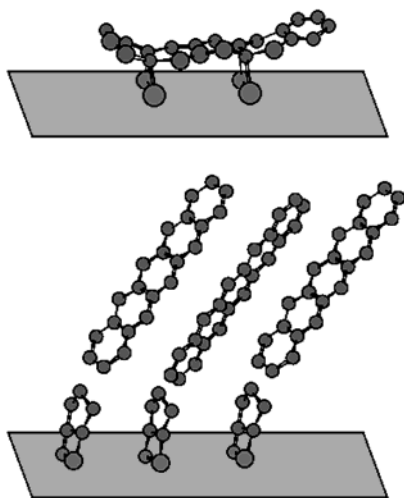
**1. Bonds Formed at the Interface with Clean Si(001).** Our data show that the interaction between pentacene and the Si(001) surface involves an initial layer of molecules whose electronic structure and crystallinity differ significantly from those of thicker multilayer pentacene films, in agreement with previous studies.<sup>3,11–14</sup> By applying more chemically sensitive methods to this problem, we are able to gain additional insight into the chemistry of the interfacial layers and their resulting impact on electronic properties of the interface and crystal growth.

FTIR spectra (Figure 1) show a clear difference in C–H stretching vibrational absorption between low pentacene coverage and multilayer coverage. The valence band spectrum also changes with dosing level as peaks in the 0–5 eV region appear only after the first monolayer is complete (Figure 2). In addition, the C(1s) core level spectrum changes dramatically as more pentacene is deposited on the surface (Figure 3). These three pieces of evidence make it very clear that the initial layer of pentacene on the Si(001) surface is different chemically and electronically from a thin film of pentacene, thus corroborating previous results.<sup>14</sup>

Since most surface analysis methods such as UPS are more easily applied to thin films than to buried interfaces, it is important to establish whether the initial interfacial layer changes when additional pentacene is deposited on top of it. We determine this by comparing the FTIR spectrum at low coverage (Figure 1b) with both that of a thicker multilayer film (Figure 1c) and that after the thick film is removed via low-temperature annealing (Figure 1d). The most significant observation is that Figures 1b and 1d both show peaks at 2870 and 2919  $\text{cm}^{-1}$ , in the region commonly ascribed to the C–H stretching vibrations of  $sp^3$ -hybridized carbon atoms. No significant structure is observed in this region in the multilayer film (Figure 1c). The spectrum after the excess layers have been desorbed from the multilayer film shows an additional peak at 2980  $\text{cm}^{-1}$  and also shows higher intensity in the Si–H region ( $\sim 2090$   $\text{cm}^{-1}$ ) compared with the spectrum produced by submonolayer deposition.

On the basis of the infrared spectra, we conclude that the interfacial layer has much more  $sp^3$ -hybridized carbon than the multilayer spectrum. This increase in  $sp^3$ -hybridized carbon can arise without dissociation via the interaction of the C=C double bonds with the Si=Si bonds of the silicon surface to form a variety of cyclic interface structures.<sup>17,18,35</sup> However, the presence of Si–H vibrational modes also suggests that cleavage of C–H bonds occurs. We conclude that heating of a multilayer pentacene thin film results in molecular desorption of all molecules but those bound at the interface and that these interfacial molecules are chemically unchanged from their initial adsorption.

As a point of comparison, we note that benzene, also an aromatic molecule with only  $sp^2$ -hybridized carbon atoms, adsorbs to the Si(001) surface and shows infrared vibrational modes at 2899 and 2944  $\text{cm}^{-1}$  that are similar to those we observe here for pentacene.<sup>35,36</sup> In the case of benzene, however, adsorption occurs entirely through the C=C bonds without any true bond cleavage; as a consequence, benzene can be reversibly adsorbed onto and desorbed from the Si(001) surface.<sup>37,38</sup>



**Figure 6.** Cartoons of (a) pentacene forming covalent C–Si bonds to the silicon surface and deforming from its planar geometry, and (b) pentacene interacting with a cyclopentene-modified silicon surface. Because the reactive dangling bonds have been terminated with an organic monolayer, pentacene is free to adopt a more electronically favorable crystal structure.

