Chapter 4

Photoelectrochemical Behavior of ntype Si(111) Electrodes Coated With a Single Layer of Graphene

4.1 Introduction and Background

In this chapter, I discuss the behavior of monolayer graphene-coated n-Si photoanodes. The behavior of graphene-coated n-type Si(111 photoanodes was compared to the behavior of H-terminated n-type Si(111) photoanodes in contact with aqueous $K_3[Fe(CN)_6]/K_4[Fe(CN)_6]$ as well as in contact with a series of outer-sphere, one-electron redox couples in non-aqueous electrolytes. The n-Si/Graphene electrodes exhibited stable short-circuit photocurrent densities of over 10 mA cm⁻² for >1000 s of continuous operation in aqueous electrolytes, whereas n-Si-H electrodes yielded a nearly complete decay of the current density within ~30 s. the values of the open-circuit photovoltages and the flat-band potentials of the Si were a function of both the Fermi level of the graphene and the electrochemical potential of the electrolyte solution, indicating that the n-Si/Graphene interface did not form a buried junction with the solution.

Various strategies have been developed to stabilize photoanodes such as n-Si against photocorrosion or photopassivation in aqueous electrolytes. Thin overlayers of metal have yielded improved anodic stability for silicon and other semiconductors, but generally form semiconductor/metal Schottky barriers that pin the Fermi level of the semiconductor, producing non-optimal photovoltages.¹⁻⁷ Furthermore, nearly complete protection from degradation generally requires the deposition of relatively thick metal layers, preventing a significant fraction of incident light from reaching the underlying semiconductor. Insulating barrier layers, such as oxides deposited by atomic layer deposition, or oxides formed via electrochemical anodization processes, can also provide some degree of protection against corrosion.⁸⁻¹⁰ However, these oxides generally require deposition of pinhole-free films that form a tunneling barrier to photogenerated holes, in many cases producing a significant series resistance that negatively affects the performance of the resulting photoelectrochemical device. Surface functionalization has led to improvements in the stability of n-Si photoanodes in H₂O-containing non-aqueous solvents, but surface-modification approaches have not yet yielded materials that remain stable under extended anodic operation in aqueous electrolytes.¹¹⁻¹³

Graphene has the potential to be an almost ideal protection layer for semiconductor photoelectrodes. Graphene can be prepared in nearly pinhole-free largearea layers and has been shown to attenuate the oxidation of metals in air as well as in aqueous electrochemical environments.¹⁴⁻¹⁹ Unlike surface functionalization techniques that are typically specific to a semiconductor and surface plane, graphene layers can be readily applied to a variety of planar electrode surfaces. Graphene also has excellent optical properties, exhibiting ~97% transmission in the visible region of the solar spectrum.²⁰ Furthermore, graphene has been used in solid-state Schottky junctions capable of generating photocurrent.^{21,22,24} The high carrier mobility in the plane of the graphene C-C bonds should allow for lateral transport of carriers to catalytically active sites on the surface of the photoelectrode.²³ The low density of states near the Fermi level of graphene, the chemical inertness of graphene, and the ability to deposit graphene at room temperature and thereby avoid high-temperature interfacial reactions, potentially provide an opportunity to deposit conductive graphene monolayers onto a variety of semiconductor photoanodes, while obtaining desirable photoelectrochemical performance from the resulting solid/liquid junctions.^{14,24,25}

4.2 Behavior of graphene-covered n-Si photoelectrodes

Graphene-covered n-Si (n-Si/Gr) electrodes were fabricated by floating graphene that had been grown using chemical vapor deposition (CVD) on to H-terminated n-Si(111) surfaces. X-ray photoelectron spectroscopic (XPS) analysis indicated that this fabrication technique resulted in an intervening 1-2 monolayer thick oxide layer between the silicon and graphene (see Chapter 4 appendix for details).

4.2.1 Stability of graphene-covered n-Si photoanode in aqueous solution

Figure 4.1a depicts the current-density vs. potential (*J*–*E*) behavior in the presence and absence of illumination of n-Si/Gr and n-Si–H electrodes in contact with CH₃CN-5 mM Fc⁺-50 mM Fc⁰-1.0 M LiClO₄. The open-circuit photovoltage, V_{oc} , was 310 mV for Si-H surfaces, and was 260 mV for the n-Si/Gr electrodes. The n-Si/Gr electrodes showed somewhat smaller fill factors (*ff*) than the n-Si–H electrodes, (0.40 vs. 0.64) indicating the presence of a resistance at the n-Si/Gr/CH₃CN contact.



