Modifying electron transfer at the silicon-molecule interface using atomic tethers

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Abstract.   We present the correlation of the electronic properties at the semiconductor-molecule interface with the nature of the covalent attachment. The chemical state, monolayer structure, and electronic properties of aliphatic monolayers with Si-O, Si-C, and Si-S covalent linkages on Si(111) surfaces were investigated with contact angle wetting, spectroscopic ellipsometry, infrared vibrational spectroscopy, x-ray photoemission spectroscopy, and ultraviolet photoemission spectroscopy. Vibrational spectra indicate aliphatic films tethered to Si with few gauche defects in agreement with hydrophobic contact angles and ellipsometric thickness measurements. Core level electronic spectra as a function of semiconductor doping reveal shifts in binding energy attributed to molecular bonding. Valence band spectra reveal the work function of the molecule-Si composite as a function of semiconductor doping and atomic tether. By combining valence band spectra with core level spectra, the electronic properties of the molecule-Si system can be understood. In particular, the relative contribution of charge transfer due to surface band bending and the polarization due to molecular dipoles was determined. The O, C, and S atomic tethers induce differing amounts of band bending and interface dipoles which can be utilized to engineer the electronic properties of molecule-semiconductor junctions.

1- Introduction.

Modifying the electrical properties of the silicon interface is of prime interest for next generation electronics. Scaling of conventional electronics is increasing the importance of electronic contributions from the near surface region while properties are less reliant on bulk contributions. Molecules have been used to engineer electronic properties at the interface of bulk devices, as demonstrated in organic field effect transistors, where assembled monolayers resulted in lowering the operating voltage of polymeric transistors. [1-3] Moreover organic monolayers have been used to add functionality to semiconductor surfaces in applications including molecular electronics, bio-electronics, CHEMFets, sensors, and photovoltaics. It is increasingly clear that next generation electronic materials and devices can take advantage of interfacial monolayers to alter the electronic properties.

In order to take electrical advantage of the organic-semiconductor system, a detailed understanding of the properties at the interface is needed. The electrical properties of the semiconductor-molecule ensemble are determined by many factors. First, the doping type and concentration of the semiconductor determines the Fermi level relative to the valence and conduction band in the bulk. At the surface, this Fermi level can move up or down depending on the surface states, defects, trapped charge, or polarization. When a molecule chemically attaches to silicon, the energy levels of the semiconductor hybridize with the molecule and charge can be transferred between the delocalized silicon wavefunction and the molecular orbitals to create new electronic states. This has been observed both experimentally and theoretically where transition voltages occur at very different energies than one would predict based purely on work function, molecular orbital levels, and Schottky barriers alone.[4-6] The molecular dipole and energy of electronic orbitals (redox capability, electron-donating ability), the molecule-substrate bonding, the molecular orientation, the surface coverage, and the molecular geometric bonding pattern are all factors in the electronic properties of the final state.

Organic monolayers have been demonstrated to tune the electronic properties of semiconductors. Selzer and Cahen have investigated the effect of varying interfacial dipoles on GaAs and SiO_2 interfaces by varying the functional group on the aromatic molecule tethered to the semiconductor/oxide surface. [7] Similar studies have recently been performed for monolayers on silicon apart from additional contributions of a top metal electrode. [8, 9] These studies indicated the electronic properties of the molecule-semiconductor composite were governed by a complex interplay between charge transfer and molecular dipole. While the effect of molecular dipole has been studied by varying the terminal functional group, there are limited reports of the electrical changes arising from changing covalent tethers at the interface. Covalently bonded molecules strongly hybridize with the delocalized silicon wavefunction causing the energy levels to broaden and facilitating transfer of fractional amounts of charge to or from the molecule. Changing the nature of the atom attached to the silicon surface can change the density and energy distribution of surface states thus altering the electrical properties of the semiconductor. It remains to be seen what happens when the atomic tether is varied. Previous reports have shown that Si-C, Si-O, and Si-S bonding can occur through the reaction of alkenes, alcohols, and thiols to the silicon surface. [4, 10-12] Silicon is an ideal substrate because of the microelectronics infrastructure and electronic doping that can be utilized to engineer desired electronic properties.

