

Optical and Electronic Anisotropy of a π -Conjugated Molecular Monolayer on the Silicon(001) Surface

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The electronic and optical properties of an oriented monolayer of a π -conjugated molecule, 9,10-phenanthrenequinone on a silicon(001) substrate were investigated. The adsorption of 9,10-phenanthrenequinone onto a single-domain, 4° -miscut Si(001) surface leads to an oriented monolayer film with intact π conjugation. Reflectance-difference spectroscopy (RDS) was used to probe the optical properties of the layer of 9,10-phenanthrenequinone, and comparison spectra were obtained on a monolayer 1,2-cyclohexanedione, a nonconjugated molecule that has a nearly identical structure at the Si–O–C interface. RDS spectra of the 9,10-phenanthrenequinone monolayer show a strong absorption feature at 5.2 eV due to π – π^* transitions within the molecule, while spectra of the nonconjugated analogue show no feature in this region. Further information about the electronic structure is provided by ultraviolet photoemission spectroscopy of the chemisorbed monolayers and by ultraviolet–visible absorption spectroscopy of the parent compounds. The experiments confirm that it is possible to create a macroscopic optical anisotropy in organic films on silicon surfaces using the Si(001) dimers to control the molecular orientation.

Introduction

Surface-tethered organic molecules are of increasing interest in a number of potential applications, including organic and molecular electronics and chemical sensors.^{1–8} Since optical and electrical properties are intimately connected, optical methods of characterization can provide complementary information about the electronic structure of organic layers. When organic monolayers are adsorbed onto semiconducting substrates such as silicon, however, measurement of the optical properties of monolayer films is difficult because the spectra are overwhelmed by bulk optical properties. The response of the near-surface region can be separated from that of the bulk by taking advantage of the fact on Si samples that are purposely miscut by $\sim 4^\circ$ from the (001) plane, the surface adopts a single-domain structure in which all the dimers are oriented along the same direction, separated by biatomic steps. (Figure 1).^{9,10} Since bulk silicon is symmetric, measurement of the optical properties using polarized light can then be used to characterize the optical response of the near-surface region.^{11,12} While this method has been applied previously to characterize the changes in optical properties of different surface reconstructions and the effects of atomic adsorbates,^{13–31} it has not been widely used to characterize the optical properties of organic molecules.^{32–36}

To use polarization spectroscopy on organic films, it is necessary to have organic layers that have a preferred orientation in the surface plane. While most means of fabricating organic monolayers leave the surface disordered or with a complex domain structure,^{37–39} we have recently shown that it is possible to prepare monolayer films of organic molecules on the Si(001) surface using a class of reactions that involve the interaction of one or more unsaturated bonds of an organic molecule with the Si=Si dimer bonds of the Si(001) surface.^{40–43} One unique

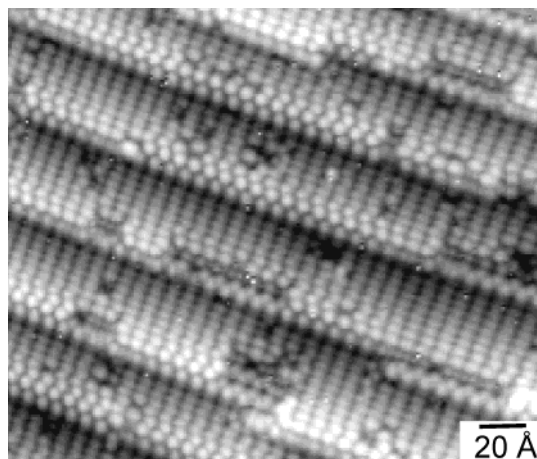


Figure 1. STM image of the 4° miscut reconstructed Si(001) surface showing double height steps leading to a surface with dimers oriented along the entire length of the sample.

feature of these reactions is that because they involve formation of two bonds between each molecule and the underlying substrate, the orientation of the underlying dimers is templated into the direction of the attached organic molecules, thereby giving rise to ordered arrays of oriented organic molecules.

Molecules with conjugated π electron systems are of particular interest because such molecules often form organic semiconductors and, when present in monolayer films, are expected to exhibit unusual electronic properties.^{5,6} In this paper, we combine the use of reflectance-difference spectroscopy with other probes of the electronic and optical properties to characterize the optical response of a monolayer of a simple π -conjugated organic molecule. By comparing molecules with similar interfacial chemistry but differing in their molecular structure, we also show that it is possible to separate transitions

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arising within the molecular layer from transitions associated with the underlying silicon substrate.