Figure 4.1. (a) *J*–*E* behavior of freshly fabricated n-Si/Gr and n-Si-H electrodes in contact with CH₃CN-Fc^{+/0} under illumination and in the dark. (b) *J-E* behavior (5 cycles at 30 mV s⁻¹) of the n-Si/Gr and n-Si-H electrodes from (a) in Fe(CN)₆^{3-/4-}_(aq) under illumination. (c) *J-E* behavior (1 cycle) of the n-Si/Gr and n-Si–H electrodes in CH₃CN-Fc^{+/0} in the presence and absence of illumination, after the data collection depicted in (b).

After five potential sweeps in contact with 50 mM Fe(CN)₆³⁻-350 mM Fe(CN)₆⁴⁻ (aq), the n-Si–H electrode exhibited negligible photocurrent over the power-producing potential range, consistent with expectations for the formation of an insulating oxide layer under photoanodic conditions.¹¹ In contrast, the n-Si/Gr photoelectrode exhibited essentially no change in *J*–*E* behavior under the same conditions, with $V_{oc} = 340$ mV and ff = 0.30 (figure 4.1b). As shown in figure 4.1c, after photoelectrochemical operation in contact with Fe(CN)₆^{3-/4-} (aq), the *J*–*E* behavior of the n-Si/Gr photoanode in contact with the CH₃CN-Fc^{+/0} redox system was almost unchanged from its initial properties in this electrolyte. In fact, a minor improvement in V_{oc} was observed, as well as an apparent decrease in the parallel shunt resistance as indicated by the decreased dependence of the current on applied potential under reverse bias. This is consistent with the passivation of shunts via oxidation in aqueous solution. The chemical nature of these shunts may be due to trace metal impurities from the fabrication procedure or 'dangling' Si bonds present due to the formation of a non-stoichiometric silicon oxide.



Figure 4.2 (a) Comparison of the *J*–*t* behavior of potentiostatically controlled n-Si/Gr and n-Si–H electrodes (E = 0 V vs. solution) in contact with Fe(CN)₆^{3-/4-} (aq) under illumination required to produce a short-circuit photocurrent density of ~11 mA cm⁻² (~33 mW/cm²). The illumination began at t = 10 s. (b) *J*–*t* behavior of an n-Si/Gr electrode in Fe(CN)₆^{3-/4-} (aq) under illumination required to produce a short-circuit photocurrent density of ~11 mA cm⁻² (~33 mV/cm²). The illumination segan at t = 10 s. (b) *J*–*t* behavior of an n-Si/Gr electrode in Fe(CN)₆^{3-/4-} (aq) under illumination required to produce a short-circuit photocurrent density of ~11 mA cm⁻² over 1000 s (E = 0 V vs. solution). The slight increase in current over 1000 s was attributed to instability in the light source.

Figure 4.2 further displays the stability toward photopassivation of the n-Si/Gr surface relative to the n-Si–H surface. Both the n-Si/Gr and the n-Si–H electrodes were immersed in Fe(CN)₆^{3./4-}(aq) and illuminated to produce ~11 mA cm⁻² of photocurrent at a potential of E=0 V vs. the Nernstian potential of the solution. The n-Si/Gr electrode exhibited stable photocurrents, whereas the n-Si–H electrode decayed back to baseline within ~30 seconds (figure 4.2a). Figure 4.2b extends the experiment on the n-Si/Gr electrodes to 1000 seconds. Additionally, comparison of the stability in Fe(CN)₆^{3./4-}(aq) of an n-Si/Gr electrode to that of methylated n-Si(111) electrodes showed that graphene was significantly more effective at preventing electrochemical performance degradation (See chapter 4 appendix), albeit without the interfacial dipole that increases the V_{oc} of n-type CH₃-Si(111) surfaces relative to H-Si(111) surfaces. Comparison of the n-Si/Gr electrode stability in Fe(CN)₆^{3./4-}(aq) to that of n-Si–H electrode stability under ~100 mW/cm² illumination indicated degradation of both electrodes, albeit at much higher rates for the n-Si–H system (See chapter 4 appendix).

4.2.2 Behavior of graphene-covered n-Si photoanodes in nonaqueous electrolyte

Figure 4.3 compares the *J*–*E* behavior of freshly prepared n-Si/Gr electrodes in contact with $CH_3CN-CoCp_2^{+/0}$ to the *J*–*E* behavior of n-Si/Gr electrodes in contact with $CH_3CN-Fc^{+/0}$ and $CH_3CN-AcFc^{+/0}$.



