Chapter 4

CONTROL OF THE BAND-EDGE POSITIONS OF CRYSTALLINE Si(111) BY SURFACE FUNCTIONALIZATION WITH 3,4,5-TRIFLUOROPHENYLACETYLENYL MOIETIES

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4.1 INTRODUCTION

The photovoltage produced by a semiconductor device is defined by the energetics of the junction.¹ Modern semiconductor devices rely heavily on p-n homojunctions to form a voltage-producing junction that is independent of the energetics of the interfacing phase, which can include metals,²⁻³ metal oxides,⁴⁻⁸ catalysts,⁹⁻¹⁰ conductive polymers,¹¹⁻¹⁴ and electrolytes.¹⁵⁻¹⁷ Many semiconductors cannot, however, be doped to form high-quality p-n homojunctions, and moreover the diffusive doping processes used to fabricate emitter layers are generally not compatible with small-grain-size polycrystalline thin-film semiconducting base layers.¹⁸⁻¹⁹ In these cases it is often necessary to form a voltage-producing junction between the semiconductor and a contacting phase, for example, a semiconductor/liquid junction. Therefore, the development of methods to tune the semiconductor energetics relative to those of the

contacting phase using thin or monolayer films could enable the use of new polycrystalline or thin-film materials in devices as well as lower the processing costs associated with device fabrication.

In the context of this work, the term "surface dipole" is used to refer to the unequal distributions of positive and negative charge at the silicon surface. This surface dipole produces an interfacial electric field that shifts the band-edge positions of the silicon relative to those in the contacting phase. Thus, shifts in band-edge positions produced by the surface dipole are reported in volts or electronvolts.

Control over the direction and magnitude of the dipole at the semiconductor surface, through chemical attachment of a molecular species, allows for manipulation of the semi- conductor's interfacial electric field to produce effective charge separation at the interface.²⁰ In principle, the barrier height, Φ_b , can be adjusted as a function of the surface dipole moment, allowing the relative band-edge positions to be tuned to drive a desired process (Figure 4.1). Control of the surface dipole for use in photoelectrochemical devices requires that the surface is stable under operational conditions and that a small or negligible fraction of the current is lost to surface recombination. A positive surface dipole has been produced on GaInP₂ and GaAs substrates by chemical functionalization.²¹⁻²³ The band-edge positions of Si(111) surfaces have also been modified to improve the energetics of junctions with metal oxides for use in catalytic applications.²⁴⁻²⁵



Figure 4.1. Effect of a surface dipole on the band-edge positions and barrier height, Φ_b , for a p-type semiconductor. The partial δ^+ and δ^- charges show the orientation of the dipole moment at the interface necessary to achieve the desired band-edge shift. The relative energy positions of the valence band, E_V , the Fermi level, E_F , the conduction band, E_C , the vacuum level, E_{Vac} , and the average electron energy of the contacting phase, $E(A/A^-)$, are indicated.

Alkyl termination of Si surfaces using wet chemical methods²⁶⁻³⁰ could provide a scalable and versatile method to control the band-edge positions. A two-step halogenation/alkylation process³¹ has been shown to produce methyl-terminated Si(111) surfaces, Si(111)–CH₃, with low surface recombination velocities, *S*, that are stable for >500 h in air.³²⁻³⁴ Relative to Si(111)–H surfaces, Si(111)–CH₃ surfaces are more stableagainst oxide formation³⁵⁻³⁷ and are readily interfaced with metals without the formation of metal silicides;³⁸⁻³⁹ however, methyl termination of Si(111) produces a –0.4 V surface dipole,³⁸⁻⁴² which on p-Si surfaces will lower Φ_b at the Si interface and reduce the electric field at the junction that drives the charge separation.

Surface functionalization with groups that contain C-F bonds, such as 3,4,5trifluorophenylacetylene (TFPA), should in principle produce a dipole moment opposite in sign to the C-H bonds in -CH3 groups and thus lead to a reversal of the negative dipole at p-type Si(111)-CH₃ surfaces. Mixed monolayer chemistry at Si(111) surfaces allows for functionalization of the surface with bulky groups that contain a desired functionality while maintaining low S and high Si-C termination.7, 34, 43-45 A mixed methyl/TFPA (MMTFPA) surface could therefore provide desirable passivation of the Si surface while allowing for the dipole to be moved more positive as a function of the fractional monolayer TFPA coverage, θ_{TFPA} . Additionally, the C-F bonds in the TFPA groups are chemically inert and are oriented with a significant portion of the dipole moment normal to the surface. MMTFPA monolayers on Si(111) surfaces could provide a robust method for controlling the semiconductor band-edge positions to impart desirable interfacial energetics without requiring formation of a p-n homojunction. Accordingly, we describe herein the synthesis and characterization of Si(111)-MMTFPA surfaces, the electrochemical properties of these surfaces in contact with Hg, and the photoelectrochemical behavior of Si(111)-MMTFPA surfaces in contact with CH₃CN solutions that contain the 1-electron redox couples decamethylferrocenium/decamethylferrocene (Cp*₂Fe^{+/0}) and methyl viologen (MV^{2+/+•}).

4.2 EXPERIMENTAL SECTION

4.2.1 Materials and Methods

Water with a resistivity of $\geq 18.2 \text{ M}\Omega$ cm was obtained from a Barnstead E-Pure system. Ammonium fluoride (NH₄F(aq), 40%, semiconductor grade, Transene, Danvers, MA) was purged with Ar(g) (99.999%, Air Liquide) for ≥ 1 h prior to use. 3,4,5-Trifluorophenylacetylene (TFPA, SynQuest Laboratories, Alachua, FL) was purified by four freeze-pump-thaw cycles, dried over activated 3 Å molecular sieves (Sigma-Aldrich), and stored in a N₂(g)-purged glovebox (<10 ppm O₂(g)) in a foil-wrapped glass Schlenk tube. All other chemicals were used as received.

Si wafers were oriented to within 0.5° of the (111) crystal plane. Float-zonegrown Si wafers (University Wafer, Boston, MA) that were used for transmission infrared spectroscopy (TIRS) were double-side polished, not intentionally doped, had a resistivity of >2 k Ω cm, and were 525 ± 15 µm thick. Float-zone-grown Si wafers (FZwafers.com, Ridgefield Park, NJ) used for *S* measurements were double-side polished, not intention- ally doped, had a resistivity of 20–40 k Ω cm, and were 300 ± 25 µm thick. Czochralski-grown n-Si wafers (University Wafer, Boston, MA) used for electrochemical experiments were single- side polished, doped with phosphorus to a resistivity of 1.1 to 1.2 Ω cm, and were 380 µm thick. Czochralski-grown p-Si wafers (Silicon Quest International, San Jose, CA or Addison Engineering, San Jose, CA) used for electrochemical experiments were single-side polished (Silicon Quest International) or double-side polished (Addison Engineering), doped with boron to a resistivity of 0.40 to 0.43 Ω cm, and were 300 ± 25 μ m thick.

1. Preparation of Lithium 3,4,5-Trifluorophenylacetylide. In a 250 mL roundbottomed flask that was connected to a Schlenk line, degassed and dried 3,4,5trifluorophenylacetylene (TFPA, 1.95 g, 12.5 mmol) was dissolved in hexanes (100 mL, anhydrous, mixture of isomers, \geq 99%, Sigma-Aldrich). The contents of the flask were cooled to -78 °C in a dry ice/acetone bath and were stirred vigorously while *n*butyllithium (*n*-BuLi, 1.68 M in hexanes, 7.3 mL, 12.3 mmol, Sigma-Aldrich) was added dropwise via a syringe. The reaction was allowed to proceed at -78 °C for 30 min, after which the flask was allowed to warm to room temperature while being stirred for an additional 60 min, yielding a white slurry. The slurry was transferred under an inert atmosphere to an amber bottle, which was stored at 8 °C. Immediately before use, tetrahydrofuran (THF, anhydrous, \geq 99.9%, Sigma-Aldrich) was added to the lithium 3,4,5-trifluorophenylacetylide (LiTFPA) slurry in 1:4 v/v THF/hexanes to solvate the product, forming a 0.10 M solution.

2. Preparation of Si(111)–H Surfaces. Wafers were cut to the desired size using a diamond-tipped scribe. The samples were washed sequentially with water, methanol (\geq 99.8%, BDH), acetone (\geq 99.5%, BDH), methanol, and water. The wafers were then immersed in a piranha solution (1:3 v/v of 30% H₂O₂(aq) (EMD)/18 M H₂SO₄ (EMD)) and heated to 95 ± 5 °C for 10–15 min. The solution was drained and the wafers were rinsed with copious amounts of water. The oxide was removed by immersing the wafers in aqueous buffered hydrofluoric acid (HF, semiconductor grade, Transene) for 18 s,

followed by a brief rinse with water. Atomically flat Si(111)–H surfaces were formed by anisotropic etching for 5.5 min in an Ar(g)-purged solution of $NH_4F(aq)$.³³ To remove bubbles that formed on the surface, the wafers were agitated at the start of every minute of etching, and the solution was purged throughout the etching process. After etching, the wafers were rinsed with water and dried under Ar(g).

3. Preparation of Si(111)–Cl Surfaces. The Si(111)–H wafers were transferred to a N₂(g)-purged glovebox with <10 ppm O₂(g) and were rinsed with chlorobenzene (anhydrous, \geq 99.8%, Sigma-Aldrich). The wafers were placed into a saturated solution of phosphorus pentachloride (PCl₅, \geq 99.998% metal basis, Alfa Aesar) in chlorobenzene, and were heated to 90 ± 2 °C for 45 min.³³ The addition of benzoyl peroxide, which has been used as a radical initiator,⁴⁶ was found not to be necessary to yield high-quality Si(111)–Cl surfaces. When the reaction finished, the wafers were removed from the reaction solution and rinsed sequentially with chlorobenzene and anhydrous THF.

4. Alkylation of Si(111)–Cl Surfaces. Si(111)–CH₃ surfaces were prepared by immersing the Si(111)–Cl surfaces in a 3.0 M solution of methylmagnesium chloride (CH₃MgCl, Acros Organics) and heating to 50 ± 2 °C for 12–24 h.³³ Mixed methyl/TFPA (MMTFPA) monolayers (Scheme 4.1) were formed by first reacting Si(111)–Cl surfaces with LiTFPA (0.10 M in 1:4 v/v THF/hexanes) for 1–20 h at 23–65 °C in the absence of light. The wafers were then rinsed with THF and submerged in 3.0 M CH₃MgCl for 12–24 h at 50 °C.^{7, 34, 43} Si(111)–TFPA surfaces were prepared by reacting Si(111)–Cl wafers with LiTFPA (0.10 M) at 65 °C for 10–20 h.



Scheme 4.1. Synthesis of Si(111)-TFPA and Si(111)-MMTFPA Surfaces

After completion of the reactions to yield the target surfaces, the wafers were removed from the reaction solution, rinsed with THF, and submerged in THF. The samples were removed from the glovebox and sonicated for 10 min in each of THF, methanol, and water. Following sonication, the wafers were rinsed with water and dried under Ar(g). For the fabrication of electrodes, wafers were broken into appropriately sized pieces, rinsed again with water, and dried under Ar(g).

5. Formation of Ohmic Contacts to the Back of n- and p-Si(111) Electrodes. After functionalization, ohmic contacts were formed to the back of n-Si(111) electrodes by application of Ga-In eutectic (78% Ga, 22% In by weight) using a diamond-tipped scribe. Prior to functionalization, ohmic contacts were formed to p-Si(111) samples by electronbeam evaporation (Denton Vacuum) of 100 nm of Al onto the backside of the wafer.⁴⁷ The wafers were then annealed in a Carbolite tube furnace at 450 °C for 30 min under an atmosphere of forming gas (5% H₂(g) in N₂(g)) flowing at 5 L min⁻¹. The Al layer was isolated from the reaction solution during the functionalization process by use of a custom Teflon reaction vessel (Figure 4.2).