Experimental Section

Three different techniques were used to probe the electronic properties of a molecular film chemically adsorbed to the silicon surface. Reflectance difference spectroscopy (RDS)^{12,44} was used to probe the anisotropic electronic transitions of molecules adsorbed on the vicinal silicon(001) surface. The valence electron structure of the molecular film was also probed with ultraviolet photoelectron spectroscopy (UPS). Both RDS and UPS experiments were performed in a UHV chamber maintaining a base pressure of $<2 \times 10^{-10}$ Torr. The electronic transitions of the molecules in the solid phase were examined using ultraviolet–visible absorption spectroscopy. Combining the information from these techniques provides a greater understanding of the electronic nature of a molecular film adsorbed on the silicon surface.

Silicon(001) Samples. The silicon(001) surface undergoes a (2×1) reconstruction in which two adjacent atoms combine to create a dimer (Si=Si), giving rise to a (2×1) reconstruction. On longer length scales, Si(001) surfaces consist of rows of dimers; dimers on adjacent terraces separated by single-layer steps are rotated 90° with respect to one another, such that (001) surfaces normally consist of equal domains of the (2×1) and the equivalent, but rotated, (1×2) structure.^{45,46} However, if the sample is purposely miscut $\sim 4^\circ$ toward the [110] direction, the surface adopts a structure in which terraces are separated by double height (bi-layer) steps, leading to a single-domain surface in which all the dimers are oriented with the Si=Si dimer bond aligned parallel to the $[1\bar{1}0]$ direction.^{9,10,47} In our experiments, we use 4.0° miscut Si(001) surfaces to prepare oriented organic monolayers for RDS and UPS experiments.

Silicon samples for RDS and UPS experiments were cut from a polished n-type, phosphorus-doped, low-resistivity (0.010–0.020 Ω cm) Si(001) wafer miscut $4 \pm 0.1^\circ$ in the (110) direction. For the UPS experiments, the samples were scored and cleaved to produce edges parallel to the [110] and $[1\bar{1}0]$ directions. For the RDS experiments, the silicon wafer was cut with a diamond saw at 45° with respect to the [110] direction, preparing two different sets of samples with the surface crystallographic axes rotated by 90° . After cutting, the samples were cleaned by sonicating in acetone, followed by electronic grade methanol. The silicon samples were exposed to ozone for 15 min to remove any residual carbon contamination prior to being placed in the UHV chamber. Inside the vacuum chamber, the samples were outgassed overnight at 850 K and then annealed at 1400 K to remove the oxide layer, producing a clean, well-ordered (2×1) -reconstructed Si(001) surface.⁴⁸ The sample orientation and tilt angle were verified using a home-built scanning tunneling microscope. Figure 1 shows a scanning tunneling microscope image of the reconstructed Si(001)- 4° miscut surface, showing the narrow terraces separated by bilayer steps.

Molecules Studied. 9,10-Phenanthrenequinone (PQ) was purchased from TCI America with a purity of 99+%. The purity was analyzed locally using gas chromatography–mass spectroscopy and was found to contain no detectable impurities when compared with a standard literature spectrum.⁴⁹ It was therefore used without further purification. Since the vapor pressure of 9,10-phenanthrenequinone is small, only 1×10^{-8} Torr at 45°C ,⁵⁰ controlled dosing of the molecule onto the surface was achieved using a special Knudsen cell, consisting of a small boron nitride crucible, ~ 5 mm diameter \times 1 cm long, with an

internal sample well encircled by heating wires and a thermocouple. The empty crucible was outgassed at 200°C , and the 9,10-phenanthrenequinone-filled crucible was outgassed at 60°C to remove any contamination. After the sample was outgassed, the crucible was extended into the main chamber and positioned approximately 5 cm from the silicon surface while keeping the temperature below 100°C . In a previous study of this molecule, we found that adsorption onto Si(001) self-terminates after the first layer;⁵¹ consequently, accurate exposure is not needed to form a monolayer film. Exposures were determined using the pressure increase measured by an ion gauge 10 in. from the dosing crucible and the time of exposure ($1\text{L} = 1$ Langmuir $\equiv 1.0 \times 10^{-6}$ Torr \cdot s). Due to the geometry of the system, actual surface exposure is much higher than the calculated exposure; the chamber background pressure reached a maximum value of 5×10^{-9} Torr.

The vapor pressure of 1,2-cyclohexanedione (CHD) is reasonably high (1.8 Torr at 25°C ⁵²), allowing us to dose the molecule using a gas line and a variable leak valve. The chemical was further purified through at least three freeze–pump–thaw cycles prior to introduction in the chamber. To minimize contamination, the gas dosing line was baked overnight at 150°C to remove any residual water and other contaminants. The cooled lines were then exposed to CHD and purged several times before introducing the chemical into the main chamber to passivate the gas lines and minimize decomposition. Since the location of the ion gauge in the chamber is comparable to that of the sample when dosing with the gas line, the calculated exposure is a fair representation of the actual exposure at the silicon surface.