Toluene and xylene, with one and two methyl groups external to the aromatic ring, have been shown to adsorb in a similar manner but less reversibly and with some dissociation of C–H bonds in the methyl group.<sup>35</sup> Pentacene exhibits slightly different behavior, undergoing some C–H bond cleavage from C atoms in the fused ring system. This cleavage results in nearly *irreversible* adsorption of the pentacene species to the Si(001) surface, an interaction which is likely stronger than that of toluene and xylene based on the thermal stability of the initial layer. This correlation to other aromatic molecules substantiates the conclusion that bonds are formed between the interfacial molecules and the substrate, but it also provides insight into how molecules with common characteristics can behave differently on the Si(001) surface.

**2. Disruption of Electronic Structure and Molecular Shape at the Interface—Influence on Nucleation and Crystal Formation.** The above experiments show that the initial pentacene layer forms covalent bonds to the underlying silicon surface, and that this bond formation necessarily disrupts the  $\pi$  conjugation within the molecule. Valence band photoemission data provide information on how these changes in hybridization alter the electronic properties of the film. While bulk valence band spectra of pentacene and other conjugated  $\pi$ -electron systems typically show  $\pi$  electron bands between 0 and 5 eV, no significant structure is observed from pentacene on Si(001) until reasonably high coverage (0.07 L, Figure 2d). The absence of significant conjugated  $\pi$  structure in the interfacial layer means that the electronic properties that make pentacene desirable for organic electronics applications (e.g., high electron mobility, good  $\pi$  overlap) will be different for the interfacial layer than for bulk pentacene. Such an interface is likely to be a hindrance to some electronics applications.

A more detailed, atomistic picture can be made on the basis of scanning tunneling microscopy images, which show that at submonolayer coverage, pentacene molecules lie approximately flat on the Si(001)-(2  $\times$  1) surface.<sup>14,39</sup> Calculations have shown that covalent bonding between the carbon atoms in pentacene and the dangling bonds from the substrate gives charge distributions that can explain the STM images.<sup>40</sup> Figure 6a is a schematic representation of a pentacene molecule bound to the surface through covalent bonds. To understand why this covalent

bond formation disrupts the crystallinity of pentacene films, it is important to note that formation of chemical bonds to the underlying silicon and the transition to  $sp^3$ -hybridization must also disrupt the planarity of the pentacene molecules. In polycyclic aromatic solids such as pentacene, the energy of crystallization arises largely from the van der Waals forces between adjacent molecules. The  $\pi$ – $\sigma$  interaction of adjacent molecules can occur most efficiently when the molecules are in a planar geometry. Thus, molecules that are bound directly to the surface and are no longer planar are likely to serve as poor sites of nucleation due to their disrupted shape. A recent study reported intense emission at 4.4 eV in UPS measurements of pentacene on SnS<sub>2</sub> surfaces, and attributed this high intensity to molecules lying nearly parallel to the surface plane.<sup>11</sup> In our experiments we observe almost no intensity at this energy at submonolayer coverage, and only a weak peak at 4.0 eV (comparable to the intensity of the other pentacene-derived peaks) in multilayer films. This result, combined with our observation of AFM-based step heights of  $\sim 1.5$  nm for multilayer films, indicate that on silicon surfaces the pentacene multilayers involve molecules aligned closer to the surface normal, as depicted in Figure 6b. Although our data suggest that on silicon the first monolayer of molecules lie approximately flat on the surface (as in Figure 6a), the absence of intense emission at 4.4 eV is consistent with the presence of significant molecular distortions from planarity and disruption of the  $\pi$  electron system due to covalent bond formation to the underlying silicon.

The idea of disrupted molecular structure leading to poor crystal structure may be one that applies to many areas of surface chemistry. Deposition onto a reactive substrate often leads to a chemical reaction on the surface, which in turn results in a physical change in molecular shape of the adsorbate. It is highly likely that this change in shape then affects the ability of subsequent layers to adopt their ideal crystalline phase. In addition, the surface reactivity of the substrate prior to deposition inhibits diffusion of the initial layer and therefore leads to a higher density of nucleation sites and an increased number of grain boundaries.