We report a detailed UPS/XPS investigation of the electronic properties of the silicon-molecule interface to understand the change in work function and the contributions due to charge transfer (band bending) and surface dipole (electron affinity) after attachment of alkane films via Si-C, Si-O, and Si-S bonds. Monolayers of decanethiol, decanol, and decene were formed on 10 Ω•cm n- and p-type Si(111). Because the molecular density, orientation, and quality affect the electronic properties, monolayers were characterized with SE, FTIR, XPS, and UPS. All of these metrics indicate the monolayers are high-quality, densely packed, hydrophobic thin films.

2- Experimental Methods

2.1 Monolayer Formation. All chemicals were American Chemical Society ACS grade or better and used as received. Double-side polished Si(111) (Czochralski grown(CZ) wafers (n-/p-type, 10 Ω·cm) were diced into approximately 1 cm by 1 cm squares and cleaned by sonication in acetone and methanol, and then dried with streaming nitrogen. The hydrogen terminated surface was prepared by immersion (3 min to 5 min) of the wafer into a 6:1 buffered oxide etch (NH$_4$F:HF). The H-Si(111) samples were then rinsed with 18.2 MΩ·cm water, dried with nitrogen, and placed in a previously cleaned reaction vessel inside a nitrogen-atmosphere glove box with water and oxygen levels < 10 ppm. All solution preparation and surface functionalization were carried out in the glove box. H-Si(111) samples, immersed in a mestilyene solution containing ≈10 mM of octadecene, octadecanol, or octadecanethiol, were maintained at 150 ^{o}C overnight. The films were rinsed and directly characterized to minimize film degradation and substrate oxidation. Characterization generally took place in ambient conditions and was completed within 24 h of monolayer preparation.

2.2 Film Characterization. *Contact Angle (CA) Measurements.* Contact angles were determined with a video camera-based commercial apparatus at room temperature and ambient relative humidity with 18.2 MΩ·cm water as the probing liquid. Sessile drop contact angles (θ) were measured by lowering a 2 μL to 3 μL drop onto the surface from a blunt-ended needle attached to a 2 mL syringe. The value of θ is reported as the average from approximately 10 samples with three measurements obtained from each sample.

Fourier-Transform Infrared Spectroscopy (FTIR) Measurements. Polarized, Brewster angle transmission FTIR were obtained by using a commercial Fourier-transform infrared spectrometer with a wire grid polarizer and a custom sample holder. The spectral intensities are reported in absorbance units; -$\log_{10}$(T/T$_o$), where T is the transmitted power of the infrared beam from the sample and T$_o$ is the transmitted power through a reference. Freshly prepared double-side polished H-Si(111) or Si(111) native oxide samples were used as the infrared references.

Spectroscopic Ellipsometry (SE) Measurements. Multiple wavelength ellipsometric measurements were performed from 190 nm to 1000 nm by using a commercial instrument at a nominal

angle of incidence of 70º from the surface normal. The optical thickness of the organic monolayer was obtained by fitting the SE data to a three-layer model (Si|organic|air) assuming an index of refraction of n=1.52 for the organic monolayers. [3] The value of 1.52 has been used extensively as the refractive index of alkanethiol self-assembled monolayers (SAMs) on gold and provides a comparison with a well-characterized aliphatic surface. [4] The average and standard deviation were obtained from approximately 10 samples of each functional group.

Photoelectron Spectroscopy (XPS and UPS) Measurements. X-ray photoelectron data were collected with a commercial instrument by using a monochromatic Al kα source (1486.3 keV) at a nominal collection angle aligned with the surface normal. A pass energy of 40 eV was used for the high resolution elemental regions and a 160 eV pass energy for the survey spectra. Ultraviolet photoemission spectroscopy (UPS) was collected using a 21.2 eV He I source with a 5 eV pass energy and an external applied voltage (5.6 V) to enable detection of the emission cutoff.