Techniques. Reflectance difference spectroscopy (RDS) was performed with an optical setup similar to that of Aspnes and co-workers,⁵³ consisting of a 100 W tungsten–halogen lamp focused through a polarizing prism to yield s-polarized light aligned to produce equal components of the electric field vector along each of the two principal crystallographic axes. The reflected light was collected at an angle of 3° from the surface normal and passed through a Hinds photoelastic modulator (PEM) resonating at 42 kHz, followed by a second polarizer rotated 45° off-axis with respect to the first polarizer and photoelastic modulator. The light was then focused into a CVI CM110 monochromator and measured with a UV-enhanced Hamamatsu photomultiplier tube. This external optical setup was coupled to a sample in UHV via a specially designed strain-free quartz window.

Because RDS measures very small changes in reflectance, small misalignments of polarizers and strain in the optics can give rise to a large birefringence, causing an increased baseline or extraneous peaks. Two checks were performed to verify the origin of the RDS features and to eliminate any effects that are not due to the sample. First, an internal isotropic standard was placed within the vacuum chamber at a position equivalent to the sample to identify features due to the optical system rather than the sample surface. This provided us with an accurate baseline to subtract from the spectra obtained from our sample. Second, analogous experiments were performed on samples prepared with the crystallographic axes rotated 90° from the original. Since $\Delta R/R$ is the normalized difference in reflectance of orthogonal crystallographic axes, spectral features arising from optical properties of the sample will exhibit a sign change between the two orientations while errors in alignment or strain in the optics will remain constant. Using these two methods of verifying the origin of RDS peaks allows us to ensure that the observed spectral features arise from the sample.

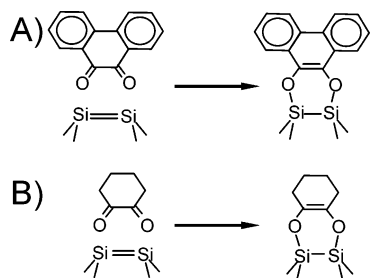


Figure 2. [4 + 2] attachment to the surface silicon(001) dimer of (A) 9,10-phenanthrenequinone and (B) 1,2-cyclohexanedione.

Ultraviolet–visible absorption spectra were obtained on solid films of 9,10-phenanthrenequinone prepared by dissolving the pure compounds in acetone, dripping the concentrated solution onto a quartz substrate and then, after allowing the acetone to dry, measuring the spectrum using a standard spectrophotometer. Ultraviolet photoelectron spectroscopy (UPS) was performed in a second UHV chamber containing a differentially pumped He discharge lamp emitting 21.2 eV ultraviolet photons. The energy distribution of the photoemitted electrons was analyzed using a Physical Electronics hemispherical electron energy analyzer with a 16-channel detector. Spectra were usually obtained for binding energies between 15 eV to -2.0 eV with respect to the Fermi energy, using a pass energy of 5.85 eV (yielding a resolution of 0.088 eV) and a step size of 0.05 eV. The Fermi energy of the molybdenum sample holder was used as an internal standard, adjusting the binding energy of the silicon by the same shift needed to bring the metal Fermi level to zero. UPS data were collected for two orientations of the Si(001)- 4° miscut sample. In one orientation the Si=Si dimer axis lies in the plane defined by the UV source, the sample, and the electron energy analyzer. In the second orientation the dimer axis is perpendicular to this plane. In both cases, the angle of incidence was typically 25° from the surface normal while a steep angle of emission (80° from the surface normal) was used to enhance surface sensitivity.

Results

Model Conjugated and Non-conjugated Systems. Two molecules, 9,10-phenanthrenequinone and 1,2-cyclohexanedione, were chosen as model systems to investigate the electronic changes at the organic-semiconductor interface. A previous study using STM, XPS, and FTIR showed that both 9,10-phenanthrenequinone and CHD react with the Si(001) surface through the oxygen atoms of the carbonyl groups, leaving a six-membered heteroatomic ring at the interface, as depicted in Figure 2.⁵¹ This reaction creates a new double bond between the two former carbonyl carbons, and is formally analogous to a heteroatomic Diels–Alder reaction.^{41,42,54} The reaction of PQ with the Si=Si dimer produces an aromatic phenanthrene-like ring exposed to vacuum, while in the case of CHD, a cyclohexene-like ring is created upon chemisorption. Scanning tunneling microscopy images with submolecular resolution that the molecules are aligned with the aromatic rings parallel to the Si–Si dimer bonds of the underlying Si substrate, and theoretical calculations show that the molecular ring is oriented perpendicular to the surface. The high degree of orientation, along with the self-terminating nature of the layer formation, makes this molecular system nearly ideal for studying the optical properties of a monolayer film.