Figure 4.3 (a) *J*–*E* behavior (forward and reverse scan) of n-Si/Gr electrodes in CH₃CN-AcFc^{+/0} ($V_{oc} = 0.43$ V), CH₃CN-Fc^{+/0} ($V_{oc} = 0.26$ V), and CH₃CN-CoCp₂^{+/0} ($V_{oc} = 0$ V) under illumination prior to exposure to [Fe(CN)₆]^{3-/4-} (aq) (b) *J*–*E* behavior of n-Si/Gr electrodes in CH₃CN-AcFc^{+/0} ($V_{oc} = 0.43$ V), CH₃CN-Fc^{+/0} ($V_{oc} = 0.28$ V), and CH₃CN-CoCp₂^{+/0} under illumination after exposure to [Fe(CN)₆]^{3-/4-} (aq). The solution potentials were as follows: $E(AcFc^{+/0}) = +0.4$ V vs. Fc^{+/0}, $E(Fc^{+/0}) = -0.1$ V vs. Fc^{+/0}, and $E(CoCp_2^{+/0}) = -1.26$ V vs. Fc^{+/0}.

The moderate V_{oc} observed for n-Si/Gr/CH₃CN-Fc^{+/0} contacts, larger V_{oc} observed for n-Si/Gr/CH₃CN-AcFc^{+/0} contacts, and negligible V_{oc} in contact with CH₃CN-CoCp₂^{+/0} is in accord with the expectation of increasing V_{oc} with increasingly oxidizing electrolyte potentials, and is also consistent with the junction energetics being controlled at least in part by the difference in electrochemical potential between the Si and liquid phase. After operation in both electrolytes, the n-Si/Gr electrodes were then operated under photoanodic conditions in contact with Fe(CN)₆^{3-/4-} (aq), in an analogous fashion to the electrodes shown in figure 4.1b.

The data in figure 4.3b indicate that the electrochemical properties of the electrodes were essentially unaffected by operation in the oxidizing $Fe(CN)_6^{3./4-}_{(aq)}$ environment. If pinholes in the graphene had controlled the junction energetics, the Si exposed through these pinholes would presumably have passivated upon treatment in $Fe(CN)_6^{3./4-}_{(aq)}$, leaving only the graphene-covered regions to control the junction energetics. Thus, the measurement of $V_{oc} > 200 \text{ mV}$ for n-Si/Gr in contact with $Fc^{+/0}$, $V_{oc} > 400 \text{ mV}$ for n-Si/Gr/AcFc^{+/0} contacts, and negligible V_{oc} for n-Si/Gr/CoCp2^{+/0} contacts indicates that the Fermi level of the n-Si/Gr electrodes was not fully pinned by the presence of graphene at the silicon/graphene/electrolyte junction. The V_{oc} of n-Si/Gr electrodes in contact with CH₃CN-Fc^{+/0} was consistently smaller than the V_{oc} of n-Si-H in contact with the same electrolyte (c.f. Figure 4.1a). The data in figures 4.1, 4.2, and 4.3 were highly reproducible between electrodes.

This behavior is consistent with expectations that a limited number of electronic states in graphene affect the junction energetics without fully pinning the Fermi level of the semiconductor. Specifically, Poisson's equation was solved while treating the n-

Si/Gr/electrolyte interface as consisting of a depleted semiconductor (Si) of known dielectric and capacitive properties in contact with an atomically thin material with the known density of electronic states as a function of energy of graphene, with this entire phase into contact with a phase consisting of the known dielectric and capacitive properties representative of a typical electrolyte solution. An initial difference in Fermi levels of ~0.8 eV between the semiconductor and the electrolyte should produce a potential drop of ~0.65 V in the Si space-charge region, with the remainder dropping across the solid/liquid interface. Mott-Schottky $(1/C^2 \text{ vs. } E)$ data vielded support for this model, in that a lower barrier height was observed for the n-Si/Gr/ CH₃CN-Fc^{+/0} contacts than for n-Si-H/CH₃CN-Fc^{+/0} contacts (see chapter 4 appendix). This behavior is consistent with a portion of the total potential drop occurring in the graphene and solution layer as opposed to the space-charge region of the semiconductor, and is also consistent with the smaller Voc of n-Si/Gr/CH₃CN-Fc^{+/0} contacts relative to n-Si-H/CH₃CN-Fc^{+/0} contacts. Many factors, including the formation of a thin insulating oxide as well as changes in charge-transfer kinetics can affect the relationship between the barrier height and Voc and could account for the somewhat smaller change in Voc relative to the change in barrier height.