2.3. Obtaining the necessary band diagram parameters
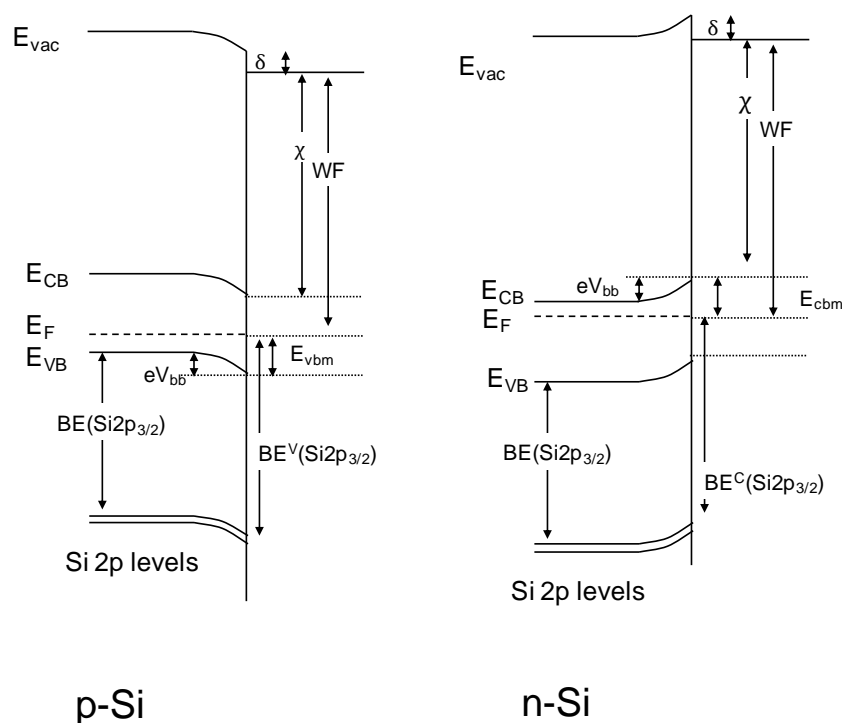
Scheme 1:   Energy level diagrams for n-type and p-type silicon surfaces.

Critical band diagram parameters can be extracted from UPS and XPS measurements. The work function (WF) is defined as the energy needed to remove an electron from the Fermi level of a material infinitely far (vacuum level). In practice, this is the cutoff of the secondary electrons in UPS data. Photoemitted electrons with energy less than the work function are not able to make it out of the sample. In order to be more sensitive to this cutoff energy, the samples were biased at 5.6 volts to accelerate any emitted electrons to the detector. The WF is then obtained from

$$WF = h\nu - E_{cutoff} \qquad (1)$$

where hv is the energy of the He I UPS source (21.2 eV) and E_{cutoff} is the secondary electron emission edge measured from the UPS data.

The work function of a semiconductor is a combination of the electron affinity, χ (which is the energy needed to bring an electron infinitely far away (vacuum level) to the conduction band), and position of the Fermi level at the surface which may be shifted by electron acceptors or donors doping or pinning the occupation of surface states in the energy gap. These effects can be separately determined by using UPS and XPS data. For a p-type surface the WF is related to the electron affinity by

$$WF = E_g - E_{vbm} + \chi \quad \text{(p-type)} \qquad (2)$$
$$WF = \chi + E_{cbm} \qquad \text{(n-type)} \qquad (3)$$

where E_g is the band gap of silicon (1.12 eV) and E_{vbm} is the valence band minimum (energy difference between the Fermi level and the valence band at the interface). For n-type samples, the work function is the sum of the electron affinity and the conduction band maximum, E_{cbm}. The E_{vbm} (E_{cbm} for n-type silicon) is obtained from the XPS Si 2p binding energy according to the following relation

$$E_{vbm} = BE(Si\ 2p_{3/2}) - BE^V(Si2p_{3/2}) \quad (4)$$

Where $BE(Si\ 2p_{3/2})$ is the measured binding energy for the Si 2p $_{3/2}$ core level relative to the Fermi level from the XPS data and $BE^V(Si\ 2p_{3/2})$ is the silicon binding energy relative to the bulk valence band and is a constant with a literature value of 98.74 eV [8, 9, 13]. Our H-Si(111) reference yielded a 98.78 eV value which is within our ±0.05eV experimental accuracy as determined from the core Si 2p binding energy to the valence band edge in the He I UPS spectra.