RDS Difference Spectra. To emphasize the changes caused by the adsorption of organic molecules, we present the RDS data as difference spectra with the spectrum from the RDS

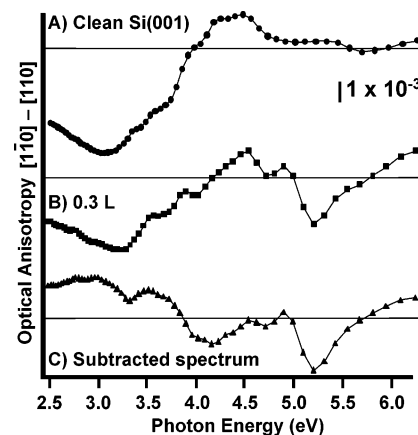


Figure 3. RDS spectra of (A) the Si(001)- 4° miscut surface annealed, (B) after exposure to 0.3 L 9,10-phenanthrenequinone, and (C) difference spectrum created by subtracting the annealed surface spectrum from the exposed surface spectrum. The horizontal lines represent zero for the individual measurement.

annealed surface subtracted from each spectrum taken after the surface was exposed to the molecule. This process is shown in Figure 3. The spectrum of annealed Si(001) (Figure 3a) shows a 3.0 eV negative peak, a less intense 3.7 eV shoulder, and a small positive 4.3 eV peak. This spectrum closely matches those in the literature.^{13,15,19,31} After exposure to 0.3 L of 9,10-phenanthrenequinone (Figure 3b), the intensity of the 3.0 and 3.7 eV features decreases, while the intensity of the 4.3 eV feature is altered asymmetrically with the lower energy portion more greatly attenuated. A new, sharp negative feature is evident at 5.2 eV. To better highlight the changes induced by the molecular layer, trace C shows the difference spectrum created by subtracting the exposed spectrum from that of the clean surface. After subtraction, the exposure-induced decrease in intensity of the 3.0 eV region is manifested in a broad rounded positive curve with a small, sharp depression at 3.3 eV. The 4.3 eV feature is altered to create a low intensity negative peak shifted to 4.2 eV after subtraction. Subtracting the two spectra does not alter the 5.2 eV feature since it was completely absent in the annealed spectrum. Representing the reflectance anisotropy of the exposed surface relative to the annealed surface allows us to clearly examine the changes occurring as a result of molecular adsorption.

Adsorption of 9,10-Phenanthrenequinone. The spectrum of the clean, 4° -miscut Si(001) surface was measured, and the sample was then exposed to 9,10-phenanthrenequinone and a new RDS spectrum was measured. RDS spectra were then obtained after successively higher exposures on the same sample. Figure 4 shows a series of spectra of a Si(001) samples exposed to PQ, after subtracting the spectrum of the clean Si(001) surface. After the first exposure of PQ (Figure 4A), the spectrum shows a small, sharp negative feature at 3.3 eV, a broad negative peak at 4.2 eV, and the appearance of a new peak near 5.2 eV. As the exposure is increased from 0.1 L up through 1.3 L, the position and intensity of the 3.3 eV feature are unchanged, but the 4.2 eV peak becomes sharper while retaining the same intensity, and the 5.2 eV peak initially increases in magnitude with exposure then decreases. For PQ bonded to the surface, the retention of aromaticity within the molecule is expected to contribute to electronic absorption within our spectral range, making electronic changes due to chemisorption a combination of both electronic absorption (ϵ'') and electronic polarizability (ϵ'). From Figure 4, it is clear that the presence of a monolayer film of organic molecules leads to significant changes in the RDS spectra. From these spectra alone, however, it cannot be

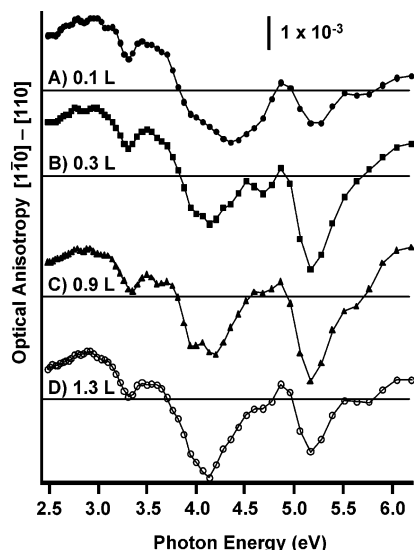


Figure 4. RDS spectra of Si(001) after various exposures to 9,10-phenanthrenequinone; (A) 0.1 L, (B) 0.3 L, (C) 0.9 L, and (D) 1.3 L. All spectra are subtracted from the spectrum of the annealed Si(001)-4° miscut surface obtained prior to exposure. The horizontal line indicates zero for each spectrum.

determined whether the molecule-induced changes arise entirely within the organic layer, or whether they might be originating from the silicon induced by changes in the surface structure.