Figure 4.2. The Teflon reaction vessels used to isolate the Al-coated side of p-Si electrodes to allow for reaction on one side of the wafer without etching away the Al layer. The assembled vessel (top) is shown along with the separate aluminum base, Teflon well, and Teflon cap.

6. Electrochemical Measurements in Contact with Hg. Electrochemical measurements in contact with Hg⁴⁰ (electronic grade, 99.9999% trace metal basis, Sigma-Aldrich or Alfa Aesar) were performed inside an Ar(g)-filled glovebox (<0.3 ppm O₂(g)) at 23 °C. The wafers were placed on a Cu plate (with the Ga-In eutectic contacting the Cu plate), and a cylindrical Teflon cell was placed on top of the wafer, to produce an electrode area of 0.314 cm². Hg was added to the Teflon cell to cover the exposed area of the wafer, and a Pt wire contacted the top of the Hg. Electrochemical measurements were collected using a two-electrode setup, with the Cu plate connected to the working electrode and the Pt wire connected to the counter electrode. All voltages measured in a two-electrode setup are indicated by *V*, while potentials measured in a three-electrode setup are indicated by *E*.

Current density versus voltage (*J-V*) measurements were performed from -0.5 to +0.5 V at a scan rate of 20 mV s⁻¹. The sampling rate was 1 mV per data point using a Solartron 1287 potentiostat operated by CorrWare software (v. 3.2c). Three *J-V* scans were collected before and after collection of differential capacitance versus voltage (C_{diff} -*V*) data. C_{diff} -*V* data were acquired with a 10 mV amplitude sinusoidal signal at an applied DC bias, with the DC bias varied in increments of 0.05 V between 0 and +0.5 V for n-Si and between 0 and -0.5 V for p-Si electrodes. The frequency was varied from 10^1 to 10^6 Hz at each DC bias. C_{diff} -*V* measurements were collected using a Schlumberger SI 1260 frequency response analyzer operated by ZPlot software (v. 3.3e).

7. Photoelectrochemical Measurements in Acetonitrile. Si working electrodes were fabricated by using high-purity conductive Ag paint (SPI Supplies, West Chester, PA) to affix a coil of tinned Cu wire to the back side of the Si electrode. The wire was threaded through a 1/4" outer diameter Pyrex tube, and the wafer was secured to the tube using Loctite 9460 epoxy (cured under ambient conditions for 12–24 h) such that the wafer surface was perpendicular to the length of the tube. Electrodes used for current density versus potential (*J-E*) and differential capacitance versus potential (C_{diff} -*E*) measurements were 0.14 to 0.61 cm² in area, as determined by analyzing scanned images of each electrode with ImageJ software. All *J-E* and C_{diff} -*E* measurements used a standard three-electrode setup.

Decamethylferrocene (Cp $*_2$ Fe, bis(pentamethylcyclopentadienyl)iron(II), 99%) was purchased from Strem Chemical and was purified by sublimation. Oxidized decamethylferrocenium (Cp $*_2$ Fe $^+$, bis(pentamethylcyclopentadienyl)iron(III) tetrafluoroborate) was synthesized by chemical oxidation of decamethylferrocene and purified by recrystallization from diethyl ether and acetonitrile.⁴⁸ Methyl viologen (MV^{2+} , 1,1'-dimethyl-4,4'-bipyridinium hexafluorophosphate) was prepared according to a literature procedure.⁴⁹ The reduced species MV^{++} was generated by controlled-potential electrolysis of MV^{2+} at –0.85 V versus AgNO₃/Ag (Bioanalytical Systems) with a Pt mesh working electrode in the main electrochemical cell compartment and a Pt mesh counter electrode located in a compartment that was separated from the main electrochemical cell by a Vycor frit. Subsequent in situ generation of the MV^{++} species was performed to maintain the cell potential within 25 mV of the initial measured open-circuit potential versus a AgNO₃/Ag reference electrode.

Photoelectrochemical measurements were performed in acetonitrile (CH₃CN, EMD, dried over columns of activated alumina) with 1.0 M LiClO₄ (battery grade, Sigma-Aldrich) inside an Ar(g)-filled glovebox that contained <0.5 ppm of O₂(g). The concentrations of the redox-couple species in solution were either 1.2 mM Cp*₂Fe⁺ and 0.92 mM Cp*₂Fe or were 1.5 mM MV²⁺ and 0.035 mM MV⁺⁺ (calculated based on charge passed during electrolysis). Open-circuit measurements were collected in the dark and also under 100 mW cm⁻² of illumination provided by a 300 W ELH-type tungstenhalogen lamp operated at 110 V. The light intensity was calibrated by use of a Si photodiode (Thor Laboratories). *J-E* data were collected from –0.5 to +0.5 V versus a Pt wire pseudoreference electrode in a three-electrode setup with a Pt mesh counter electrode, using a Gamry Reference 600 potentiostat operated by Gamry Instruments Framework software (v. 5.61). A four- port, cylindrical, flat-bottomed, borosilicate glass

cell was used for the photoelectrochemical measurements. C_{diff} -E measurements were collected using a Gamry Reference 600 potentiostat with the same specifications used for the measurements performed in contact with Hg.

4.2.2 Instrumentation

1. Transmission Infrared Spectroscopy. TIRS data were collected using a Thermo Scientific Nicolet 6700 optical spectrometer³³ equipped with a thermoelectrically cooled deuterated L-alanine-doped triglycine sulfate (DLaTGS) detector, an electronically temperature-controlled (ETC) EverGlo mid-IR source, a N₂(g) purge, and a KBr beam splitter. A custom attachment allowed the wafers $(1.3 \times 3.2 \text{ cm})$ to be mounted with the incident IR beam at 74° (Brewster's Angle for Si) or 30° with respect to the surface normal. Spectra collected at 74° show modes that are either perpendicular or parallel to the surface, while spectra collected at 30° show primarily modes parallel to the surface.⁵⁰ The spectra reported herein are averages of 1500 scans at 4 cm⁻¹ resolution. The baseline was flattened and the residual water peaks were subtracted in the reported spectra. Spectra were collected and processed using OMNIC software v. 9.2.41. The background SiO_x and Si(111)–H spectra were recorded separately for each sample.

2. X-ray Photoelectron Spectroscopy. X-ray photoelectron spectroscopy (XPS) data were collected using a Kratos AXIS Ultra spectrometer.^{7, 33, 51} The instrument was equipped with a hybrid magnetic and electrostatic electron lens system, a delay-line detector (DLD), and a monochromatic Al K α X-ray source (1486.7 eV). Data were collected at pressures $<9 \times 10^{-9}$ Torr, and the photoelectron ejection vector was 90° with

respect to the sample surface plane. The electron-collection lens aperture was set to sample a $700 \times 300 \ \mu\text{m}$ spot, and the analyzer pass energy was 80 eV for survey spectra and 10 eV for high-resolution spectra. The instrument energy scale and work function were calibrated using clean Au, Ag, and Cu standards. The instrument was operated by Vision Manager software v. 2.2.10 revision 5.

3. Surface Recombination Velocity. Surface recombination velocity (S) measurements were performed using a contactless microwave conductivity apparatus.^{7, 33-34, 43} A 20 ns laser pulse at 905 nm provided by an OSRAM laser diode and an ETX-10A-93 driver generated electron-hole pairs. The charge-carrier lifetime was determined by monitoring the change in reflected microwave intensity using a PIN diode connected to an oscilloscope. The data were collected using a custom LabView program. All photoconductivity decay curves were averages of 64 consecutive decays. Reported data were collected after the *S* value had stabilized in the presence of air, usually 24–72 h after preparation of the surface.

4.2.3 Data Analysis

1. Fitting and Quantification of XPS Data. High-resolution XPS data were analyzed using CasaXPS software v. 2.3.16. A Shirley background was applied to all C 1s, F 1s, and Si 2p spectra, except when analyzing small amounts of SiO_x in the 102–104 eV range, for which a linear background was used. C 1s and F 1s data were fitted using a Voigt GL(30) function that consisted of 70% Gaussian and 30% Lorentzian character. Cl 2p data were fitted using a Voigt GL(90) function that consisted of 10% Gaussian and 90% Lorentzian

character. Bulk Si 2p spectra were fitted with asymmetric Lorentzian convoluted with Gaussian line shapes of the form LA(e, f, g), where *e* and *f* determine the asymmetry of the line shape and *g* determines the Gaussian width of the function. LA(1.2, 1.4, 200) fit the obtained Si 2p spectra consistently, and the peak widths were set to be equal to each other. The SiO_x contributions from 102–104 eV were fitted using the GL(30) function.

The Si(111)–MMTFPA surfaces were terminated by mixed monolayers that had a large difference in thickness of the two terminating species. As such, a modified two-layer substrate-overlayer model was used to determine the thickness of the desired overlayer species. An initial average overlayer thickness was estimated by assuming that all surface Si sites were terminated by either $-CH_3$ or TFPA groups, and the ratio of the C 1s photoemission signal at 284.2 eV (C_{Si}) was determined relative to the signal at 288.0 eV (C_F). The fractional coverage of TFPA groups was estimated using this method, and the average overlayer thickness was estimated using the calculated fractional coverage of $-CH_3$ and TFPA groups in conjunction with the estimated thickness of each species shown in Scheme 4.2. With an estimated average overlayer thickness, a two-layer substrate-overlayer model was used to determine the thickness of the F monolayer (d_A), as expressed by eq 4.1:

$$\left(\frac{I_{\rm A}}{I_{\rm Si}}\right)\left(\frac{SF_{\rm Si}}{SF_{\rm A}}\right)\left(\frac{\rho_{\rm Si}}{\rho_{\rm A}}\right) = \left(\frac{1 - e^{-\frac{d_{\rm A}}{\lambda_{\rm A}\sin\varphi}}}{e^{-\frac{d_{\rm A}+d_{\rm B}}{\lambda_{\rm Si}\sin\varphi}}}\right)$$
(4.1)

 I_A and I_{Si} are the core level peak areas for the overlayer species A and for the Si substrate, respectively, SF_A and SF_{Si} are the sensitivity factors for the overlayer species A ($SF_{F1s} =$ 1.00) and for the Si substrate ($SF_{Si 2p} = 0.328$), respectively, ρ_A and ρ_{Si} are the densities of the overlayer species A (3.0 g cm⁻³ for hydrocarbon overlayers) and the Si substrate (2.3 g cm⁻³), respectively, and λ_A and λ_{Si} are the attenuation lengths for the photoelectrons arising from the overlayer species A ($\lambda_{F1s} = 1.6 \text{ nm}$)⁵² and from the Si 2p core level ($\lambda_{Si} = 4.0 \text{ nm}$), respectively. The angle between the photoelectron ejection vector and the surface plane (φ) was 90°. The quantity ($d_A + d_B$) is the thickness of the mixed monolayer, which was estimated using the method described above.

Scheme 4.2. Estimated Thickness of -CH3 and TFPA Groups



Samples with $\theta_{\text{TFPA}} > 0.15$ ML often showed the presence of unreacted Si–Cl sites. The fractional ML coverage of Si–Cl was determined using eq 4.1, with $SF_{\text{Cl}\,2s} = 0.493$ and $\lambda_{\text{Cl}\,2s} = 2.8 \text{ nm}.^{52}$ The overlayer density, ρ_A , was assumed to be the same as for hydrocarbon overlayers, and the average overlayer thickness ($d_A + d_B$) was estimated as described above. The thickness of 1 ML of Cl atoms was estimated to be the length of the Si–Cl bond (0.20 nm). The Cl 2p photoelectrons were assumed to be unattenuated by neighboring TFPA groups.