Fitting the forward-bias dark J-E behavior of the n-Si/Gr/CH₃CN-Fc^{+/0} contact to the diode equation, $J = J_0 * [\exp(-q\Delta V/\eta kT)-1]$ where J_0 is the exchange current density, qis unsigned charge on an electron, k is Boltzmann's constant, T is the absolute temperature, η is the diode quality factor, and ΔV is the difference between the applied potential and the Nernst potential of the solution, yielded $J_0 = 9.61 \times 10^{-7}$ A cm⁻² (± 6.10 $\times 10^{-8}$) and $\eta = 1.65$ (± 0.02). Analysis of the dark *J-E* behavior of a freshly HF-etched n-Si–H electrode in contact with CH₃CN-Fc^{+/0} yielded $J_0 = (6.80 \pm 0.51) \times 10^{-8}$ A cm⁻² and $\eta = 1.25 \pm 0.012$. The $J_{0,n-Si-H}$ and $J_{0, n-Si/Gr}$ values for these contacts were much smaller than the values obtained for Si/Gr/CH₃CN-CoCp₂^{+/0} contacts ($J_0 \sim 10^{-3}$ A cm⁻²), and were comparable to J_0 values reported for highly rectifying n-Si/organic conducting polymer contact ($J_0 \sim 2 \times 10^{-8}$ A cm⁻²). Similar to the reported results for n-Si/polymer contacts, the J_0 values for n-Si/Gr in contact with varying redox species spanned approximately five orders of magnitude, in comparison to n-Si/metal contacts, which are generally limited to a range of three orders of magnitude in J_0 . This further supports the conclusion that the Si/Gr/electrolyte interface was only partially pinned by the presence of graphene. ²⁶ The higher than unity ideality factor could result from a number of factors, including the voltage drop across the small amount of interfacial oxide as well as the expected voltage-dependent surface charge density that results from the observations and modeling of the interfacial energetics.

4.3 Conclusion

The ability of graphene to protect metallic electrodes against corrosion is controversial.^{14-16,27} Herein we have clearly demonstrated that graphene markedly enhances the stability of silicon towards passivation by oxide formation under illumination, even in the stressing case of anodic operation in contact with aqueous solutions. In addition, we have elucidated the effects of graphene on the interfacial energetics of semiconductor/liquid contacts, which is not accessible on metallic electrodes and thus has not been defined or elucidated previously. The V_{oc} vs. solution potential relationships observed from the *J*–*E* data demonstrate that Fermi-level pinning by graphene did not fully limit the observed photovoltages. Further study is required to

determine whether the photovoltage is maximized for the n-Si/Gr system in contact with $CH_3CN-AcFc^{+/0}$. Extended studies of the stability imparted by graphene to silicon surfaces and the electronic and chemical effects of graphene on the silicon surface are currently underway to elucidate the extent of the graphene-imparted stability especially for bilayer and multi-layer of grapshene coatings, as well as the effect of graphene on the surface chemistry and recombination characteristics of the underlying Si and the effect of graphene on n-Si/oxygen-evolution catalyst systems.

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4.5 References

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4.6 Appendix

4.6.1 Methods

4.6.1.1 Chemicals/Materials

All experiments employed single-crystalline, Czochralski grown, (111)-oriented, planar, 380 µm thick, phosphorus doped, 1.1 Ω -cm resistivity (doping density, $N_D \approx 5 \times 10^{15}$ cm⁻³) n-type silicon (University Wafer).

Water was obtained from a Barnstead Nanopure system and had a resistivity \geq 18.0 MΩ-cm. Copper Etch Type CE – 100 (FeCl₃-based, Transene Company, Inc., Danvers, MA), Copper Etch Type APS – 100 (Ammonium persulfate-based, Transene), buffered HF_(aq) (semiconductor grade, Transene Company, Inc., Danvers, MA), and 11 M NH₄F (semiconductor grade, Transene) were used as received. Acetone (HPLC grade, Sigma-Aldrich) was used as received. Acetonitrile (99.8% anhydrous, Sigma-Aldrich) that was used in electrochemical measurements was dried over Al₂O₃ prior to use.