The band bending at the silicon interface, eV_{bb} is determined from the following relation

$$eV_{bb} = E_{vbm} - (E_F - E_{VB})_{bulk} \quad \text{(n-type Si)} \quad (5)$$
$$eV_{bb} = E_{cbm} - (E_{CB} - E_F)_{bulk} \quad \text{(p-type Si)} \quad (6)$$

where $(E_F - E_{VB})_{bulk}$ is the energy difference between the Fermi level and the valence band in the bulk semiconductor determined from the dopant type and concentration. The substrates used in this study were 10 Ω·cm doped with P and B. This yields a bulk energy offset of 0.28 eV for our n-type ((E_{CB}-$E_F)_{bulk}$) samples and 0.30 eV for our p-type ((E_F-$E_{VB})_{bulk}$) samples. A positive eV_{bb} value indicates the difference between the VB/CB and Fermi level increases at the interface.

The interface dipole, δ, is the voltage drop going from one material to another due to a combination of differing work function and redox potential. It is determined from the following relation

$$\delta = WF - E_g - \chi_{Si} + E_{vbm} \quad (7)$$

by using the convention that an increase in the WF leads to a positive interface dipole where χ_{Si} is the electron affinity of bulk silicon (4.05 eV).

3. Results

3.1. Monolayer Characterization. Because the monolayer quality directly contributes to the electrical properties of the ensemble, the physical and chemical properties were thoroughly characterized. The IR C-H vibrations for decene, decanol, and decanethiol attached to Si(111) are shown in Figure 1 with the peak intensity and position of the most intense, methylene stretch reported in Table 1. The energy of the CH_2 asymmetric stretch has been used as an indication of film order, with 2919 cm^{-1} associated with an all-trans chain conformation and 2925 cm^{-1} associated with a liquid like heterogeneous configuration. All of the aliphatic monolayers exhibit methylene peaks at energies consistent with some gauche disorder within the films as expected from a relatively short chain. The intensity of the peaks is a combination of molecular density and chain tilt. While the intensity of the alcohol and thiol are roughly equivalent, the intensity of the alkene spectrum is nearly a factor of two larger. This suggests that the monolayers are likely ordered differently due to a combination of different packing density and chain tilting. There was no observation of oxide in the vibrational spectra despite the thin monolayers. The SE thickness and water contact angle are reported in Table 1. The contact angles greater than 100° indicate the monolayers are hydrophobic consistent with a CH_3 termination and the thickness is somewhat larger than expected (1.25 nm) for the short chain molecules but comparable to similar monolayers on Au and Si.[11, 14] Overall, the monolayers are high-quality with only slight differences observed for the decene, decanol, and decanethiol starting materials.

3.2 Shift in Si 2p after molecular grafting. Because XPS photoelectrons are from the near surface region, an analysis of the Si 2p binding energy as a function of covalent bonding gives an indication of the electronic structure at the organic-semiconductor interface. Shown in Figure 2 are the XPS core level spectra of Si 2p for the organic-modified surfaces, a SiH reference and a native oxide references. The binding energy position value was obtained from fitting the spectra to a Gaussian-

Lorentzian peak with a $2p_{3/2}$:$2p_{1/2}$ spin orbit split intensity ratio of 2:1. The binding energies (shown in Table 2) for the n-type samples are shifted higher relative to the p-type silicon indicating more energy is needed to remove the electrons due to screening from the electron deficient interface. This is consistent with the upward band bending at the interface for n-type silicon depicted in Scheme 1. Molecular attachment causes the Si 2p binding energy to shift to slightly higher energies than the Si-H surface (lower BE than the SiO_2) indicating slightly more energy is needed to remove electrons from the organic-modified silicon surface. The trend in binding energy is the same for both p- and n-type silicon, indicating the binding energy shifts are attributed to Si-molecule bonding rather than the silicon substrate doping.