Small concentrations of SiO_x were detected on Si(111)–MMTFPA surfaces with $\theta_{\text{TFPA}} > 0.15$ ML and on Si(111)–TFPA surfaces. For estimating the thickness of SiO_x using eq 4.1, the quantity $(SF_{\text{Si}}/SF_{\text{A}})(\rho_{\text{Si}}/\rho_{\text{A}})$ reduces to 1.3, and the quantity $d_{\text{A}} + d_{\text{B}}$ reduces simply to d_{A} . For this estimate, all photoelectrons originate in Si, so $\lambda_{\text{A}} = \lambda_{\text{Si}} = 3.4$ nm for photoelectrons attenuated by a SiO_x overlayer.⁵³⁻⁵⁴ The thickness of 1 ML of SiO_x was assumed to be 0.35 nm.^{33, 35, 52}

2. Calculation of Surface Recombination Velocity and Surface Trap State Density. The minority-carrier lifetime, τ , was determined by fitting the photoconductivity decay versus time data to an exponential decay equation.³⁴ The surface recombination velocity (*S*) was estimated for a given value of τ using:

$$S = \frac{a}{2\tau} \tag{4.2}$$

where *a* is the thickness of the Si wafer. The effective surface trap-state density, N_t , was determined from *S* using:

$$N_{\rm t} = \frac{S}{\sigma v_{\rm th}} \tag{4.3}$$

where σ is the trap-state capture cross section (10⁻¹⁵ cm²) and v_{th} is the thermal velocity of the charge carriers (10⁷ cm s⁻¹).

3. Determination of the Barrier Height by Current Density Versus Voltage Curve Analysis. Barrier heights, Φ_b , and ideality factors (*n*) were estimated for 2-electrode measurements performed in contact with Hg by fitting the linear region of the forward-bias portion of a semi-log current density versus voltage (*J-V*) plot to the thermionic emission model.

$$J = A^{**}T^2 e^{-\frac{q\Phi_b}{k_B T}} \left(e^{\frac{qV}{nk_B T}} - 1 \right)$$
(4.4)

 A^{**} is the modified Richardson's constant for Si (112 A cm⁻² K⁻² for n-Si and 32 A cm⁻² K⁻² for p-Si), $k_{\rm B}$ is Boltzmann's constant (1.381 × 10⁻²³ J K⁻¹), and *T* is the temperature in Kelvin (296 K). By convention, the forward-bias region of the *J-V* curves was depicted and analyzed in the first quadrant.

4. Determination of the Barrier Height by Analysis of Differential Capacitance Versus Voltage Data. Differential capacitance versus voltage (C_{diff} -V) data were collected for Si/Hg junctions using a 2-electrode setup. Nyquist plots were hemispherical, indicating a parallel RC circuit in series with a resistance R_s (Randles Circuit). C_{diff} -V data were fitted across frequencies for which the measured phase angle was >80° and for which Bode plots were linear. The Mott-Schottky equation was used to determine the flat-band potential, V_{fb} , of the Si

$$C^{-2} = \frac{2}{q\varepsilon\varepsilon_0 N_{\rm D} A_{\rm S}^2} \left(V_{\rm fb} + \frac{k_{\rm B}T}{q} - V \right)$$
(4.5)

where *C* is the differential capacitance, *q* is the absolute value of the elementary charge $(1.602 \times 10^{-19} \text{ C})$, ε is the dielectric constant of silicon (11.8), ε_0 is the vacuum permittivity $(8.85 \times 10^{-14} \text{ F cm}^{-1})$, N_D is the dopant density determined from the measured resistivity, and A_S is the junction area in cm². By convention, the applied DC bias was negative, and the obtained V_{fb} was positive for n- and p-type Si. The barrier height ($\Phi_{\text{b,n}}$ for n-Si and $\Phi_{\text{b,p}}$ for p-Si) was calculated using:

$$\Phi_{\rm b,n} = V_{\rm fb} - \frac{k_{\rm B}T}{q} \ln\left(\frac{N_{\rm D}}{N_{\rm C}}\right)$$
(4.6)

$$\Phi_{\rm b,p} = V_{\rm fb} - \frac{k_{\rm B}T}{q} \ln\left(\frac{N_{\rm D}}{N_{\rm V}}\right)$$
(4.7)

where $N_{\rm C}$ is the effective density of states in the Si conduction band (2.8 × 10¹⁹ cm⁻³), $N_{\rm V}$ is the effective density of states for the Si valence band (1.0 × 10¹⁹ cm⁻³), and $N_{\rm D}$ is the dopant density determined by four-point probe measurement to be 4.4 × 10¹⁵ cm⁻³ for n-Si and 4.0 × 10¹⁶ cm⁻³ for p-Si.

5. Determination of the Barrier Height by Analysis of Differential Capacitance Versus Potential Data. Differential capacitance versus potential (C_{diff} -E) data were collected in contact with decamethylferrocenium/decamethylferrocene ($Cp^*_2Fe^{+/0}$) or methyl viologen^{2+/+} in CH₃CN using a three-electrode setup. The data were collected versus a platinum wire pseudoreference electrode, and the flat-band potential E_{fb} was determined versus the potential of the solution using eq 4.8 for n-Si and eq 4.9 for p-Si.

$$C^{-2} = \frac{2}{q\varepsilon\varepsilon_0 N_{\rm D} A_{\rm S}^2} \left(E - E_{\rm fb} - \frac{k_{\rm B}T}{q} \right)$$
(4.8)
$$C^{-2} = \frac{2}{q\varepsilon\varepsilon_0 N_{\rm D} A_{\rm S}^2} \left(E_{\rm fb} + \frac{k_{\rm B}T}{q} - E \right)$$
(4.9)

where *E* is the DC potential applied versus the potential of the solution. The barrier heights, $\Phi_{b,n}$ and $\Phi_{b,p}$, were determined versus the potential of the solution using

$$\Phi_{\rm b,n} = E_{\rm fb} + \frac{k_{\rm B}T}{q} \ln\left(\frac{N_{\rm D}}{N_{\rm C}}\right)$$
(4.10)
$$\Phi_{\rm b,p} = E_{\rm fb} - \frac{k_{\rm B}T}{q} \ln\left(\frac{N_{\rm D}}{N_{\rm V}}\right)$$
(4.11)

The calculated values for $\Phi_{b,n}$ were negative and the calculated values of $\Phi_{b,p}$ were positive. The reported values of Φ_b are unsigned in order to align with the common conventions for reporting Φ_b and to provide a direct comparison with the magnitudes of Φ_b determined by two-electrode measurements in contact with Hg.

6. Determination of the Effective Solution Potentials for Photoelectrochemical Cells. The Nernstian cell potential, $E(Cp*_2Fe^{+/0})$, for $Cp*_2Fe^{+/0}$ in CH₃CN with 1.0 M LiClO₄ was measured to be +0.023 V versus the formal potential of the redox couple, which is $E^{\circ\prime}(Cp*_2Fe^{+/0}) = -0.468$ V versus ferrocenium/ferrocene.⁴⁷ The reference potential was converted to the saturated calomel electrode (SCE) by use of the experimentally determined value of $E^{\circ\prime}(Fc^{+/0}) = +0.311$ versus SCE.⁴⁷ $E(MV^{2+/+*})$ for the $MV^{2+/+*}$ couple in CH₃CN with 1.0 M LiClO₄ was measured as -0.781 V versus AgNO₃/Ag. The cell reference potential was converted to SCE using $E(AgNO_3/Ag) = +0.393$ V versus SCE.⁵⁵ The measured cell potentials were converted to effective cell potentials, for which a normalizing 10 mM concentration was used for comparison with previous results. The effective cell potential for n-Si electrodes, $E_{eff,n}$ (A/A⁻) was determined by⁴⁷

$$E_{\rm eff, n}\left(A / A^{-}\right) = E\left(A / A^{-}\right) + \frac{k_{\rm B}T}{q} \ln \frac{\left[A_{\rm eff}^{-}\right]}{\left[A^{-}\right]}$$
(4.12)

and the effective cell potential for p-Si electrodes $E_{eff,p}$ (A/A⁻) was determined by

$$E_{\rm eff, p}\left(A / A^{-}\right) = E\left(A / A^{-}\right) - \frac{k_{\rm B}T}{q} \ln \frac{\left[A_{\rm eff}\right]}{\left[A\right]}$$
(4.13)

Here, $[A_{eff}^{-}]$ and $[A_{eff}]$ are the effective 10 mM concentrations of the reduced and oxidized species, respectively, and $[A^{-}]$ and [A] are the solution concentrations of the reduced and oxidized species, respectively. For the Cp*₂Fe^{+/0} cell, $E_{eff,n}$ (Cp*₂Fe^{+/0}) = -0.073 V versus SCE and $E_{eff,p}$ (Cp*₂Fe^{+/0}) = -0.188 V versus SCE. For the MV^{2+/+•} cell, $E_{eff,n}$ (MV^{2+/+•}) = -0.244 V versus SCE and $E_{eff,p}$ (MV^{2+/+•}) = -0.436 V versus SCE.

4.3 RESULTS

4.3.1 Spectroscopic Characterization and Surface Recombination Velocity of Si(111)–TFPA and Si(111)–MMTFPA Surfaces

Figure 4.3 presents TIRS data for a Si(111)–TFPA surface collected at 74° and 30° incidence with respect to the surface normal. The spectrum collected at 74° incidence exhibited an intense peak at 1533 cm⁻¹, which was ascribed to primary skeletal phenyl C–C stretching vibrations.⁵⁶⁻⁵⁷ This peak was reduced in intensity at 30° incidence, indicating that this motion has a significant component that is perpendicular to the surface. At 74° incidence, weak peaks were observed at 1612, 1584, 1432, 1366, and 1351 cm⁻¹ and were characteristic of aromatic systems.⁵⁷ At 30° incidence, the signal at 1432 cm⁻¹ was readily observed, while the other characteristic aromatic C–C stretching peaks were not present. A sharp signal observed for 74° incidence at 1251 cm⁻¹ of C–F stretching,⁵⁷⁻⁵⁹ and this peak was greatly reduced in intensity at 30° incidence. A very weak signal at 2160 cm⁻¹ was observed only at 74° incidence, indicating the presence of C≡C triple bond stretching perpendicular to the surface.⁵⁷ Weak C–H stretching signals were observed only for 74° incidence at 2962 and 2853 cm⁻¹, which can be ascribed to



Figure 4.3. TIRS data for a Si(111)–TFPA surface collected at 74° (top) and 30° (bottom) with respect to the surface normal. The symbols v and δ indicate stretching and bending motions, respectively, and the subscript "Ph" indicates modes associated with the phenyl ring. The spectrum collected at 74° had $\theta_{\text{TFPA}} = 0.16$ ML and $\theta_{\text{SiO}_x} = 0.17$ ML, while the spectrum collected at 30° had $\theta_{\text{TFPA}} = 0.25$ ML and $\theta_{\text{SiO}_x} = 0.03$ ML. The spectra were referenced to the Si(111)–H surface. The peak at 1533 cm⁻¹ and the surrounding satellite peaks were attributed to skeletal C–C stretching in the phenyl ring. The C–F stretch was observed at 1251 cm⁻¹, and a weak C≡C stretch was observed at 2160 cm⁻¹. The inset shows a magnified portion of the spectrum from 2250 to 2000 cm⁻¹.

adventitious saturated hydrocarbon species.⁵⁰ No distinct aromatic C–H stretching signal (typically near 3050 cm⁻¹) was observed for the surface-bound TFPA group. A broad peak centered near 1050 cm⁻¹ was ascribed to transverse optical (TO) Si–O–Si stretching.⁵⁰ The observation of this mode indicated the presence of subsurface SiO_x, consistent with the oxidation of unreacted Si–Cl sites on the functionalized surface. A sharp signal overlapped by the Si–O–Si stretching peak was observed at both angles of incidence centered at 1055 cm⁻¹ and was ascribed to in-plane aromatic C–H bending. No

residual Si–H signal was detected when a SiO_x surface was used as a reference, indicating that the surface sites were only terminated by TFPA or Cl moieties.

TIRS data for a Si(111)–MMTFPA sample with $\theta_{\text{TFPA}} = 0.16$ ML are presented in Figure 4.4. The Si(111)–MMTFPA surface showed the modes associated with the phenyl ring and aromatic C–F stretching observed in Figure 4.3 in addition to reduced SiO_x content. The symmetric C–H bending, δ_s (C–H),⁵⁰ mode overlapped significantly with the C–F stretching peak, resulting in a single peak at 1253 cm⁻¹. Additionally, the –CH₃ rocking mode was observed at 762 cm⁻¹.⁵⁰ The presence of these peaks demonstrates that the Si(111)–MMTFPA exhibits both TFPA and –CH₃ functionality.