Ferrocene (Fc, bis(cyclopentadienyl)iron(II) ,99%,Strem), cobaltocene (CoCp₂, bis(cyclopentadienyl)cobalt(II), 98%, Strem), and acetylferrocene (AcFc, (acetylcyclopentadienyl)-cyclopentadienyl iron(II), 99.5%, Strem) were purified via sublimation. Ferrocenium tetraflouroborate ($Fc^+[BF_4]^-$, bis(cyclopentadienyl)iron(III) tetraflouroborate,technical grade,Sigma-Aldrich) was recrystallized from a mixture of diethyl ether (ACS grade, EMD) and acetonitrile (ACS grade, EMD) and dried under vacuum. Cobaltocenium hexafluorophosphate ($CoCp_2^+$, bis(cyclopentadienyl)cobalt(III) hexafluorophosphate, 98%, Sigma-Aldrich) was recrystallized from a mixture of ethanol

(ACS grade, EMD) and acetonitrile (ACS grade, EMD) and dried under vacuum. Acetylferrocenium ($AcFc^+$) was generated in situ via electrochemical oxidation of AcFc with the concomitant reduction reaction occurring in a compartment separated from the electrochemical cell using a Vycor frit.

Potassium ferricyanide ($K_3[Fe(CN)_6]$, 99.2%, Sigma-Aldrich) and potassium ferrocyanide ($K_4[Fe(CN)_6] \cdot 3H_2O$, ACS Certified, Fischer Scientific) were used as received. LiClO₄ (battery grade, Sigma-Aldrich) was used as received. Petri dishes used were Falcon OptiluxTM branded and were cleaned with water prior to use. All chemicals were used as received unless otherwise noted.

4.6.1.2 Electrode Fabrication

A monolayer film of graphene was formed via chemical-vapor deposition (CVD) of carbon onto a Cu foil. A 25 μ m-thick Cu foil (99.999%, Alfa Aesar) was heated in a tube furnace to 800 °C at a pressure of 50 mTorr and annealed for 10 h under a 2 sccm flow of H_{2(g)}. Graphene was subsequently synthesized on the surface of the copper foil by flowing CH_{4(g)} (35 sccm) and H_{2(g)} (2 sccm) at 1000 °C and 250 mTorr. This method of graphene growth has been shown to grow polycrystalline monolayer graphene and figure 4A.1 shows a representative Raman spectrum of the starting material graphene on 300 nm SiO₂.¹ After growth of the graphene, the gas flow rates and chamber pressure were maintained and the Cu foil was rapidly cooled to room temperature by removing the furnace from the growth section of the process tube. The graphene synthesis resulted in grains that were 0.2 to 5 μ m on a side, and an analysis of the grain size and grain distribution of the resulting polycrystalline graphene film has been presented in Petrone, et al., 2008.¹ The surface was then covered with a coating of 495K A4 polymethyl

for 60 s, followed by a 10-min bake at 185 °C. This procedure was repeated for a total of two PMMA applications. The Cu was etched away using either a 15% (v:v) NH₄(S₂O₈₎₂ (aq) solution or a 40% FeCl₃/1% HCl (aq) solution (Transene).² Cu removal was determined visually and confirmed by XPS analysis (figure 4A.6). To remove etchant residue, the resultant PMMA/graphene stack was transferred consecutively to three fresh baths of 18 M Ω -cm resistivity H₂O in petri dishes. The transfer was executed using a freshly piranha-cleaned (7:3 H₂SO₄:H₂O₂, aqueous solution) SiO₂-coated Si wafer to collect the PMMA/Gr stack from one bath and release the stack in a fresh H₂O bath. Ntype Si samples were washed consecutively with H₂O, methanol, acetone, methanol, and H₂O, and were then submerged in a piranha solution for 10 min and etched for 30 s in buffered HF_(aq) (Buffer HF Improved, semiconductor grade, Transene). The cleaned PMMA/graphene stack was transferred from a water bath to the cleaned, freshly $HF_{(aq)}$ etched Si(111) surface, and a gentle stream of N_{2(g)} was used to remove H₂O from the intervening space between the graphene and the Si. The PMMA/graphene/Si stack was then heated at 80 °C for 10 min in air, followed by submersion for 10 min in acetone to remove the PMMA layer. The resulting Si/graphene (Si/Gr) stack was annealed for ~8 h at 300 °C under forming gas (95:5 v:v N₂:H₂) to further remove PMMA residue from the surface of the graphene.¹ Si/Gr electrodes $\sim 0.02 \text{ cm}^2$ in area were then fabricated with the use of GaIn (75:25 mass:mass) eutectic as a back ohmic contact. The electrodes were affixed to a Cu wire with Ag paint, and all surfaces, except the electrode, were insulated from the electrolyte by use of Loctite Hysol 9460 epoxy. On average, out of ten fabricated electrodes, two to three showed very low shunt resistances in non-aqueous