3.3 Valence band spectra after molecular grafting. Shown in Figure 3 are the UPS valence band spectra of the Si-organic, SiH, and SiO_2 samples. The Si-H spectra contain a broad density of states between 2-4 eV which has been observed previously.[15, 16] A peak appears at 3.5 eV for all of the molecular modified samples which is most likely due to the Si 2p orbitals.[17, 18] Enhancement of this feature for the thiol linkage may be due to contributions from the sulfur p orbitals. The valence band spectra contain a strong absorption ~6 eV which is due to bulk silicon absorption which has been previously reported to overlap with C 2p character.[15, 17] The presence of a weakened feature at similar energies in the SiH spectra indicates the majority of the intensity is bulk silicon related. Because of the large energy difference between these features and the Fermi level, they are unlikely to be involved in conduction of charge across the interface, although valence band spectra indicate mixing of the silicon and molecular orbitals.

The work function can be determined from the secondary electron cutoff in the UPS data shown in Figure 3. Electrons with energy smaller than the work function cannot escape the sample to be detected. The cutoff energy for the molecular modified samples is much closer to that of the SiO_2 sample than the SiH sample for both n-and p-type silicon samples, indicating the work function for the molecular modified silicon is closer to the work function of oxide terminated silicon. The cutoff energy for the alkene and thiol molecular films are nearly equivalent, while the cutoff energy for the alcohol

monolayers is shifted approximately 0.2 eV higher. This indicates that attachment of the alcohol species creates the most electron rich interface for both n- and p-type Si surfaces. Because the work function is a combination of charge transfer at the interface (band bending) and electrostatics of surface dipoles, a detailed analysis of both the XPS and UPS data is needed to separate these two electronic effects at the molecule-silicon interface.

4. Discussion

4.1 Determining the band structure. The work function is the energy difference between the Fermi level and the conduction band in the bulk and is affected at the surface by band bending and surface dipoles. The shift in silicon 2p binding energy is sensitive to the electron environment at the interface making the XPS data sensitive to adsorbate induced charge transfer and interface band bending. The band bending calculated from the XPS data is given in Table 3. The band bending, like the Si 2p binding energy, is similar for the SiH surface and molecular-terminated samples. There is little difference among the different atomic tethers, but there is a large difference for the two dopant types. To a first approximation, the shift in core level binding energy can be associated with adatom induced charge transfer, especially for monovalent linkages as in this case. Previous theoretical studies have shown that approximately half of the charge density in the interfacial region is localized within two atomic layers. [19] Recent photoemission studies have also observed an exponential drop-off of charge density within the first four layers with the majority contained at the silicon-molecule atomic link.[5] Due to the localized nature of the charge, early surface science studies of adsorbed elements on clean silicon surfaces in UHV are a good comparison with solution-prepared molecular layers chemically bonded to Si. Bonding of dissimilar atoms results in a dipole described by the partial ionic character of the covalent bond. The respective charge transfer changes the electrostatic potential of the core electrons of both the substrate and bonding molecule. Previous low energy photoemission studies of methyl terminated Si have observed the surface silicon shifts 0.30 eV higher than bulk silicon, consistent with less electron density resulting from the chemical bond formation.[17, 20] Early surface

science studies of hydrogen-terminated silicon prepared in vacuum have also observed a shift in binding energy of ~0.3 eV.[21] The binding energies and derived band bending for the alkene and Si-H surfaces are nearly identical in our studies, consistent with these previous reports.

The surface band bending is roughly the same for the molecules but differs between the two substrates. The different atomic tethers have equivalent effects on the band bending indicating nearly equivalent transfer of charge between the different covalent bonds. This is in stark contrast to the diazo reports with strong electron acceptor/donor groups creating significant charge transfer at the interface[8, 9] and presumably due to the weaker electrochemical groups and the lack of aromatic pi orbitals to facilitate charge transfer. The band bending and surface dipole changes after organic modification are shown in Figure 4.