Figure 4.5 shows the surface recombination velocity (*S*) as a function of the composition of the functionalized Si surfaces. The Si(111)–CH₃ surface exhibited $S = 13 \pm 5$ cm s⁻¹, which corresponds to a trap-state density, N_t , of ~1.3 × 10⁹ cm⁻², that is, one trap for every 6.0 × 10⁵ surface sites. This low trap-state density has been shown to be stable over >500 h of air exposure.³²⁻³³ A substantial increase in *S* was observed for surfaces with $\theta_{TFPA} > 0.1$ ML, which is consistent with an increase in *S* observed for increased fractional coverages of bulky groups in mixed monolayers on Si(111) surfaces.^{34, 43} A Si(111)–MMTFPA surface with $\theta_{TFPA} = 0.10$ ML exhibited $S = (1.6 \pm 0.5) \times 10^2$ cm⁻¹, corresponding to $N_t = 1.6 \times 10^{10}$ cm⁻². With $\theta_{TFPA} = 0.22$ ML, a Si(111)–MMTFPA surface had $S = (1.9 \pm 0.1) \times 10^3$ cm s⁻¹, corresponding to $N_t = 1.9 \times 10^{11}$ cm⁻². The Si(111)–TFPA surface, which had higher θ_{TFPA} than the measured Si(111)–MMTFPA samples, exhibited substantially higher *S* than was observed for the measured Si(111)–MMTFPA samples.



Figure 4.4. TIRS data for a Si(111)–MMTFPA surface with $\theta_{\text{TFPA}} = 0.16$ ML collected at 74° with respect to the surface normal. The symbols v, δ , and ρ indicate stretching, bending, and rocking motions, respectively, and the subscript "Ph" indicates modes associated with the phenyl ring. The spectrum was referenced to the Si(111)–H surface. The peak at 1533 cm⁻¹ and the surrounding satellite peaks were attributed to skeletal C–C stretching in the phenyl ring. The C–F stretching was convoluted with the symmetric C–H bending peak, appearing at 1253 cm⁻¹.



Figure 4.5. *S* values for Si(111)–CH₃, Si(111)–MMTFPA, and Si(111)–TFPA surfaces as a function of fractional monolayer coverage with TFPA groups. For $\theta_{\text{TFPA}} > 0.1$ ML, *S* increased rapidly.

Figure 4.6a presents a representative XP survey spectrum of a Si(111)–MMTFPA surface with $\theta_{TFPA} = 0.11$ ML. Survey spectra were free of contaminants and only showed the presence of Si, C, O, and F core-level peaks. A high-resolution C 1s spectrum showed the presence of C bound to Si at 284.2 eV,^{33, 41, 60} C bound to C at 285.3 eV, C bound to O at 286.8 eV, and C bound to F at 288.0 eV (Figure 4.6b).^{45, 61-62} Figure 4.6c shows the high-resolution Si 2p XP spectrum, which showed only bulk Si⁰ and no detectable high-order SiO_x in the 102–104 eV region. The F 1s high-resolution spectrum exhibited a single peak at 688.3 eV (Figure 4d), indicative of a single source of F on the surface.⁶² In general, samples with $\theta_{TFPA} < 0.15$ ML exhibited no detectable SiO_x in the 102–104 eV range, while samples with $\theta_{TFPA} > 0.15$ ML exhibited $\theta_{SiO_x} = 0.07 \pm 0.02$ ML. Samples with $\theta_{TFPA} > 0.2$ ML also often exhibited a small amount of residual Cl, which gave an average Si–Cl coverage, θ_{Cl} , of 0.11 ± 0.01 ML.

Figure 4.7 shows analogous XP spectra for a Si(111)–TFPA surface with $\theta_{\text{TFPA}} = 0.35$ ML. Without subsequent methylation, the Si(111)–TFPA surface exhibited residual Cl, as seen in the survey spectrum (Figure 4.7a) and in the high-resolution Cl 2s spectrum (Figure 4.7e). The C 1s spectrum similarly showed contributions from C bound to Si (284.1 eV), C bound to C (285.0 eV), C bound to O (286.2 eV), and C bound to F (287.6 eV) (Figure 4.7b). The Si 2p spectrum shown did not exhibit detectable levels of SiO_x, while $\theta_{\text{SiO}_x} = 0.11 \pm 0.07$ ML across multiple Si(111)–TFPA sample preparations (Figure 4.7c). The F 1s spectrum exhibited a single signal centered at 687.9 eV (Figure 4.7d).



Figure 4.6. XPS data for an n-Si(111)–MMTFPA surface with $\theta_{\text{TFPA}} = 0.11$ ML. The survey spectrum (a) exhibited signals from Si, C, O, and F. The high-resolution C 1s spectrum (b) showed signals ascribed to C bound to Si (C_{Si}), C bound to C (C_C), C bound to O (C_O), and C bound to F (C_F). The Si 2p high-resolution spectrum (c) showed peaks attributed to bulk Si⁰ with no detectable high-order SiO_x (magnified region). The F 1s high-resolution spectrum (d) exhibited a single peak ascribed to F bound to C.



Figure 4.7. XPS data for the Si(111)–TFPA surface with $\theta_{\text{TFPA}} = 0.35$ ML. The survey spectrum (a) exhibited signals from Si, C, O, F, and Cl. The high-resolution C 1s spectrum (b) showed signals ascribable to C bound to Si (C_{Si}), C bound to C (C_C), C bound to O (C_O), and C bound to F (C_F). The Si 2p high-resolution spectrum (c) showed peaks attributed to bulk Si⁰ with no detectable high-order SiO_x (magnified region). The F 1s high-resolution spectrum (d) showed a single peak ascribable to F bound to C. The Cl 2s high-resolution spectrum (e) showed a single peak indicative of unreacted Cl bound to Si.

4.3.2 Hg Contacts to Si(111)-MMTFPA Surfaces

Figure 4.8a displays the *J-V* behavior for n-Si(111)–MMTFPA/Hg contacts having a range of θ_{TFPA} . By convention, measured values of Φ_b and of the built-in voltage were unsigned for two-electrode measurements in contact with Hg. The n-Si(111)– CH₃/Hg contact exhibited strongly rectifying behavior ($\Phi_b = 0.9$ V), evidenced by small, near-constant current at reverse bias.⁴⁰ The n-Si(111)–MMTFPA/Hg contacts exhibited less rectification as θ_{TFPA} increased, suggesting that the molecular dipole induced by the



Figure 4.8. Representative two-electrode J-V behavior for (a) n-type and (b) p-type Si(111)–MMTFPA/Hg junctions. The fractional ML coverage of TFPA for a given curve is indicated below each curve. By convention, the forward bias region is depicted in the first quadrant.

C–F bonds in the TFPA group shifted the band-edge positions to produce a smaller builtin voltage at the n-Si(111)–MMTFPA/Hg junction. At high θ_{TFPA} , the n-Si– MMTFPA/Hg contact was ohmic to Hg, indicating $\Phi_b \leq 0.3$ V and corresponding to a shift of ≥ 0.6 V in the Si band-edge positions compared with n-Si(111)–CH₃ surfaces. Samples that exhibited low values for Φ_b generally did not exhibit clear linear regions in the forward-bias portion of the semilog *J-V* plot, which precluded analysis of the *J-V* data within a thermionic emission model. The diode-ideality factor, *n*, for the n-Si(111)–MMTFPA/Hg junctions was estimated as 1.5 ± 0.2 (eq 4.4), which is comparable to previous observations on junctions between alkyl-terminated n-Si and Hg.⁴⁰

Figure 4.8b shows J-V data for p-Si(111)–MMTFPA surfaces in contact with Hg. The p-Si(111)–CH₃ samples exhibited ohmic behavior in contact with Hg, and previous work has indicated that $\Phi_b < 0.15$ V for this junction.⁴⁰ The addition of TFPA to the alkyl monolayer resulted in increased rectification of the junction, producing measurable values for Φ_b . Similar to n-Si/Hg junctions, p-Si/Hg junctions that exhibited low values for Φ_b gave semilog *J-V* response curves with no definitive linear portion in the forwardbias region, thereby limiting the determination of Φ_b for these samples. The p-Si(111)– MMTFPA samples showed increased rectification with increasing θ_{TFPA} , which indicated an increase in the built-in voltage for p-Si/Hg junctions as θ_{TFPA} increased. Analysis of the *J-V* response yielded a maximum measured value for Φ_b of 0.7 V on p-Si(111)–MMTFPA/Hg junctions, which indicated a shift in the band-edge positions of ≥ 0.5 V relative to p-Si(111)–CH₃ surfaces. The value of the diode-ideality factor, *n*, for p-Si(111)–MMTFPA/Hg junctions was 1.3 ± 0.2 (eq 4.4).

 C_{diff} -V data were also collected for the functionalized n-Si/Hg and p-Si/Hg junctions. The flat-band position was calculated from the C_{diff} -V data using eq 4.5, and the flat-band values were used to determine Φ_{b} (eq 4.6 or 4.7). As with *J*-V measurements, samples with small Φ_{b} in contact with Hg generally did not exhibit ideal behavior by C_{diff} -V measurements, precluding determination of Φ_{b} for samples that did not show strong rectification. The dopant density, N_{D} , was also calculated from these measurements and was compared with the value of N_{D} determined by four-point probe measurements. For n-Si, N_{D} determined by C_{diff} -V analysis was (2.7 ± 0.3) × 10¹⁵ cm⁻³, and N_{D} determined by four-point probe data was 4.4 × 10¹⁵ cm⁻³. For p-Si, N_{D} determined by C_{diff} -V analysis was (1.7 ± 0.4) × 10¹⁶ cm⁻³ and 4.0 × 10¹⁶ cm⁻³ by four-point probe.

For either n-Si and p-Si samples, the values of N_D were thus within a factor of ~2 when calculated by the C_{diff} -V or by four-point probe measurements.

Figure 4.9 presents the values of Φ_b calculated from the *J-V* response and C_{diff} -*V* analysis for Si(111)–MMTFPA/Hg junctions as a function of θ_{TFPA} . The n-Si(111)–MMTFPA/ Hg junctions exhibited values of Φ_b that were in close agreement for both methods. Samples for which the junction appeared ohmic are plotted with a value of $\Phi_b = 0.15 \pm 0.15$ V. The p-Si(111)–MMTFPA/Hg junctions showed values of Φ_b that generally were not in good agreement for the two analytical methods used, and Φ_b determined by C_{diff} -*V* measurements exhibited significantly greater spread for a given θ_{TFPA} than Φ_b determined from *J-V* measurements. For high θ_{TFPA} , the p-Si/Hg junctions



Figure 4.9. Correlation between the calculated barrier height for Si(111)–MMTFPA/Hg junctions and the fractional monolayer coverage of TFPA for (a) n-type and (b) p-type samples. The barrier heights calculated from fitting the forward bias region of the *J-V* curves using eq 4.4 are shown as black circles, and the barrier heights calculated from fitting the C_{diff} -*V* data using eqs 4.5–4.7 are shown as red triangles. Samples that showed low Φ_{b} values did not exhibit ideal junction behavior, precluding analysis of Φ_{b} for samples with poor rectification. Error bars represent the statistical variation in Φ_{b} for samples from the same preparation.

exhibited values of Φ_b determined by Mott-Schottky analysis near the Si band gap, while apparent Φ_b values determined from analysis of the *J-V* response were considerably lower, at ~0.65 V.