Comparison of Conjugated vs Non-conjugated Molecular Layers. To better understand the molecular origin of the RDS features, we examined the RDS spectra of 1,2-cyclohexanedione adsorbed on the silicon. While both PQ and CHD link to the surface via two carbonyl groups, the surface adduct produced by CHD has only a single C=C bond in a cyclohexene-like structure. This single C=C bond is expected to have its lowest-lying π - π^* transition between 6.0 and 7.1 eV.^{55,56} Since this value is beyond the range of our measurement system, the CHD molecule is not expected to have any electronic transitions detectable in our RDS system. However, we expect any perturbations of the silicon dielectric function to be similar to those exhibited by PQ since the Si-O-C linkages for these molecules are similar.

After the spectrum of the annealed silicon surface was obtained, the sample was exposed to 1,2-cyclohexanedione, and a new spectrum was collected for the molecule-exposed surface. Figure 5 shows a set of difference RDS spectra collected for increasing exposure to CHD. After initial 10 L exposure, a sharp negative peak at 3.3 eV and a broader negative peak at 4.2 eV are apparent. With increasing exposure, neither the intensities nor positions of these peaks appear to change. The 3.3 and 4.2 eV features are very similar in the RDS spectra of both CHD and PQ exposed silicon surfaces. The most significant difference between the spectra of the two molecules investigated is the presence of the 5.2 eV peak in the RDS spectra of 9,10-phenanthrenequinone, which is completely absent in the spectra of 1,2-cyclohexanedione. Thus, the comparison of CHD and PQ shows that the 3.3 and 4.2 eV peaks arise from surface termination-induced perturbation of the bulk reflectivity, while the 5.2 eV feature is associated with the aromatic ring of the PQ molecule.

To further separate dielectric changes and electronic absorption events, we also measured the absorption spectra of the intact molecules. Figure 6 shows UV-vis absorption spectra of thin films of 9,10-phenanthrenequinone (Figure 6a) and phenanthrene (Figure 6b). The spectrum of phenanthrene shows a series of

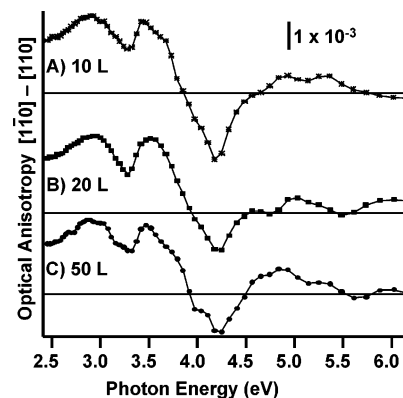


Figure 5. RDS spectra of the Si(001)-4° miscut surface after various exposures to 1,2-cyclohexanedione; (A) 10 L, (B) 20 L, and (C) 50 L. All spectra are subtracted from the spectrum of the annealed Si(001)-4° miscut surface obtained prior to exposure. The horizontal line indicates zero for each spectrum.

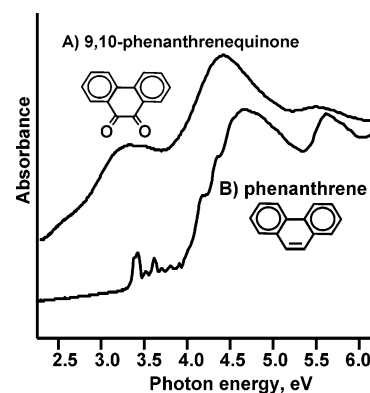


Figure 6. Ultraviolet-visible absorption spectra obtained from solid films of (A) 9,10-phenanthrenequinone and (B) phenanthrene. Vertical scales are not calibrated.

weak vibrationally coupled peaks at 3.6, 3.7, and 3.9 eV, a more intense absorption peak at 4.8 eV with shoulders at 4.4 and 4.3 eV, and a final peak at 5.7 eV. 9,10-Phenanthrenequinone shows a weak, barely resolvable feature at 2.7 eV, and more intense peaks at 3.4, 4.5, and 5.5 eV. These intensities and energies of these features are also very similar to those observed in solution-phase spectra.⁵⁷ After 9,10-phenanthrenequinone bonds to the silicon surface, the energy and intensity of electronic transitions are not expected to be identical to those measured in solid-phase UV-vis spectra, since bonding to the surface modifies the electronic structure. However, identifying the energy of electronic absorption in the solid-phase allows us to predict the spectral region in which an electronic absorption event would occur in the RDS spectra, thereby, separating absorption events from changes in the dielectric constant.