The difference in work function for the covalent bonding does not arise from differences in interface charge transfer as indicated by similar interfacial band bending for the Si-O-C, Si-C-C, and Si-S-C covalent bonds. Thus, we examine the changes in electron affinity due to a potential drop across the molecular interface. The size of this potential drop is related to the size of the molecular dipole, the direction/orientation of the dipole at the surface, and the density of molecules within this dipole. The dipole, δ, obtained from analysis of XPS and UPS data, is shown in the band diagrams of Figure 4. Si-C and Si-S bonding induced nearly the same dipole while the Si-O bonding induces a dipole roughly twice the size. For both substrates, the dipole is negative indicating a decrease in the electron affinity, i.e. emitted electrons are accelerated within the dipole field. The substrate independence indicates that this dipole is not due to charge transfer at the covalent bond, as discussed earlier, but rather due to space charge affected by the molecular dipole. Because these molecules differ only by the atomic tether, differences in the molecular dipole can be extracted from the dipole of the Si-atom covalent bond. The bond dipole can be calculated by using established means that take into account the electronegativity differences and bond lengths. The calculated dipole associated with the Si-C bond is 0.23 eV, the Si-O is 0.76 eV, and the Si-S is 0.21 eV.[19] Clearly the dipole for the Si-O is much larger, indicating that electrons emitted from the Si surface will be accelerated by this dipole field, relative to the Si-C and Si-

S fields. Comparison with longer chain C18 monolayers using the same three linkage chemistries show similar work functions and surface dipoles as the C10 monolayers, indicating interface attachment dominates the electrical properties. This implies that the Si-O-C bonding should facilitate electronic coupling in functional electronic devices. Recent theoretical studies comparing Si-O-C and Si-S-C linkages have predicted that charge transfer at the Si-O-C interface should be enhanced by a broadening of the density of states near the interface. [22-24]

4.2 Coverage Differences. Molecules bond to silicon through a strong covalent bond. Thus, changing the atom that bonds to the surface can affect the monolayer density, order, and quality. The monolayers are dense and covalently bonded to the silicon surface but differ slightly in coverage. Relative coverage of the monolayers can be determined from the SE, FTIR, and XPS[25] data. Comparison of these results indicates the alcohol molecular density is 3.9($\pm$0.1) x 10^{14} molecules/cm^2, while alkene molecular coverage is 3.2($\pm$0.1) x 10^{14} molecules/cm^2 and thiol coverage is 2.5($\pm$0.1) x 10^{14} molecules/cm^2. There appears no difference between the coverage of the n-type and p-type species. This XPS derived coverage is likely higher than reality due to adventitious carbon, however, the relative density for the different molecules is in agreement with the SE thickness data and allows comparison between the molecular films.

A correction of the dipole from these Si-O, Si-C, and Si-S species as a function of coverage is relatively straightforward by analogy with adsorbed elements on UHV-prepared silicon surfaces. [19] As the molecular coverage increases, the dipole polarization decreases due to screening by neighboring molecules. Thus, the coverage corrected dipoles are calculated to be 0.22 eV for the alkene, 0.74 eV for the alcohol, and 0.20 eV for the thiol; nearly identical to the isolated molecule. It is not surprising that coverage differences are a minimal contribution to the surface dipole. First, the dipole in gas-phase has been shown to be larger than the dipole of the molecule in a thin film due to dipole-dipole intermolecular interactions. [26]   Second, the effect of monolayer coverage on the work function is geometry dependent where pinhole domains smaller than the depletion region(>30 nm for N_d ~10^{15}) have little effect on electronic properties. [27]   The dense monolayers in this study will not have

pinholes large enough to alter the work function. The band bending for the molecular linkers studied is relatively constant, indicating the density and energy of interface charge is not determined by altering the charge transfer at the atomic linker or surface coverage. The dipole, however, is different for the monolayers studied and the molecule with the largest dipole also has the largest coverage.

5. Summary and Conclusions. The first direct evidence of the relative contributions of interfacial charge transfer and dipole to the change in work function for the Si-O, Si-C, and Si-S linked aliphatic molecules was presented. Modification of the semiconductor-molecule electronic properties is possible through judicious choice of atomic linkage. Covalently bonding molecules with different atomic linkages can be used to alter the barriers to charge transfer and provide favorable electrical response in next-generation devices. Moreover, the use of atomic tethers can be applied to other semiconductors or gate stacks to passivate surface reactions as well as engineer charge transfer across interfaces.