4.3.3 Photoelectrochemical Behavior of Si(111)–TFPA and Si(111)–MMTFPA Surfaces in Contact with CH₃CN-Cp*₂Fe^{+/0}

Figure 4.10 presents representative *J-E* data for functionalized n- and p-Si(111) samples in contact with CH₃CN-Cp*₂Fe^{+/0} (1.2, 0.92 mM) under 100 mW cm⁻² of simulated solar illumination. The effective cell potential, E_{eff} (Cp*₂Fe^{+/0}), was determined using eqs 4.12 and 4.13, to give $E_{eff,n}$ (Cp*₂Fe^{+/0}) = -0.073 V and $E_{eff,p}$ (Cp*₂Fe^{+/0}) = -0.188 V versus SCE. Data for the Si(111)–CH₃ surface were collected for comparison with Si(111)–MMTFPA and Si(111)–TFPA samples. The photocurrent density was limited by mass transport because the electrode areas were relatively large and the redox couple concentrations were low. Large electrode areas were required to produce reliable C_{diff} -*E* measurements with minimal edge effects. Table 4.1 presents the measured values of the open circuit potential (E_{oc}) for the functionalized electrodes under 100 mW cm⁻² illumination as well as the values of Φ_b determined from C_{diff} -*E* measurements. Values of Φ_b are reported as unsigned magnitudes.

The E_{oc} , shown in Table 4.1, of n-Si(111)–MMTFPA and n-Si(111)–TFPA samples shifted by +0.27 V and +0.36 V, respectively, compared with the E_{oc} for n-Si(111)–CH₃ samples in contact with CH₃CN-Cp*₂Fe^{+/0}. The calculated values of Φ_b for



Figure 4.10. Representative *J*-*E* data under 100 mW cm⁻² simulated sunlight illumination for functionalized Si(111) surfaces in contact with Cp*₂Fe^{+/0} (1.2, 0.92 mM) in dry CH₃CN for (a) n-type and (b) p-type samples. Si(111)–CH₃ samples (solid black) are shown for comparison with Si(111)–MMTFPA (dashed red) and Si(111)–TFPA (blue dotted) samples.

Table 4.1. E_{oc} and Φ_b measurements for functionalized Si surfaces in contact with CH₃CN-Cp*₂Fe^{+/0}.

Surface	$E_{\rm oc}$ in Cp* ₂ Fe ^{+/0} (V) ^a	$\Phi_{\rm b}$ in Cp* ₂ Fe ^{+/0} (V) ^b	$\theta_{\mathrm{TFPA}}(\mathrm{ML})$
n-Si-CH3	-0.43 ± 0.02	1.07	0
n-Si-MMTFPA	-0.16 ± 0.03	0.56 ± 0.01	0.23 ± 0.01
n-Si–TFPA	-0.072 ± 0.001	0.427 ± 0.001	0.307 ± 0.007
p-Si–CH ₃	$+0.03 \pm 0.03$	_	0
p-Si-MMTFPA	$+0.095 \pm 0.004$	0.56 ± 0.07	0.193 ± 0.007
p-Si-TFPA	$+0.12 \pm 0.02$	0.35 ± 0.01	0.27 ± 0.02

^{*a*}The redox couple concentrations were 1.2 mM Cp*₂Fe⁺ and 0.92 mM Cp*₂Fe. The effective cell potentials calculated from eq 4.12 and eq 4.13 were $E_{eff,n}$ (Cp*₂Fe^{+/0}) = -0.073 V and $E_{eff,p}$ (Cp*₂Fe^{+/0}) = -0.188 V versus SCE. ^{*b*}The values of Φ_b were determined by C_{diff} -*E* measurements using eq 4.8 through 4.11 and are reported as unsigned magnitudes. No value for Φ_b is reported for samples that formed weakly rectifying junctions with the redox solution.

n-Si(111)–MMTFPA and n-Si(111)–TFPA samples were lowered in magnitude by 0.51 and 0.64 V, respectively, compared with Φ_b for n-Si(111)–CH₃ samples in contact with CH₃CN-Cp*₂Fe^{+/0}. The dopant density, N_D , for functionalized n-Si samples was found to be $(4.6 \pm 0.8) \times 10^{15}$ cm⁻³, which agreed well with N_D determined from four-point probe measurements $(4.4 \times 10^{15} \text{ cm}^{-3})$.

For p-Si samples in contact with CH₃CN-Cp*₂Fe^{+/0}, the E_{oc} shifted positively and Φ_b increased in magnitude for surfaces that contained TFPA functionality compared with p-Si(111)–CH₃ surfaces. The p-Si(111)–CH₃ samples exhibited very low photovoltages (Table 4.1), and Φ_b was too small to be accurately determined by C_{diff} -E measurements. The p-Si(111)–MMTFPA samples exhibited a moderate shift in E_{oc} of +0.07 V relative to p-Si(111)–CH₃ samples, and p-Si(111)–TFPA samples showed a slightly greater shift in E_{oc} of +0.09 V. The p-Si(111)–MMTFPA samples yielded $\Phi_b = 0.56 \pm 0.07$ V, while p-Si(111)–TFPA samples yielded an apparent Φ_b of 0.35 \pm 0.01 V despite the higher E_{oc} observed for these samples relative to p-Si(111)–MMTFPA samples. The value of N_D determined from C_{diff} -E measurements in contact with CH₃CN-Cp*₂Fe^{+/0} was 2.0 \pm 0.3 \times 10¹⁶ cm⁻³, compared with the value of $N_D = 4.0 \times 10^{16}$ cm⁻³ determined from four-point probe measurements.

4.3.4 Photoelectrochemical Behavior of Si(111)–TFPA and Si(111)–MMTFPA Surfaces in Contact with CH₃CN- MV^{2+/+•}

Figure 4.11 shows representative *J-E* data for functionalized n- and p-Si(111) samples in contact with CH₃CN-MV^{2+/+•} (1.5, 0.035 mM) under 100 mW⁻² simulated solar illumination. The effective cell potential, $E_{eff}(MV^{2+/+•})$, was determined using eqs 4.12 and 4.13 to give $E_{eff,n}$ (MV^{2+/+•}) = -0.244 V and $E_{eff,p}$ (MV^{2+/+•}) = -0.436 V versus SCE. Low concentrations (0.035 mM) of the radical MV^{+•} species resulted in very low anodic photocurrent densities. Table 4.2 presents the measured values of E_{oc} determined for the functionalized electrodes under 100 mW cm⁻² illumination, in addition to the absolute values of Φ_b determined from C_{diff} -*E* measurements.



Figure 4.11. Representative *J*-*E* data under 100 mW cm⁻² illumination for functionalized Si(111) surfaces in contact with MV^{2+/+•} (1.5, 0.035 mM) in dry CH₃CN for (a) n-type and (b) p-type samples. Si(111)–CH₃ samples (solid black) are shown for comparison with Si(111)–MMTFPA (dashed red) and Si(111)–TFPA (blue dotted) samples.

The E_{oc} , shown in Table 4.2, of n-Si(111)–MMTFPA samples in contact with CH₃CN-MV^{2+/+•} shifted by +0.24 V relative to the E_{oc} of n-Si(111)–CH₃ samples. This

shift is comparable to the shift observed for the same samples in contact with CH₃CN-Cp*₂Fe^{+/0}. The n-Si(111)–TFPA samples in contact with CH₃CN-MV^{2+/+•} exhibited a slightly larger shift in E_{oc} of +0.25 V compared with the E_{oc} for n-Si(111)–CH₃ samples. The value of Φ_b for n-Si(111)–CH₃ samples in contact with CH₃CN-MV^{2+/+•} was 0.64 ± 0.06 V, while the low barrier at n-Si(111)–MMTFPA and n-Si(111)–TFPA junctions with CH₃CN-MV^{2+/+•} precluded determination of Φ_b by C_{diff} -E measurements. The change in measured E_{oc} and Φ_b for n-Si samples containing TFPA functionality is consistent with an overall positive shift in the composite molecular dipole present at the interface. The dopant density, N_D , for functionalized n-Si samples was found to be (4.7 ± 0.2) × 10¹⁵ cm⁻³ in contact with CH₃CN-MV^{2+/+•}.

Table 4.2. E_{oc} and Φ_b measurements for functionalized Si surfaces in contact with CH₃CN-MV^{2+/+•}.

Surface	$E_{\rm oc}$ in ${\rm MV}^{2+/+\bullet}$ ${\rm (V)}^a$	$\Phi_{\rm b}$ in ${ m MV}^{2+/+ \bullet}({ m V})^b$	$\theta_{\mathrm{TFPA}}(\mathrm{ML})$
n-Si–CH ₃	-0.26 ± 0.02	0.64 ± 0.06	0
n-Si-MMTFPA	-0.021 ± 0.007	_	0.23 ± 0.01
n-Si–TFPA	-0.01 ± 0.01	_	0.310 ± 0.007
p-Si–CH ₃	$+0.15 \pm 0.01$	0.51 ± 0.08	0
p-Si-MMTFPA	$+0.254 \pm 0.009$	0.99 ± 0.07	0.196 ± 0.002
p-Si–TFPA	$+0.24 \pm 0.02$	0.7 ± 0.1	0.26 ± 0.02

^{*a*}The redox couple concentrations were 1.5 mM MV²⁺ and 0.035 mM MV⁺. The effective cell potentials calculated from eq 4.12 and eq 4.13 were $E_{\text{eff,n}}$ (MV^{2+/+*}) = -0.244 V and $E_{\text{eff,p}}$ (MV^{2+/+*}) = -0.436 V versus SCE. ^{*b*}The values of Φ_b were determined by C_{diff} -*E* measurements using eq 4.8 through 4.11 and are reported as unsigned magnitudes. No value for Φ_b is reported for samples that formed weakly rectifying junctions with the redox solution.

As observed for p-Si samples in contact with CH₃CN-Cp*₂Fe^{+/0}, the E_{oc} for p-Si(111)–MMTFPA and p-Si(111)–TFPA samples in contact with CH₃CN-MV^{2+/++} shifted positively relative to E_{oc} for p-Si(111)–CH₃ surfaces (Table 4.2). The positive shift in E_{oc} was accompanied by an increase in the magnitude of Φ_b . The p-Si(111)–MMTFPA samples exhibited a modest shift in E_{oc} , of +0.10 V in contact with MV^{2+/++} relative to the E_{oc} of p-Si(111)–CH₃ samples, and p-Si(111)–TFPA samples showed a very similar shift in E_{oc} of +0.09 V relative to p-Si(111)–CH₃ samples. For p-Si(111)–CH₃ samples, Φ_b was determined by C_{diff} -E measurements to be 0.51 ± 0.08 V, while $\Phi_b = 0.99 \pm 0.07$ V for p-Si(111)–MMTFPA surfaces; that is, the barrier height of this junction is close to the Si band gap. As was observed in contact with Cp*₂Fe^{+/0}, p-Si(111)–TFPA samples yielded a lower Φ_b of 0.7 ± 0.1 V, despite the nearly identical E_{oc} observed for these samples as compared with p-Si(111)–MMTFPA samples. The value of N_D determined from C_{diff} -E measurements was (2.4 ± 0.4) × 10¹⁶ cm⁻³.

4.4 DISCUSSION

4.4.1 Si(111)–TFPA Surface Characterization

The TIRS data for Si(111)–TFPA surfaces yielded modes consistent with the presence of a phenyl ring, aryl C–F bonds, and a C=C bond (Figure 4.3). The observation of the C=C stretch at 2160 cm⁻¹ at 74° incidence but not at 30° incidence indicates that the TFPA groups are predominantly oriented perpendicular to the surface. The large reduction in intensity of the primary aromatic C–C stretching peak at 1533 cm⁻¹ for 30° incidence relative to 74° incidence demonstrates that this mode is primarily oriented

perpendicular to the surface. Similarly, the C–F stretching signal at 1251 cm⁻¹ was greatly reduced at 30° incidence relative to 74° incidence, indicating that the majority of this mode is oriented perpendicular to the surface. The residual intensity observed for the 1533 and 1251 cm⁻¹ modes at 30° incidence indicates that a fraction of each mode is not perpendicular to the surface, in accord with expectations based on the geometry of the TFPA group. The in-plane aromatic C–H bend was observed at both angles of incidence at 1055 cm⁻¹, indicating that this mode is not primarily oriented perpendicular to the surface. The aryl C–H stretching peaks near 3050 cm⁻¹ were not observed by TIRS, suggesting that substitution of the phenyl group with C–F bonds weakens the C–H stretching signal for the TFPA group.