Valence-Band Photoemission. To better understand the origin of these electronic transitions within the monolayer, we obtained valence-band photoemission spectra of PQ monolayers on single-domain Si(001) surfaces. Figure 7 shows UPS spectra of a 9,10-phenanthrenequinone monolayer on two different silicon samples that were prepared such that the dimer orientations differ by 90°, as indicated in the figure. These spectra were obtained at glancing angle emission to increase the contribution of valence band electrons parallel to the surface and the higher energy peaks. Sample A was prepared such that the Si=Si dimer bond axis, [110], lies in the plane defined by the UV source, the sample, and the analyzer input aperture, while sample B is oriented with the dimer bond perpendicular to this plane. Thus, with sample A the collected electrons have

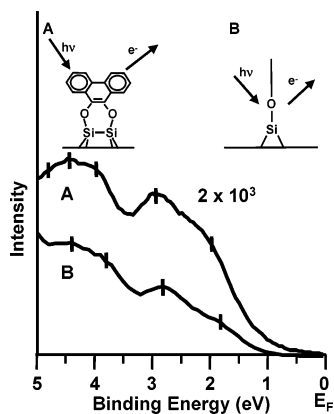


Figure 7. UPS spectra for 9,10-phenanthrenequinone-saturated Si(001)-4°-miscut surface. The inset indicates the orientation being probed. Spectrum A was aligned with the $[1\bar{1}0]$ axis parallel to the plane defined by the UV source, sample, and electron analyzer. Spectrum B was obtained with the $[1\bar{1}0]$ axis perpendicular to this axis. The spectra were normalized based on the peak intensity of higher binding energy features. Tick marks indicate peak energies.

momentum along $[1\bar{1}0]$ and $[001]$ directions, while with sample B the electrons have momentum along the $[110]$ and $[001]$ directions. Although in Figure 7 the spectra have been individually normalized, we find that dimer orientation of sample A consistently produces a much larger overall photoelectron yield, as well as differences in the relative intensities of various individual peaks. The spectrum obtained from sample A shows peaks at 2.0, 2.9, 4.0, 4.5, and 4.8 eV, while the spectrum obtained from sample B contains peaks at 1.8, 2.8, 3.8, and 4.3 eV. The difference in the photoelectron spectra for the two orthogonal directions indicate that the presence of a monolayer film of organic molecules leads to significant changes in the valence band compared to the annealed surface and obvious anisotropy between the two surface directions.

Discussion

Electronic Structure of the Silicon Surface. Before discussing the molecule-induced changes in the electronic structure at the interface, we first consider the optical response of the clean surface. The optical response of the Si(001)-4° surface and other, similar vicinal surfaces has been studied extensively with RDS, both experimentally^{29,31,58} and theoretically.^{18,22,28} There are a number of bulk and surface effects that contribute to the spectrum, and the relative importance of these has been the subject of some debate.^{12–14,16–18,21–25,28–30,58,59} The most pronounced features are usually seen near the bulk critical point energies associated with transitions between valence and conduction bands within the bulk crystal. For silicon, the (E'_0, E_1) and E_2 critical point energies are located at 3.4 and 4.3 eV.^{60,61}

As noted earlier, although bulk Si is isotropic, the steps and the (2×1) reconstruction induce some optical anisotropy in the RDS spectra of the clean single-domain Si(001) samples. Our spectra, such as in Figure 3, are very similar to those reported previously by other groups.^{11,16,18,23,28,29,31,58} In all cases, the clean surface gives rise to a negative peak at 3.0 eV, a small derivative-like structure near 3.4 eV, and a positive peak at ~ 4.2 eV. Since the sign of the peaks is indicative of orientation at the surface, the broad negative feature at 3.0 eV indicates lower reflectivity along the $[110]$ crystallographic direction, parallel to both the dimer bond and the step edge. This peak has been attributed to optical transitions involving both unoccupied dangling bonds of the clean silicon surface^{15,25,28} and, more recently, to a step-induced perturbation of the bulk dielectric

function.^{18,29,59} The origin of the 4.2 eV peak in the annealed spectrum has remained ambiguous for some time, appearing for nearly every silicon surface and reconstruction. Recently, it has been fit to a surface-modified bulk wave function caused by the localization of the optical response at the surface or interface.^{18,19} While the silicon surface gives rise to features detectable in RDS, it is significant that these features all occur at energies less than 5 eV.

A comparison of the raw RDS spectra in Figure 3a and 3b shows that adsorption of 9,10-phenanthrenequinone alters the RDS spectrum in four distinct ways: (1) it reduces the intensity of the broad peak near 3 eV, (2) the derivative-like structure near 3.3 eV that is barely apparent on the clean surface becomes significantly enhanced, (3) the shape and intensity of the 4.2 eV peak are altered, and (4) a new, negative peak arises at 5.2 eV. Although these changes can all be observed by comparing the raw spectra in Figure 3a and Figure 3b, they are more apparent in the subtracted spectra in Figure 3c and in Figure 4, which reflect the changes induced by the molecular adsorption.