electrolytes and/or displayed minimal protection of the Si surface from oxidation. The remaining 7-8 electrodes gave data consistent with that shown figures 4.1, 4.2, and 4.3. An analogous process was used to fabricate electrodes that were not coated with graphene (n-Si–H and n-Si–Me electrodes). Methylated silicon wafers were prepared using a previously reported procedure.³ Before use, the graphene-free, non-methylated Si electrodes were terminated with Si-H bonds by exposure to buffered $HF_{(aq)}$ for 30 seconds. Electrodes were also fabricated by exposing silicon wafers to the same conditions as the graphene-transfer procedure, except that no graphene was present between the PMMA and Cu. Such electrodes were not HF-etched prior to use.

4.6.1.3 Instrumentation

X-ray photo- electron spectroscopy (XPS) data was collected at $\sim 5 \times 10^{-9}$ Torr using a Kratos AXIS Ultra DLD with a magnetic immersion lens that consisted of a spherical mirror and concentric hemispherical analyzers with a delay-line detector (DLD). An Al K α (1.486 KeV) monochromatic source was used for X-ray excitation. Ejected electrons were collected at an angle of 90° from the horizontal. The CASA XPS software package v 2.3.16 was used to analyze the collected data.

Electrochemical data were obtained using a Princeton Applied Research Model 2273 or a Gamry Reference 600 potentiostat. A Pt wire reference electrode (0.5 mm dia., 99.99% trace metals basis, Sigma-Aldrich) and a Pt mesh counter electrode (100 mesh, 99.9% trace metals basis, Sigma-Aldrich) were used for the electrochemical measurements. The cell potentials for the non-aqueous redox species were determined using cyclic voltammetry to compare the solution potential to the formal potential of the redox species. The potential difference between cells was calculated using the difference

between the formal potentials for each redox couple using standard potentials from the literature.⁴ The CH₃CN-CoCp₂^{+/0} solution (CoCp₂ [3 mM]/ CoCp₂⁺ [50 mM]) was calculated to have a solution potential of -1.4 V vs Fc/Fc^+ , the CH₃CN-Fc^{+/0} solution (Fc $[55 \text{ mM}]/\text{ Fc}^+[3 \text{ mM}])$ was calculated to have a solution potential of -0.10 V vs Fc/Fc⁺, and the CH₃CN-AcFc^{+/0} solution (pre-electrolysis AcFc concentration = [50 mM]) was calculated to have a solution potential of +0.40 V vs Fc/Fc⁺. The non-aqueous electrochemical solutions each contained 1.0 M LiClO₄. The aqueous $K_3[Fe(CN)_6]/K_4[Fe(CN)_6]$ ([Fe(CN)_6]⁻³, 50mM; [Fe(CN)_6]⁻⁴, 350mM) solution contained no additional supporting electrolyte due to the high intrinsic salt concentration. The current under forward bias saturated at much larger values in the $Fe(CN)_6^{3-/4-}$ solution relative to in the Fc⁺/Fc solution because of the increased concentration of electronaccepting species in the $Fe(CN)_6^{3-/4-}$ solution. CH₃CN-Fc[BF₄] is a highly colored species that at high concentrations absorbs a significant fraction of the light prior to photons striking the photoelectrode. The electrolyte solution was rapidly stirred with a small, Teflon-covered stir bar. Illumination was provided with an ELH-type tungsten-halogen lamp. Illumination intensities were set to provide either 3-5 mA cm⁻² or ~10-11 mA cm⁻². These values corresponded to $\sim 1/10^{th}$ and $\sim 1/3^{rd}$ of a Sun ($\sim 10 \text{ mW cm}^{-2}$ and $\sim 33 \text{ mW}$ cm⁻²), respectively, as determined through the concurrent use of a Si photodiode (Thor Laboratories) that was calibrated relative to a secondary standard photodetector that was NIST-traceable and calibrated at 100 mW cm⁻² of AM1.5 illumination. Non-aqueous electrochemistry was performed anaerobically in an Ar(g)-filled glovebox. Aqueous electrochemistry was performed in air. Electrodes were washed with H₂O and isopropanol and dried prior transfer between electrolyte solutions.