TIRS data for the Si(111)–MMTFPA surface, presented in Figure 4.4, showed a single peak at 1253 cm⁻¹ that was ascribed to the overlap of the symmetric C–H bending and C–F stretching modes. The energy of this mode falls between the TFPA C–F stretch, observed at 1251 cm⁻¹, and the symmetric C–H bend of the –CH₃ group, observed at 1257 cm^{-1.50} The Si(111)–TFPA sample exhibited a 0.18 height ratio of the peak at 1253 cm⁻¹ relative to the peak at 1533 cm⁻¹, while the Si(111)–MMTFPA sample yielded a 0.22 height ratio of the peak at 1251 cm⁻¹ relative to the peak at 1251 cm⁻¹ relative to the peak at 1251 cm⁻¹ relative to the peak at 1253 cm⁻¹. Thus, the peak at 1253 cm⁻¹ on the Si(111)–MMTFPA sample results from a convolution of the symmetric C–H bending and C–F stretching modes, indicating that both TFPA and –CH₃ groups are present on the surface.

The shoulder observed in the C 1s XPS signal of the Si(111)–TFPA surface (Figure 4.7b) centered at 284.1 eV provides evidence of the formation of a Si–C bond.

The residual Cl observed on Si(111)–MMTFPA surfaces for samples with $\theta_{\text{TFPA}} > 0.2$ ML is consistent with steric crowding on the surface that prevented the reaction of a small fraction of residual Si–Cl sites with CH₃MgCl. This behavior suggests considerable steric crowding that limited further passivation of the remaining Si–Cl sites on surfaces with $\theta_{\text{TFPA}} > 0.2$ ML.

A small amount of SiO_x was observed in the Si 2p spectrum from 102–104 eV on Si(111)–MMTFPA surfaces containing $\theta_{TFPA} > 0.15$ ML and on Si(111)–TFPA surfaces. Mixed monolayers with high concentrations of bulky groups can prevent passivation of neighboring Si–Cl sites with –CH₃ groups for steric reasons, leaving the surface sites more susceptible to oxidation.³⁴ Consistently, slightly more SiO_x was observed on Si(111)–TFPA surfaces compared with Si(111)–MMTFPA surfaces with high θ_{TFPA} .

Si(111)–MMTFPA samples exhibited high *S* compared with previously reported mixed monolayers.^{7, 34, 43} High concentrations of bulky groups in mixed monolayers can sterically block passivation of Si–Cl sites with –CH₃ groups, leaving the unreacted sites susceptible to oxidation and formation of surface states.^{7, 34, 43} This expectation is consistent with the behavior of Si(111)–MMTFPA surfaces with $\theta_{TFPA} > 0.2$ ML, which had unreacted Si–Cl sites that likely contributed to increased surface recombination velocity, *S*, for surfaces with high θ_{TFPA} . Mixed methyl/allyl³⁴ and mixed methyl/propionaldehyde⁷ monolayers, which were formed using Grignard reagents only, exhibited *S* < 100 cm s⁻¹. Mixed methyl/thienyl monolayers,⁴³ prepared using 2-thienyllithium, exhibited *S* < 100 cm s⁻¹ for $\theta_{SC_4H_3} < 0.3$ ML. However, the Si(111)–MMTFPA surface exhibited significantly higher *S*, even for $\theta_{\text{TFPA}} = 0.15$ ML (Figure 4.5), than has been observed for other mixed monolayers.

Small-molecule silanes have been shown to undergo cleavage of the Si-Si bonds in the presence of organolithium reagents, such as methyllithium.⁶³⁻⁶⁴ Furthermore, addition of organolithium reagents to H-terminated porous Si surfaces has been proposed to proceed by cleavage of Si-Si bonds.⁶⁵⁻⁶⁶ The reaction of 1-propynyllithium with Si(111)-Cl surfaces also yields samples with $S = 1.0 \times 10^3$ cm s⁻¹ (72 h after preparation), despite near complete termination of the Si atop sites with Si-C bonds.³³ However, reaction of CH₃Li with Si(111)-Cl surfaces is known to yield samples with S values comparable to those of samples prepared by reaction with CH₃MgCl.⁴³ Thus, the chemical nature of the organolithium reagent plays an important role in properties of the resulting functionalized surfaces. CH₃Li could form surfaces with low S because the small size of the $-CH_3$ group kinetically allows for passivation of all Si(111) atop sites without the breaking of Si-Si bonds. Hence, a route that utilizes only Grignard reagents to attach the bulky group to Si(111)–Cl surfaces for the synthesis of mixed methyl monolayers could be required to obtain low S values at functionalized Si(111) surfaces. Grignard reagents formed from terminal acetylides have been observed to undergo undetectable or slow reaction with Si(111)-Cl surfaces,³³ and consistently, reaction of the Grignard reagent 3,4,5trifluorophenylethynylmagnesium chloride with Si(111)-Cl at 50 °C yielded a maximum $\theta_{\text{TFPA}} < 0.05$ ML. Thus, the organolithium reagent, LiTFPA, used herein for the synthesis of Si(111)-TFPA and Si(111)-MMTFPA surfaces, was necessary to achieve the reported monolayer compositions and shifts in the band-edge positions.

4.4.2 Hg Contacts to Si(111)–MMTFPA Surfaces

The work function of Hg is 4.49 eV,⁶⁷ which lies between the energies of the bottom of the conduction band and the top of the valence band of bulk Si and is very near the estimated energy of the absolute electrochemical potential for the standard hydrogen electrode (SHE), which is 4.44 eV at 25 °C.⁶⁸⁻⁶⁹ Hg can also be readily applied to and removed from the Si surface at room temperature without the formation of metal silicides.⁴⁰

The *J*-*V* data presented in Figure 4.8 and the plots of Φ_b versus θ_{TFPA} in Figure 4.9 show a clear trend in the value of Φ_b as a function of θ_{TFPA} for functionalized n- and p-Si(111) surfaces in contact with Hg. The surface composition played an essential role in the electrical behavior of the junction. The composite dipole at the interface between the Si and the Hg results in a net electric field that can be tuned to energetically favor the transfer of electrons from p-Si to Hg or holes from n-Si to Hg, respectively. The n-Si/Hg junction exhibited maximum rectification for surfaces terminated by –CH₃ groups, and addition of TFPA to the monolayer yielded junctions with lower Φ_b . The decrease in Φ_b with increase in θ_{TFPA} resulted from a shift in the band-edge positions of the Si relative to those of the Hg contacting phase. The electrical behavior of n-Si(111)–MMTFPA/Hg junctions that showed ohmic behavior by *J*-*V* analysis could have also been influenced by a high surface recombination velocity, which was measured for samples with high θ_{TFPA} .

For p-Si, the Si(111)–CH₃ surface formed an ohmic contact with Hg. The addition of TFPA to the monolayer resulted in an increase in Φ_b as θ_{TFPA} increased. Therefore, as

 θ_{TFPA} increased, the band-edge positions of the Si shifted relative to the band-edge positions of Si(111)–CH₃ surfaces. This behavior is consistent with the formation of a surface dipole in the orientation shown in Figure 4.1b due to the addition of surficial TFPA. The resulting electric field at the interface is favorable for the flow of electrons from p-Si to the Hg contacting phase.

The values of Φ_b for Hg contacts to n-Si electrodes determined by *J-V* analysis agreed well with those obtained by C_{diff} -*V* analysis. In contrast, C_{diff} -*V* analysis for p-Si/Hg contacts with θ_{TFPA} near 0.2 ML yielded $\Phi_b = 1.07$ V, that is, close to the Si band gap, while *J-V* data of the same samples yielded $\Phi_b = 0.68$ V. The C_{diff} -*V* analysis is performed while the sample is in reverse bias and passes only small amounts of current to measure the real and imaginary impedance as well as the current-voltage phase shift. C_{diff} -*V* analysis thus minimizes the effects of recombination current on the calculated Φ_b . *J-V* analysis, in contrast, is performed in forward bias, for which significantly more current passes, and where the effects of high surface recombination are greater. The difference in Φ_b determined for p-Si(111)–MMTFPA/Hg by *J-V* versus C_{diff} -*V* methods indicates that high *S* values yield lower Φ_b when measured by *J-V* analysis.

Si(111)–H surfaces have been widely used for fabrication of Si-based optoelectronic devices, and comparison of the band- edge positions of Si(111)–H surfaces with the results reported in this work is informative. For n-Si, the electrical behavior of Si(111)–H surfaces in contact with Hg produced a junction with $\Phi_b = 0.3$ V, which appeared ohmic when measured at 296 K.⁴⁰ The n-Si(111)–MMTFPA samples with $\theta_{TFPA} > 0.17$ ML in contact with Hg produced behavior similar to the n-Si(111)–H

samples. Previous results for p-Si(111)–H/Hg junctions yielded $\Phi_b = 0.8$ V by both *J-V* and C_{diff} -V measurements,⁴⁰ while p-Si(111)–MMTFPA samples achieved a maximum Φ_b of 0.68 V when measured by *J-V* analysis. The near-band gap Φ_b measured by C_{diff} -V analysis for p-Si(111)–MMTFPA samples indicated that the band-edge positions were energetically closer to the vacuum level than the band-edge positions of Si(111)–H surfaces, but high *S* values for these surfaces limited the Φ_b measured under *J-V* operation.

4.4.3 Photoelectrochemical Measurements of Si(111)–TFPA and Si(111)–MMTFPA Surfaces in CH₃CN

Photoelectrochemical measurements for n- and p- Si(111)–CH₃ samples in contact with CH₃CN-Cp*₂Fe^{+/0} were in good agreement with previously reported results;⁴⁷ however, n- and p-Si(111)–CH₃ samples in contact with CH₃CN-MV^{2+/++} exhibited E_{oc} values of -0.26 ± 0.02 and $+0.15 \pm 0.01$ V, respectively, that were not within the error of previously reported results of -0.10 ± 0.03 and $+0.31 \pm 0.02$ V, respectively.⁴⁷ The calculated values of $E_{eff,n}$ (MV^{2+/++}) and $E_{eff,p}$ (MV^{2+/++}) were shifted by -0.16 and -0.13 V, respectively, compared with previous work. This difference in effective solution potential likely arose because the previous work used 1,1'-dimethyl-4,4'-bipyridinium hexafluorophosphate. The reversible potential for the MV^{2+/++} couple has previously been found to be dependent on the nature of the anion in the electrolyte.⁷⁰ For the calculated values of $E_{eff,n}$ (A/A⁻) and $E_{eff,p}$ (A/A⁻), extrapolation of

the results previously reported predicts E_{oc} values that are within close agreement with the values measured in this work.

Photoelectrochemical measurements under 100 mW cm⁻² illumination demonstrated that the E_{oc} exhibited by the semiconductor-liquid junctions was sensitive to the surface composition. Compared with Si(111)–CH₃ samples, E_{oc} for n-Si(111)– MMTFPA samples shifted by +0.27 V in contact with CH₃CN-Cp*₂Fe^{+/0} and by +0.24 V in contact with CH₃CN-MV^{2+/+•}. The n-Si(111)-TFPA samples exhibited a greater shift in E_{oc} , suggesting that the residual Si–Cl sites, with a molecular dipole in the positive direction (Figure 4.1b), and greater θ_{TFPA} contributed to the positive shift in the bandedge positions. Despite higher S observed for Si(111)-TFPA samples (Figure 4.5), Si(111)–TFPA samples showed larger shifts in E_{oc} than those observed for Si(111)– MMTFPA samples. This behavior indicated that the overall greater θ_{TFPA} observed for Si(111)–TFPA samples and inclusion of Si(111)–Cl sites contributed more to the overall $E_{\rm oc}$ than the high S measured for Si(111)–TFPA samples. The observation of different $E_{\rm oc}$ values for n-Si(111)-MMTFPA and n-Si(111)-TFPA samples in contact with different redox species indicates that the Fermi level of the semiconductor is not fully pinned by surface states, evidenced by the high observed S. The observed decrease in the magnitude of $\Phi_{\rm b}$ for n-Si(111)–TFPA and n-Si(111)–MMTFPA samples was indicative of a substantial positive shift in the band-edge positions of these surfaces relative to Si(111)-CH3 samples. The Eoc observed for n-Si(111)-MMTFPA samples in contact with $Cp*_2Fe^{+/0}$ and $MV^{2+/+}$ was further shifted positively by the high S observed for samples with high θ_{TFPA} .