The reduction in intensity of the broad 3 eV feature that we observe here parallels previous work with H-terminated samples. A previous study reported that increasing H-coverage reduces the intensity of this peak, leading to the conclusion that the 3 eV peak arises from transitions involving the “dangling bond” π state of the Si=Si dimers.^{16,25} Previous detailed studies of the 9,10-phenanthrenequinone/Si(001) system^{51,62} show that the chemical bond formation similarly eliminates the π bond of the reacting Si=Si dimers (as illustrated in Figure 2), as further confirmed by the photoemission data in Figure 7. Thus, our results showing a reduction in intensity of this peak after chemisorption are consistent with the idea that it may arise from transitions of the Si=Si dimer π bond.

The sharper feature at 3.2–3.3 eV observed after exposure to 9,10-phenanthrenequinone and 1,2-cyclohexanedione are similar to those observed in many previous RDS spectra of silicon samples in a variety of crystallographic orientations (including Si(001), Si(115), Si(114), Si(113), Si(110), and Si(111)), and a variety of terminations (including $-H$, $-O$, and Si/SiO₂).^{14,16,20,22,24,25} This insensitivity to the detailed surface structure or composition indicates that this feature arises from anisotropy in the bulk dielectric function induced by the symmetry-breaking at the interface. Previous studies have likewise observed the 4.2 eV peak, and have shown that it inverts in sign with increasing miscut angle.²³ Our data indicates that although this feature is mildly positive on the clean surface, it is strongly negative after dosing with either of the molecules investigated here. It appears that this feature may be more pronounced on our chemically modified samples than on the previously studied high-index samples.

While the features at 3 eV, ~ 3.3 eV, and ~ 4.2 eV all have parallels in previous measurements of silicon samples, the intense 5.2 eV feature we observed after dosing the 9,10-phenanthrenequinone has not been seen in previous studies of adsorbates on the silicon surface, and the energy of this peak does not coincide with any critical point energy of bulk silicon. Even more significant is that this feature is observed for Si(001) surfaces exposed to PQ (Figure 4), but not for samples exposed to CHD (Figure 5). Since our previous study showed that these molecules bond to the surface in a nearly identical manner, we conclude that the 5.2 eV feature arises from a discrete electronic absorption *within* the phenanthrenequinone molecule. Even more specifically, we attribute the 5.2 eV feature to an electronic transition involving the aromatic rings.

A peak at 5.5 eV in 9,10-phenanthrenequinone and 5.7 eV in phenanthrene is seen in the solid-phase absorbance spectrum that has been attributed to a π - π^* transition.⁶³ This electronic transition is likely the same transition observed in the RDS spectra. Our previous results⁵¹ have shown that phenanthrenequinone and cyclohexanedione molecules bond to the Si(001) surface with their molecular plane parallel to a Si=Si dimer bond and oriented perpendicular to the surface plane. For PQ, this orientation is further supported by STM images showing individual PQ molecules chemisorbed on the Si(001) surface with the molecular plane parallel to the Si=Si dimer bond.⁵¹ Since most planar aromatic molecules have the π - π^* transition dipole in the plane of the molecule,^{64,65} the negative sign of the 5.2 eV peak further supports a transition within the molecule aligned with the dimer bond axis. Combining the electronic absorption data with RDS indicates the presence of an electronic transition within the phenanthrenequinone molecule tethered to the silicon surface.

The 5.2 eV feature could, in principle, arise from anisotropy in the molecular polarizability or from absorption due to electronic transitions. Since the intensity of reflected light is smaller when the electric field is parallel to the Si=Si dimer bonds, and since the molecules are known to be oriented with their molecular plane perpendicular to the surface and parallel to the dimer bond,⁵¹ electronic transitions of the π system are expected to lie along the $[1\bar{1}0]$ direction (parallel to the Si=Si dimer bonds, perpendicular to the dimer rows) and $[001]$ directions (along the surface normal).⁶⁶ Solution-phase spectra show a molar extinction coefficient of 3×10^4 moles⁻¹ L cm⁻¹ for phenanthrene.⁶⁷ Assuming this value, a molecular density of 1×10^{14} molecules/cm² (one molecule per two Si=Si dimers, on average) would yield an absorbance of $\sim 5 \times 10^{-3}$. This is in good agreement with the observed value of 2.7×10^{-3} (Figure 4).