Figure 4A.1. Representative Raman spectrum of starting material graphene on 300 nm $SiO_2 (\lambda = 532 \text{ nm})$. Sharp G (1594 cm⁻¹, FWHM: 10 cm⁻¹) and 2D (2684 cm⁻¹, FWHM: 32 cm⁻¹), as well as a small defect peak (~1350 cm⁻¹) confirm the monolayer, defect-free nature of the starting material.^{5,6}

4.6.2 Mott-Schottky Fitting Procedure

To perform the Mott-Schottky analysis, a 10 mV sinusoidal AC signal was superimposed over DC biases of 0.25, 0.30, 0.35, 0.4, 0.45, 0.50, 0.55, and 0.60 V versus the Nernstian potential of the solution. The frequency of the AC signal was varied from 50 to 300 kHz at each DC bias. The impedance data were modeled by the equivalent Randle's circuit shown in figure 4A.2, and best fits were obtained using the fitting procedure executed by the ZView electrochemical software (Scribner Associates, Inc.). The data in table 4A.1 and table 4A.2 were used to approximate the area-normalized series resistance imparted to the n-Si/Gr electrodes by the fabrication procedure at approximately 9 Ω cm² by comparing the average area-normalized resistance of the n-Si/Gr and n-Si–H electrodes (24.4 Ω cm² and 15.1 Ω cm², respectively. The *J-E* data of n-Si/Gr under illumination in contact with CH₃CN-Fc^{0/+} electrolyte indicated a series resistance of 23.1 ± 5.1 Ω cm² (6 electrodes), in excellent accord with data found via electrochemical impedance spectroscopy.



Figure 4A.2. Equivalent circuit used to analyze the impedance data. C1 was treated as the space-charge capacitance (C_{sc}).

Voltage (V)	$R1(\Omega \text{ cm}^2)$	R2(Ω cm ²)	C1 (μ F cm ²)
0.25	25.6	7656.2	2.89E-02
0.3	24.7	7685.7	2.73E-02
0.35	23.9	7641.1	2.62E-02
0.4	24.3	7642.4	2.53E-02
0.45	24.4	7577.3	2.47E-02
0.5	24.2	7615.4	2.39E-02
0.55	24.2	7661.3	2.33E-02
0.6	24.1	7688.3	2.27E-02

Table 4A.1. Results obtained from the fitting of the impedance data at each applied voltage for the representative n-Si/Gr electrode.

Voltage (V)	R1(Ω cm ²)	R2(Ω cm ²)	C1 (μ F cm ²)
0.25	12.9	154180.5	4.07E-03
0.3	13.7	95594.4	3.99E-03
0.35	14.2	84057.0	3.91E-03
0.4	15.0	60479.1	3.83E-03
0.45	15.5	49401.7	3.74E-03
0.5	16.1	47259.1	3.67E-03
0.55	16.7	49229.5	3.60E-03
0.6	17.4	41858.1	3.54E-03

Table 4A.2. Results obtained from the fitting of the impedance data at each applied voltage for the representative n-Si-H electrode.



Figure 4A.3-I. Mott-Schottky (C_{diff}^{-2} vs *E*) behavior of (a) n-Si–H and (b) n-Si/Gr electrodes in contact with CH₃CN-Fc^{+/0} in the dark. The differential capacitance (C_{diff}) at each voltage was determined by fitting the impedance vs. frequency data between 50 kHz and 300 kHz to an equivalent Randle's circuit at each voltage. The doping density measured by 4-point probe technique was calculated to be $N_D \sim 5 \times 10^{15}$ cm⁻³.



Figure 4A.3-II Bode plot of n-Si–H and n-Si/Gr electrodes in contact with $CH_3CN-Fc^{+/0}$ in the absence of illumination at E = 0.40 V vs. the Nernst potential of the solution. The deviation from linearity that can be seen in this figure suggests that the Randles circuit is an incomplete description of the graphene-covered Si photoelectrode interface.