The p-Si(111)–MMTFPA and p-Si(111)–TFPA samples exhibited a maximum shift in E_{oc} of +0.10 V relative to p-Si(111)–CH₃ samples in contact with Cp*₂Fe^{+/0} and MV^{2+/+*}. The increase in Φ_b observed for p-Si(111)–MMTFPA samples relative to p-Si(111)–CH₃ samples was ~0.5 V, which should produce a larger increase in E_{oc} than was observed. The E_{oc} observed for p-Si(111)–MMTFPA samples in contact with Cp*₂Fe^{+/0} and MV^{2+/+*} was shifted negatively by the high *S* observed for samples with high θ_{TFPA} . For p-Si samples, the effect on E_{oc} of high *S* opposes the effect on E_{oc} produced by the surface dipole, so the reduced positive shift in E_{oc} achieved for p-Si samples as compared with n-Si samples is consistent with the presence of significant surface recombination at such interfaces.

Monolayer chemistry on Si(111) surfaces can effectively control the interfacial energetics at Si(111) interfaces. Moreover, alkyl monolayers can be applied to a broad range of crystalline, polycrystalline, and thin-film semiconductors without requiring expensive, specialized processing equipment. The electrochemical measurements presented in this work demonstrate that mixed monolayers on Si(111) can produce measurable shifts in the band-edge positions to yield junctions with tunable energetics. The development of methods to reduce S while maintaining a surface composition comparable to that of the MMTFPA monolayers presented in this work may enable the use of a broad range of materials in semiconductor devices.

4.5 CONCLUSIONS

The electrochemical behavior of n- and p-Si(111)–MMTFPA samples in contact with Hg showed that the addition of TFPA to the monolayer produced shifts in the bandedge positions, relative to Si(111)–CH₃ surfaces, by ≥ 0.6 V for n-Si and ≥ 0.5 V for p-Si samples. Photoelectrochemical measurements in contact with $CH_3CN-Cp*_2Fe^{+/0}$ and $CH_3CN\text{-}MV^{2^{+/+\bullet}}$ demonstrated that the composition of the organic monolayer on the surface yielded shifts in E_{oc} consistent with a net positive molecular dipole at the Si surface. The n-Si(111)–MMTFPA samples exhibited E_{oc} values that shifted by as much as +0.27 V compared with n-Si(111)-CH₃ surfaces, and the p-Si(111)-MMTFPA samples showed E_{oc} values that shifted by up to +0.10 V with respect to the p-Si(111)- CH_3 surface. The change in E_{oc} for p-Si was limited by high surface recombination, suggesting that larger changes in E_{oc} could be achieved by maintaining low S while allowing for comparable levels of F coverage on the surface. Si(111)-MMTFPA surfaces provide a versatile and scalable means of tuning the Si band-edge positions, especially for samples with low θ_{TFPA} . Semiconductor surface chemistry therefore holds promise to allow for control of the interface between semiconductors and functional components, such as metals, metal oxides, catalysts, and conductive polymers.

4.6 REFERENCES

- Walter, M. G.; Warren, E. L.; McKone, J. R.; Boettcher, S. W.; Mi, Q.; Santori, E. A.; Lewis, N. S. Solar Water Splitting Cells. *Chem. Rev.* 2010, *110*, 6446-6473.
- Huang, Z.; McKone, J. R.; Xiang, C.; Grimm, R. L.; Warren, E. L.; Spurgeon, J. M.; Lewerenz, H.-J.; Brunschwig, B. S.; Lewis, N. S. Comparison Between the Measured and Modeled Hydrogen-Evolution Activity of Ni- or Pt-Coated Silicon Photocathodes. *Int. J. Hydrogen Energy* 2014, *39*, 16220-16226.
- McKone, J. R.; Warren, E. L.; Bierman, M. J.; Boettcher, S. W.; Brunschwig, B. S.; Lewis, N. S.; Gray, H. B. Evaluation of Pt, Ni, and Ni-Mo Electrocatalysts for Hydrogen Evolution on Crystalline Si Electrodes. *Energy Environ. Sci.* 2011, *4*, 3573-3583.
- Sun, K.; Saadi, F. H.; Lichterman, M. F.; Hale, W. G.; Wang, H.-P.; Zhou, X.; Plymale, N. T.; Omelchenko, S. T.; He, J.-H.; Papadantonakis, K. M.; Brunschwig, B. S.; Lewis, N. S. Stable Solar-Driven Oxidation of Water by Semiconducting Photoanodes Protected by Transparent Catalytic Nickel Oxide Films. *Proc. Natl. Acad. Sci. U.S.A.* 2015, *112*, 3612-3617.
- Sun, K.; McDowell, M. T.; Nielander, A. C.; Hu, S.; Shaner, M. R.; Yang, F.; Brunschwig, B. S.; Lewis, N. S. Stable Solar-Driven Water Oxidation to O₂(g) by Ni-Oxide-Coated Silicon Photoanodes. *J. Phys. Chem. Lett.* 2015, *6*, 592-598.
- Hu, S.; Shaner, M. R.; Beardslee, J. A.; Lichterman, M.; Brunschwig, B. S.; Lewis, N. S. Amorphous TiO₂ coatings stabilize Si, GaAs, and GaP photoanodes for efficient water oxidation. *Science* 2014, *344*, 1005-1009.

- O'Leary, L. E.; Strandwitz, N. C.; Roske, C. W.; Pyo, S.; Brunschwig, B. S.; Lewis, N. S. Use of Mixed CH₃–/HC(O)CH₂CH₂–Si(111) Functionality to Control Interfacial Chemical and Electronic Properties During the Atomic-Layer Deposition of Ultrathin Oxides on Si(111). *J. Phys. Chem. Lett.* 2015, *6*, 722-726.
- Kim, H. J.; Kearney, K. L.; Le, L. H.; Pekarek, R. T.; Rose, M. J. Platinum-Enhanced Electron Transfer and Surface Passivation through Ultrathin Film Aluminum Oxide (Al₂O₃) on Si(111)–CH₃ Photoelectrodes. *ACS Appl. Mater. Inter.* 2015, *7*, 8572-8584.
- Roske, C. W.; Popczun, E. J.; Seger, B.; Read, C. G.; Pedersen, T.; Hansen, O.; Vesborg, P. C. K.; Brunschwig, B. S.; Schaak, R. E.; Chorkendorff, I.; Gray, H. B.; Lewis, N. S. Comparison of the Performance of CoP-Coated and Pt-Coated Radial Junction n⁺p-Silicon Microwire-Array Photocathodes for the Sunlight-Driven Reduction of Water to H₂(g). *J. Phys. Chem. Lett.* **2015**, *6*, 1679-1683.
- Warren, E. L.; McKone, J. R.; Atwater, H. A.; Gray, H. B.; Lewis, N. S. Hydrogen-Evolution Characteristics of Ni-Mo-Coated, Radial Junction, n⁺p-Silicon Microwire Array Photocathodes. *Energy Environ. Sci.* 2012, *5*, 9653-9661.
- Juang, A.; Scherman, O. A.; Grubbs, R. H.; Lewis, N. S. Formation of Covalently Attached Polymer Overlayers on Si(111) Surfaces Using Ring-Opening Metathesis Polymerization Methods. *Langmuir* 2001, *17*, 1321-1323.
- Sailor, M. J.; Klavetter, F. L.; Grubbs, R. H.; Lewis, N. S. Electronic Properties of Junctions between Silicon and Organic Conducting Polymers. *Nature* 1990, *346*, 155-157.

- Giesbrecht, P. K.; Bruce, J. P.; Freund, M. S. Electric and Photoelectric Properties of 3,4–Ethylenedioxythiophene-Functionalized n-Si/PEDOT:PSS Junctions. *ChemSusChem* 2016, 9, 109-117.
- Bruce, J. P.; Oliver, D. R.; Lewis, N. S.; Freund, M. S. Electrical Characteristics of the Junction between PEDOT:PSS and Thiophene-Functionalized Silicon Microwires. *ACS Appl. Mater. Inter.* 2015, *7*, 27160-27166.
- 15. Warren, E. L.; Boettcher, S. W.; Walter, M. G.; Atwater, H. A.; Lewis, N. S. pH-Independent, 520 mV Open-Circuit Voltages of Si/Methyl Viologen^{2+/+} Contacts Through Use of Radial n⁺p-Si Junction Microwire Array Photoelectrodes. *J. Phys. Chem. C* 2011, *115*, 594-598.
- Johansson, E.; Boettcher, S. W.; O'Leary, L. E.; Poletayev, A. D.; Maldonado, S.; Brunschwig, B. S.; Lewis, N. S. Control of the pH-Dependence of the Band Edges of Si(111) Surfaces Using Mixed Methyl/Allyl Monolayers. *J. Phys. Chem. C* 2011, *115*, 8594-8601.
- Boettcher, S. W.; Warren, E. L.; Putnam, M. C.; Santori, E. A.; Turner-Evans, D.;
 Kelzenberg, M. D.; Walter, M. G.; McKone, J. R.; Brunschwig, B. S.; Atwater, H. A.;
 Lewis, N. S. Photoelectrochemical Hydrogen Evolution Using Si Microwire Arrays. *J. Am. Chem. Soc.* 2011, *133*, 1216-1219.
- Heller, A., Chemical Control of Surface and Grain Boundary Recombination in Semiconductors. In *Photoeffects at Semiconductor-Electrolyte Interfaces*, AMERICAN CHEMICAL SOCIETY: 1981; Vol. 146, pp 57-77.
- Zhou, X.; Liu, R.; Sun, K.; Friedrich, D.; McDowell, M. T.; Yang, F.; Omelchenko, S. T.; Saadi, F. H.; Nielander, A. C.; Yalamanchili, S.; Papadantonakis, K. M.;

Brunschwig, B. S.; Lewis, N. S. Interface Engineering of the Photoelectrochemical Performance of Ni-Oxide-Coated n-Si Photoanodes by Atomic-Layer Deposition of Ultrathin Films of Cobalt Oxide. *Energy Environ. Sci.* **2015**, *8*, 2644-2649.

- Smith, W. A.; Sharp, I. D.; Strandwitz, N. C.; Bisquert, J. Interfacial Band-Edge Energetics for Solar Fuels Production. *Energy Environ. Sci.* 2015, *8*, 2851-2862.
- Kocha, S. S.; Turner, J. A. Displacement of the Bandedges of GaInP₂ in Aqueous Electrolytes Induced by Surface Modification. *J. Electrochem. Soc.* 1995, *142*, 2625-2630.
- Hilal, H. S.; Turner, J. A. Controlling Charge-Transfer Processes at Semiconductor/Liquid Junctions. *Electrochim. Acta* 2006, *51*, 6487-6497.
- MacLeod, B. A.; Steirer, K. X.; Young, J. L.; Koldemir, U.; Sellinger, A.; Turner, J. A.; Deutsch, T. G.; Olson, D. C. Phosphonic Acid Modification of GaInP₂ Photocathodes Toward Unbiased Photoelectrochemical Water Splitting. *ACS Appl. Mater. Inter.* 2015, 7, 11346-11350.
- 24. Kim, H. J.; Seo, J.; Rose, M. J. H₂ Photogeneration Using a Phosphonate-Anchored Ni-PNP Catalyst on a Band-Edge-Modified p-Si(111)|AZO Construct. ACS Appl. Mater. Inter. 2016, 8, 1061-1066.
- Seo, J.; Kim, H. J.; Pekarek, R. T.; Rose, M. J. Hybrid Organic/Inorganic Band-Edge Modulation of p-Si(111) Photoelectrodes: Effects of R, Metal Oxide, and Pt on H₂ Generation. *J. Am. Chem. Soc.* 2015, *137*, 3173-3176.
- 26. Ciampi, S.; Harper, J. B.; Gooding, J. J. Wet Chemical Routes to the Assembly of Organic Monolayers on Silicon Surfaces via the Formation of Si–C Bonds: Surface Preparation, Passivation and Functionalization. *Chem. Soc. Rev.* 2010, *39*, 2158-2183.