A recent study showed that when depositing pentacene on a clean Si(001) surface, nucleation of bulk pentacene-like crystals does not occur until after an initial coverage of  $\sim 20\%$  of a “monolayer equivalent”.<sup>21</sup> After this “dead layer” has been formed, subsequent deposition leads to many layers of pentacene, such as those shown in Figure 4. In these earlier experiments, 20% of a monolayer equivalent was based upon the amount of pentacene needed to produce a complete layer in an orientation similar to a single-crystal orientation. However, STM experiments at low coverage, along with our studies showing a high degree of electronic disruption, indicate that the molecules are likely lying approximately flat on the surface. In this case 20% of a monolayer equivalent actually covers an area substantially larger than 20% of the surface. If each pentacene molecule is modeled as a rectangle 14.1 Å by 5.0 Å (the approximate length and width of a pentacene molecule<sup>5</sup>), a full monolayer of flat-lying molecules would correspond to  $1.4 \times 10^{14}$  molecules/cm<sup>2</sup>. For comparison, our XPS measurements suggest that the monolayer corresponds to a molecular density of  $1.1 \times 10^{14}$  molecules/cm<sup>2</sup>, while 20% of a crystalline pentacene monolayer corresponds to  $8.2 \times 10^{13}$  molecules/cm<sup>2</sup>. Within the combined error limits of each measurement, the data are consistent with a model in which the initial pentacene molecules interact strongly with the surface, lying approximately flat and excluding further adsorption within an area slightly



larger than the planar projection of the molecule. Once this layer is completed, further pentacene molecules adsorb, forming more weakly bound pentacene layers.

**3. Pentacene on Chemically Modified Silicon.** The passivating effect of an organic monolayer can improve the nucleation and growth of pentacene on the Si(001) surface by reducing the surface energy of the Si=Si double bonds, leaving only a simple hydrocarbon-like surface that has no available reactive sites for bonding to pentacene.<sup>21</sup> By reducing the possibility of bond formation with the pentacene layer, the crystal formation can more readily be controlled by the pentacene–pentacene interactions instead of surface-to-molecule bond formation. This situation is represented schematically in Figure 6b, where the initial layer of pentacene is shown adopting a crystalline orientation instead of the disrupted planar configuration shown in Figure 6a. When the surface is exposed to cyclopentene-*d*<sub>8</sub> followed by pentacene, the absence of available sites leaves the pentacene molecules unperturbed, so that they retain their original *sp*<sup>2</sup> hybridization and planar geometry. This is clearly evidenced through the FTIR spectra in Figure 5a–c by the absence of any C–H vibrational features at 2870 or 2919 cm<sup>−1</sup> that might be ascribed to *sp*<sup>3</sup>-hybridized carbon atoms.

The appearance of an intense C–D peak at 700 K (Figure 5d) indicates that this temperature is hot enough to desorb the terminating monolayer of deuterated cyclopentene. Another interesting feature that appears in this same temperature region is the absorption at 2082 and 2106 cm<sup>−1</sup>. The fact that they are positive peaks indicates that Si–H bonds are *forming* at high temperatures. This most likely arises from some pentacene molecules remaining on the surface until the cyclopentene desorbs and then undergoing a reaction with the exposed surface, in a manner similar to submonolayer coverages. This reaction, however, takes place only when the surface is heated enough to remove the passivating layer and open up reactive sites.

## Conclusion

We have shown that the initial layer of pentacene, an aromatic molecule with semiconducting properties well-suited to thin-film transistors, adsorbs strongly to the Si(001)-(2 × 1) surface. FTIR data confirm the formation of Si–C bonds and indicates that there is a limited amount of dissociation of the interfacial molecules upon adsorption. The chemisorbed layer remains the same both chemically and electronically throughout the deposition and heating process. The formation of a chemisorbed layer inhibits the growth of pentacene crystals on the clean silicon surface and is undesirable for organic electronic applications. Passivation of the reactive Si surface with a molecule such as cyclopentene prior to pentacene deposition leads to a surface that interacts weakly with the thin film and therefore is likely to have superior electronic characteristics as well as wider application in organic electronics.

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