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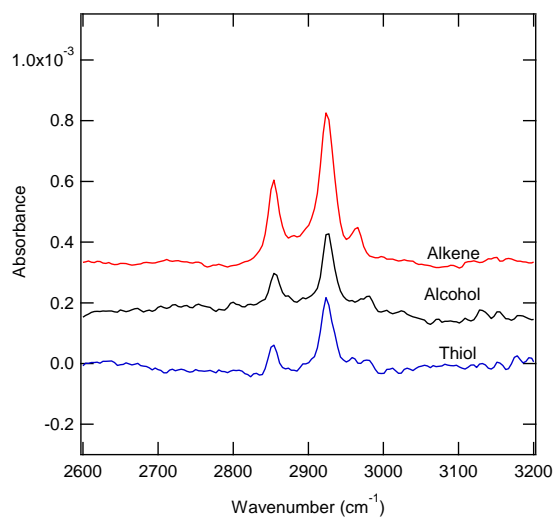
Figure 1. Transmission infrared spectra of the organic modified silicon surfaces.
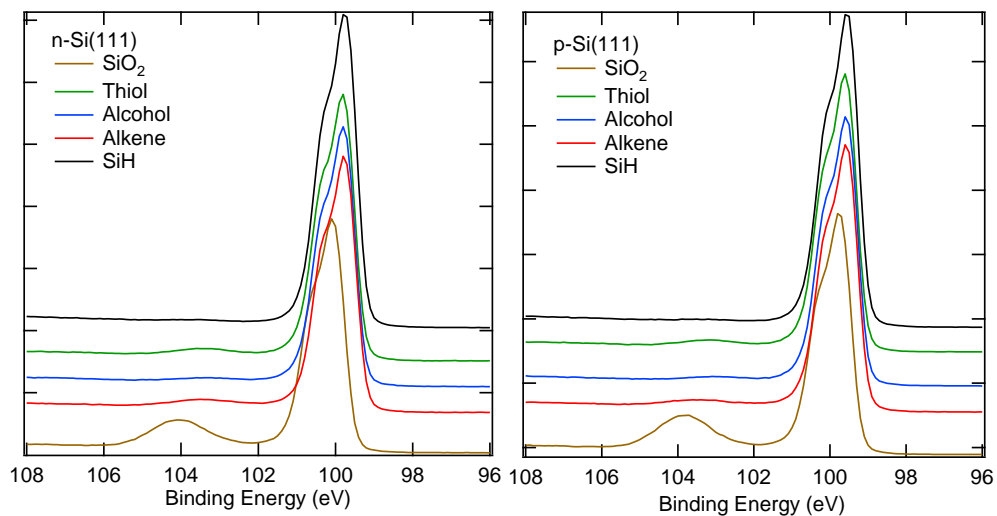
Figure 2. XPS core level spectra of Si 2p for the organic modified surfaces and SiH and native oxide references.
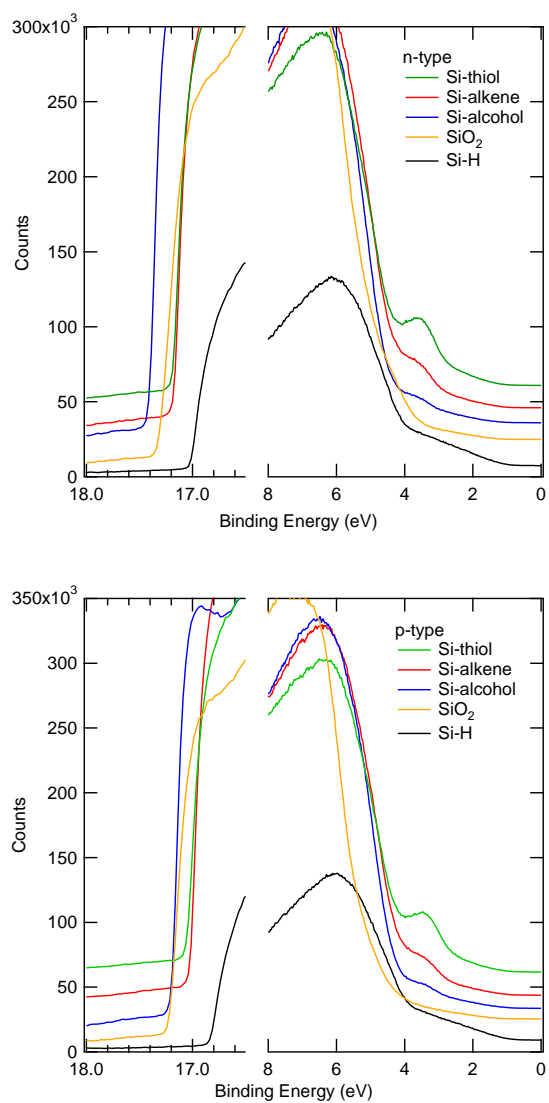
Figure 3. UPS valance level spectra of the organic modified surfaces and SiH and native oxide references.
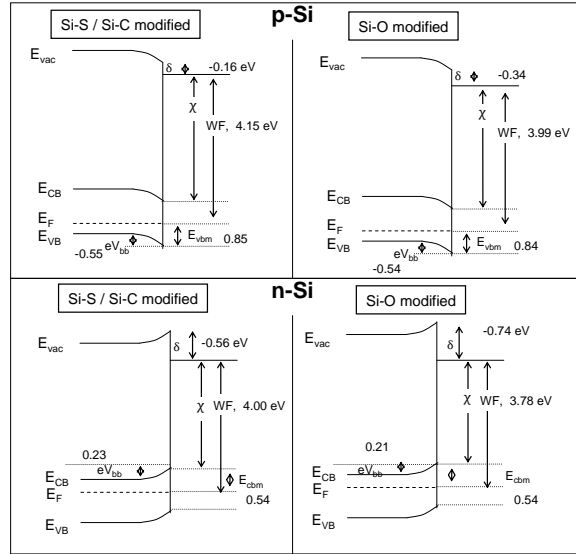
Figure 4. Band diagrams calculated from XPS and UPS data of the organic-silicon interface. All values are in eV, error is ± 0.1 eV.