- Ciampi, S.; Luais, E.; James, M.; Choudhury, M. H.; Darwish, N. A.; Gooding, J. J. The Rapid Formation of Functional Monolayers on Silicon under Mild Conditions. *Phys. Chem. Chem. Phys.* 2014, *16*, 8003-8011.
- Linford, M. R.; Chidsey, C. E. D. Alkyl Monolayers Covalently Bonded to Silicon Surfaces. J. Am. Chem. Soc. 1993, 115, 12631-12632.
- Buriak, J. M. Illuminating Silicon Surface Hydrosilylation: An Unexpected Plurality of Mechanisms. *Chem. Mater.* 2014, *26*, 763-772.
- Buriak, J. M.; Sikder, M. D. H. From Molecules to Surfaces: Radical-Based Mechanisms of Si–S and Si–Se Bond Formation on Silicon. *J. Am. Chem. Soc.* 2015, *137*, 9730-9738.
- Bansal, A.; Li, X.; Lauermann, I.; Lewis, N. S.; Yi, S. I.; Weinberg, W. H. Alkylation of Si Surfaces Using a Two-Step Halogenation/Grignard Route. *J. Am. Chem. Soc.* 1996, 118, 7225-7226.
- Royea, W. J.; Juang, A.; Lewis, N. S. Preparation of Air-Stable, Low Recombination Velocity Si(111) Surfaces through Alkyl Termination. *Appl. Phys. Lett.* 2000, 77, 1988-1990.
- Plymale, N. T.; Kim, Y.-G.; Soriaga, M. P.; Brunschwig, B. S.; Lewis, N. S. Synthesis, Characterization, and Reactivity of Ethynyl- and Propynyl-Terminated Si(111) Surfaces. J. Phys. Chem. C 2015, 119, 19847-19862.
- 34. O'Leary, L. E.; Johansson, E.; Brunschwig, B. S.; Lewis, N. S. Synthesis and Characterization of Mixed Methyl/Allyl Monolayers on Si(111). *J. Phys. Chem. B* 2010, *114*, 14298-14302.

- 35. Webb, L. J.; Lewis, N. S. Comparison of the Electrical Properties and Chemical Stability of Crystalline Silicon(111) Surfaces Alkylated Using Grignard Reagents or Olefins with Lewis Acid Catalysts. J. Phys. Chem. B 2003, 107, 5404-5412.
- Webb, L. J.; Michalak, D. J.; Biteen, J. S.; Brunschwig, B. S.; Chan, A. S. Y.; Knapp,
 D. W.; Meyer, H. M.; Nemanick, E. J.; Traub, M. C.; Lewis, N. S. High-Resolution
 Soft X-ray Photoelectron Spectroscopic Studies and Scanning Auger Microscopy
 Studies of the Air Oxidation of Alkylated Silicon(111) Surfaces. *J. Phys. Chem. B* 2006, *110*, 23450-23459.
- Bansal, A.; Lewis, N. S. Stabilization of Si Photoanodes in Aqueous Electrolytes through Surface Alkylation. J. Phys. Chem. B 1998, 102, 4058-4060.
- Maldonado, S.; Knapp, D.; Lewis, N. S. Near-Ideal Photodiodes from Sintered Gold Nanoparticle Films on Methyl-Terminated Si(111) Surfaces. J. Am. Chem. Soc. 2008, 130, 3300-3301.
- Maldonado, S.; Lewis, N. S. Behavior of Electrodeposited Cd and Pb Schottky Junctions on CH₃-Terminated n-Si(111) Surfaces. *J. Electrochem. Soc.* 2009, *156*, H123-H128.
- Maldonado, S.; Plass, K. E.; Knapp, D.; Lewis, N. S. Electrical Properties of Junctions between Hg and Si(111) Surfaces Functionalized with Short-Chain Alkyls. *J. Phys. Chem. C* 2007, *111*, 17690-17699.
- Hunger, R.; Fritsche, R.; Jaeckel, B.; Jaegermann, W.; Webb, L. J.; Lewis, N. S. Chemical and Electronic Characterization of Methyl-Terminated Si(111) Surfaces by High-Resolution Synchrotron Photoelectron Spectroscopy. *Phys. Rev. B* 2005, *72*, 045317.

- Wong, K. T.; Lewis, N. S. What a Difference a Bond Makes: The Structural, Chemical, and Physical Properties of Methyl-Terminated Si(111) Surfaces. *Acc. Chem. Res.* 2014, 47, 3037-3044.
- 43.O'Leary, L. E.; Rose, M. J.; Ding, T. X.; Johansson, E.; Brunschwig, B. S.; Lewis, N. S. Heck Coupling of Olefins to Mixed Methyl/Thienyl Monolayers on Si(111) Surfaces. J. Am. Chem. Soc. 2013, 135, 10081-10090.
- 44. Lattimer, J. R. C.; Blakemore, J. D.; Sattler, W.; Gul, S.; Chatterjee, R.; Yachandra, V. K.; Yano, J.; Brunschwig, B. S.; Lewis, N. S.; Gray, H. B. Assembly, Characterization, and Electrochemical Properties of Immobilized Metal Bipyridyl Complexes on Silicon(111) Surfaces. *Dalton Trans.* 2014, *43*, 15004-15012.
- Lattimer, J. R. C.; Brunschwig, B. S.; Lewis, N. S.; Gray, H. B. Redox Properties of Mixed Methyl/Vinylferrocenyl Monolayers on Si(111) Surfaces. *J. Phys. Chem. C* 2013, *117*, 27012-27022.
- Rivillon, S.; Chabal, Y. J.; Webb, L. J.; Michalak, D. J.; Lewis, N. S.; Halls, M. D.;
 Raghavachari, K. Chlorination of Hydrogen-Terminated Silicon (111) Surfaces. *J. Vac. Sci. Technol. A* 2005, *23*, 1100-1106.
- 47. Grimm, R. L.; Bierman, M. J.; O'Leary, L. E.; Strandwitz, N. C.; Brunschwig, B. S.; Lewis, N. S. Comparison of the Photoelectrochemical Behavior of H-Terminated and Methyl-Terminated Si(111) Surfaces in Contact with a Series of One-Electron, Outer-Sphere Redox Couples in CH₃CN. *J. Phys. Chem. C* 2012, *116*, 23569-23576.
- Hendrickson, D. N.; Sohn, Y. S.; Gray, H. B. Magnetic Susceptibility Study of Various Ferricenium and Iron(III) Dicarbollide Compounds. *Inorg. Chem.* 1971, 10, 1559-1563.

- Megehee, E. G.; Johnson, C. E.; Eisenberg, R. Optical versus Thermal Electron Transfer between Iridium(I) Maleonitriledithiolate Complexes and Methyl Viologen. *Inorg. Chem.* 1989, 28, 2423-2431.
- Webb, L. J.; Rivillon, S.; Michalak, D. J.; Chabal, Y. J.; Lewis, N. S. Transmission Infrared Spectroscopy of Methyl- and Ethyl-Terminated Silicon(111) Surfaces. *J. Phys. Chem. B* 2006, *110*, 7349-7356.
- Li, Y.; O'Leary, L. E.; Lewis, N. S.; Galli, G. Combined Theoretical and Experimental Study of Band-Edge Control of Si through Surface Functionalization. *J. Phys. Chem. C* 2013, *117*, 5188-5194.
- 52. Haber, J. A.; Lewis, N. S. Infrared and X-ray Photoelectron Spectroscopic Studies of the Reactions of Hydrogen-Terminated Crystalline Si(111) and Si(100) Surfaces with Br₂, I₂, and Ferrocenium in Alcohol Solvents. *J. Phys. Chem. B* **2002**, *106*, 3639-3656.
- Seah, M. P.; Spencer, S. J. Ultrathin SiO₂ on Si II. Issues in Quantification of the Oxide Thickness. *Surf. Interface Anal.* 2002, *33*, 640-652.
- 54. van der Marel, C.; Yildirim, M.; Stapert, H. R. Multilayer Approach to the Quantitative Analysis of X-ray Photoelectron Spectroscopy Results: Applications to Ultrathin SiO₂ on Si and to Self-Assembled Monolayers on Gold. *J. Vac. Sci. Technol. A* 2005, *23*, 1456-1470.
- 55. Kratochvil, B.; Lorah, E.; Garber, C. Silver-Silver Nitrate Couple as Reference Electrode in Acetonitrile. *Anal. Chem.* **1969**, *41*, 1793-1796.
- 56. Kim, N. Y.; Laibinis, P. E. Derivatization of Porous Silicon by Grignard Reagents at Room Temperature. J. Am. Chem. Soc. 1998, 120, 4516-4517.

- 57. Socrates, G. Infrared and Raman Characteristic Group Frequencies: Tables and Charts, 3rd ed.; John Wiley & Sons Ltd.: Chichester, West Sussex, England, 2001.
- Larkin, P. J. *IR and Raman Spectroscopy: Principles and Spectral Interpretation*; Elsevier: Waltham, MA, USA, 2011.
- Stuart, B. H. Infrared Spectroscopy: Fundamentals and Applications; John Wiley & Sons Ltd.: Chichester, West Sussex, England, 2004.
- Jaeckel, B.; Hunger, R.; Webb, L. J.; Jaegermann, W.; Lewis, N. S. High-Resolution Synchrotron Photoemission Studies of the Electronic Structure and Thermal Stability of CH₃- and C₂H₅-Functionalized Si(111) Surfaces. *J. Phys. Chem. C* 2007, *111*, 18204-18213.
- 61. Moulder, J. F.; Stickle, W. F.; Sobol, P. E.; Bomen, K. D. Handbook of X-ray Photoelectron Spectroscopy: A Reference Book of Standard Spectra for Identification and Interpretation of XPS Data; Physical Electronics USA, Inc.: Chanhassen, Minnesota, 1995.
- Collins, G.; O'Dwyer, C.; Morris, M.; Holmes, J. D. Palladium-Catalyzed Coupling Reactions for the Functionalization of Si Surfaces: Superior Stability of Alkenyl Monolayers. *Langmuir* 2013, 29, 11950-11958.
- Still, W. C. Conjugate Addition of Trimethysilyllithium. A Preparation of 3-Silyl Ketones. J. Org. Chem. 1976, 41, 3063-3064.
- Hevesi, L.; Dehon, M.; Crutzen, R.; Lazarescu-Grigore, A. Kinetic Control in the Cleavage of Unsymmetrical Disilanes. *J. Org. Chem.* 1997, *62*, 2011-2017.

- 65. Song, J. H.; Sailor, M. J. Functionalization of Nanocrystalline Porous Silicon Surfaces with Aryllithium Reagents: Formation of Silicon–Carbon Bonds by Cleavage of Silicon–Silicon Bonds. J. Am. Chem. Soc. 1998, 120, 2376-2381.
- 66. Kim, N. Y.; Laibinis, P. E. Improved Polypyrrole/Silicon Junctions by Surfacial Modification of Hydrogen-Terminated Silicon Using Organolithium Reagents. *J. Am. Chem. Soc.* 1999, *121*, 7162-7163.
- 67. *Handbook of Chemistry and Physics*, 75th ed.; CRC Press, Inc.: Boca Raton, Florida, 1994.
- Trasatti, S. The Absolute Electrode Potential: An Explanatory Note. *Pure Appl. Chem.* **1986**, *58*, 955-966.
- Dekker, M. Standard Potentials in Aqueous Solution; CRC Press, Inc.: New York, 1985.
- Bird, C. L.; Kuhn, A. T. Electrochemistry of the Viologens. *Chem. Soc. Rev.* 1981, 10, 49-82.