Alternatively, the 5.2 eV feature could arise from differences in the polarizability along the two different molecular orientations. Experimental measurements of phenanthrene show that the static (i.e., DC) polarizability is approximately 43 Å³ along the long molecular axis, 31 Å³ along the short molecular axis, and 16 Å³ perpendicular to the molecular plane.⁶⁸ Thus, we should expect similar values of ~ 43 Å³ along the $[1\bar{1}0]$ direction (parallel to the Si=Si dimer bond), and ~ 16 Å³ along the $[110]$ direction (perpendicular to the dimer bond). Although these are *static* polarizabilities, we expect the frequency-dependent polarizability to also have a higher value parallel to the molecular plane, since the transitions in the spectral region of interest arise from the π -orbital system. If one assumes a polarizability of 35 Å³ and a molecular packing of 0.004 molecules/Å³, then using the Lorentz-Lorenz formula one obtains a permittivity of ~ 5.2 for phenanthrene. A simple Fresnel 3-layer analysis shows that an increase in the permittivity by ~ 0.1 leads to a decrease in reflectivity of 10^{-4} . Since we expect the permittivity to be greater parallel to the molecular plane, the 5.2 eV feature might also be attributed to a resonance involving an increase in the permittivity parallel to the molecular plane. We note, however, that a frequency-dependent change in permittivity would be expected to have a dispersive line shape, while our experimental data appear to be better represented by a simpler negative-going peak. Thus, we believe that the observed peak shape is determined primarily by the real part of the dielectric function, but additional smaller contributions from the imaginary part cannot be ruled out.

Previous studies examining the reflected intensity of polarized light were able to calculate the frequency-dependent dielectric

functions (both molecular polarizability and absorbance) along the crystallographic orientations of single-crystal anthracene.⁶⁹ Their data indicate a large absorbance peak between 4.5 and 5.5 eV with a corresponding derivative-like permittivity feature in this same range for incident light polarized along the long molecular axis of crystalline anthracene. In addition, incident light polarized normal to the molecular plane exhibits very little absorbance (as expected) and only slight changes in permittivity. Assuming that phenanthrenequinone would exhibit very similar optical characteristics, we have subtracted the frequency-dependent data along the long axis ($[1\bar{1}0]$) from that aligned normal to the molecular plane ($[110]$), to determine the anisotropic dielectric functions. Using a Fresnel 3-phase model, approximating the response of the silicon substrate with the measured isotropic dielectric functions⁷⁰ and the response of the phenanthrenequinone monolayer with that obtained from crystalline anthracene,⁶⁹ we calculated the reflectance difference, by first determining the reflectance along the $[1\bar{1}0]$ and $[110]$ directions and then subtracting 110 from $1\bar{1}0$ as in the RDS. The line shape and energy position of the permittivity and absorbance features indicate that the 5.2 eV RDS peak can be attributed to a π - π^* transition within the adsorbed phenanthrene rather than anisotropic molecular polarizabilities.

Anisotropy in Valence-Band Photoemission. Electronic transitions at the phenanthrenequinone-silicon interface have shown anisotropy in the RDS spectra. Anisotropy of the valence electronic properties is also shown in the UPS spectra of Figure 7. The spectra for the two orientations of the silicon substrate appear quite different in the intensity and position of peaks, as expected from the bonding geometry. We attribute these peaks in the UPS spectra to the phenanthrenequinone molecule rather than the silicon substrate for two reasons. First, UPS spectra for the clean silicon showed peaks at 0.7 and 2.2 eV closely matching those attributed to the silicon surface dimer features⁷¹ while the UPS spectra of adsorbed phenanthrenequinone do not contain peaks at these energies. Second, after applying a rigid shift, the spacing between the UPS peaks matches those seen for gas-phase values of phenanthrene and diazo-substituted phenanthrene within ± 0.3 eV.⁷²⁻⁷⁵ Comparison of UPS data from similar phenanthrene molecules and the clean silicon surface leads us to assign these UPS peaks to the phenanthrenequinone molecule. The spectrum obtained along the dimer bond axis, the plane of adsorbed phenanthrenequinone, shows a much larger intensity than the spectrum obtained along the perpendicular direction. It is also evident from the UPS data that there is anisotropy among the peak positions along the two crystallographic directions. This difference in photoelectron yield most arises from the fact that the molecular conjugation involves redistribution of electron density parallel to the molecular plane, so that photoionization is more likely to eject electrons in this same plane. Differences in electron mean free path along different azimuthal directions could also affect the signal intensity, but because the inelastic mean free path is long compared with the thickness of the organic layer, we believe that the azimuthal dependence most likely arises from the electron ejection step.

Conclusion

We have shown that the use of reflectance-difference spectroscopy permits measurement of the optical changes produced by a single monolayer of organic molecules. Previous studies have shown that interpretation of even clean surfaces and surfaces covered by simple atomic adsorbates can be quite complicated.^{14,16,20,22,24,25} By comparing different molecular

adsorbates that give rise to very similar interfacial structure, we have shown that it is possible to distinguish the features associated with the molecular layer (i.e., molecular electronic transition) from those that are due to symmetry-breaking and other changes within the underlying silicon substrate. One particularly unique feature of RDS spectroscopy on an aligned molecular layer is that it is also possible to directly observe the orientation of the electronic transition dipole associated with the molecular absorption phenomena. Our results with 9,10-phenanthrenequinone show that the use of cycloaddition chemistry to prepare oriented molecular layers can also be used to produce monolayer films exhibiting strong anisotropy in optical properties.

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