Table 1: Comparison of C10 Aliphatic Monolayers on H-SI(111) from Different Starting Material

Molecule	SE (nm; ±0.1)	CA (°; ±2)	IR ν ch$_{2(a)}$ (cm^{-1}; ±1)	IR ν ch$_{2(a)}$ (abs; ±5 x 10^{-5})
Alcohol	1.50	105	2928	2.7 x 10^{-4}
Alkene	1.35	100	2925	4.8 x 10^{-4}
Thiol	1.21	101	2923	2.4 x 10^{-4}

Table 2: Data obtained during band diagram calculation

	BE(Si 2p$_{3/2}$) (eV; ±0.05)		Band offset (eV; ±0.05)		E$_{cutoff}$ (eV; ±0.05)		WF (eV; ±0.05)	
	p-Si(111)	n-Si(111)	p-Si E$_{vbm}$	n-Si E$_{cbm}$	p-Si(111)	n-Si(111)	p-Si(111)	n-Si(111)
Alkene	99.58	99.76	0.83	0.55	17.03	17.20	4.17	4.00
Alcohol	99.58	99.81	0.84	0.49	17.21	17.42	3.99	3.78
Thiol	99.61	99.81	0.87	0.49	17.06	17.20	4.14	4.00
Si-H	99.55	99.75	0.81	0.55	16.85	17.03	4.35	4.17
SiO$_2$	99.78	100.08	1.07	0.22	17.23 - 17.04	17.32 - 17.27	3.97 - 4.16	3.88 - 3.93

Table 3: More Data relevant to the band diagram

	eV$_{bb}$ (eV; ±0.05)		Electron Affinity, χ (eV; ±0.05)		Interface Dipole, δ (eV; ±0.05)	
	p-Si(111)	n-Si(111)	p-Si (111)	n-Si (111)	p-Si(111)	n-Si(111)
Alkene	0.53	0.26	3.88	3.47	-0.16	-0.58
Alcohol	0.54	0.21	3.70	3.29	-0.34	-0.76
Thiol	0.57	0.21	3.89	3.51	-0.16	-0.54
Si-H	0.51	0.27	4.04	3.62	-0.01	-0.43
SiO$_2$	0.74	-0.04	3.92 – 4.05	3.68	-0.07	-0.35