4.6.3 Description of Semiconductor/Gr/Electrolyte Model

To gain a better understanding of the electrochemical and photoelectrochemical effects of graphene, the equilibration of the three-phase semiconductor/graphene/electrolyte system was analyzed. The following assumptions were made:

- The Fermi level of all three phases is the same at equilibrium.
- Equilibrium is obtained through charge transfer between the three phases.
- The initial Fermi level of the semiconductor $(E_{F,SC})$ is closer to the vacuum level than the initial Fermi level of graphene $(E_{F,Gr})$, which is in turn closer to the vacuum level than the initial Fermi level of the electrolyte $(E_{F,electrolyte})$.
- The sum of the net charge in the three phases is zero, as required by electroneutrality: $Q_{sc} + Q_{Gr} + Q_{liquid} = 0$, where Q_{sc} is the net charge in the semiconductor, Q_{Gr} is the net charge in the graphene, and $Q_{electrolyte}$ is the net charge in the liquid electrolyte.
- The potential drop in the semiconductor (V_{bi}) is well-modeled by the potential drop of a semiconductor under depletion conditions.
- The potential drop in the electrolyte ($V_{\rm H}$) is well-modeled using the known capacitive and dielectric properties of a typical electrolyte solution.
- The Fermi level of the graphene phase may be strongly shifted by the addition or loss of electrons, due to the low density of states and atomically thin structure of the grapheme. This shift (V_{Gr}) can be predicted

using the theoretically calculated DOS of graphene.⁷ V_{Gr} is a shift in the graphene Fermi level and not an electrostatic potential drop.

• The potential drop in the interfacial layer between the semiconductor and graphene, as well as the potential drop the interfacial layer between graphene and the liquid electrolyte contact, is negligible.

Essentially, Poisson's equation was solved while treating the n-Si/Gr/electrolyte interface as consisting of a depleted semiconductor (Si) of known dielectric and capacitive properties in contact with an atomically thin material with the known density of electronic states as a function of energy of graphene, with this entire phase in contact with a phase consisting of the known dielectric and capacitive properties representative of a typical electrolyte solution. This treatment parallels, and is consistent with, the interfacial charge equilibration and surface state models that have been developed previously for semiconductor surfaces and are extensively described in the literature.^{8,9} To calculate the equilibrium values of Q_{sc} , Q_{Gr} , and $Q_{electrolyte}$, as well as V_{bi} and V_{H} , the analysis was broken down into two steps and iterated. First, the equilibrium values for the two-phase Gr/electrolyte system were determined using Poisson's equation. Then, using these values as the starting condition, the final self-consistent state for the twophase Si/Gr system was solved using Poisson's equation. These values were then used as starting conditions for the first two-phase Gr/electrolyte system, and the process was iterated until the values converged to a global minimum. Poisson's equation was solved using a method previously described for equilibration of a two-phase system.⁸

The constants used in the modeling were as follows. The electron affinity of Si was taken to be -4.05 eV vs. vacuum.¹⁰ The Fermi level of phosphorous-doped Si (N_D = 10¹⁵ cm⁻³) was calculated to be ~ -4.3 eV. The intrinsic Fermi level of graphene was taken to be -4.6 eV vs. vacuum.¹¹ The empirical built-in potential difference in the absence of graphene ($V_{bi} = 0.8$ V) was used to calculate the Fermi level of the liquid electrolyte contacting phase, q $E(A/A^-) = -5.1$ eV versus vacuum (Figure 4A.3-I). The DOS of graphene is known,⁷ and from this, [d(DOS)/dE_{F, Gr}] was taken to be 1.5x10⁻⁵ C/eV. The thickness of the Helmholtz layer was set to 5x10⁻⁸ cm and κ_1 was set to 4.0.^{12,13}

The potential distribution in the two-phase Gr/electrolyte system was modeled by the following equations:

$$\phi_{Gr} - \phi_{Electrolyte} = V_{Gr} + V_H \tag{1}$$

where ϕ_{Gr} is the Fermi level of the graphene with respect to vacuum, $\phi_{electrolyte}$ is the Fermi level of the liquid electrolyte with respect to vacuum,

$$V_{Gr} = \pm \sqrt{\frac{|Q_{Gr} + \Delta Q|}{0.5 * \frac{dDOS}{dE_{F,Gr}}}}$$
(2)

and

$$V_{H} = \frac{D * |Q_{Electrolyte} + \Delta Q|}{\varepsilon_{0} * \kappa_{l}}$$
(3)

where $Q_{\text{Gr}} = Q_{\text{electrolyte}} = 0$, ΔQ is the change in charge required to reach equilibrium, $[d(\text{DOS}_{\text{Gr}})/dE_{\text{F, Gr}}]$ is determined from the reported DOS of graphene with respect to $E_{\text{F, Gr}}$, G_{r} , D is the thickness of the Helmholtz layer, ε_0 is the permittivity of free space, and κ_1 is the relative permittivity of the liquid phase.⁷ The solution to this system of equations results in two values for ΔQ because of its quadratic dependence; however, only one of the results is physical. The equilibrium charge distributions for the two-phase Gr/liquid system are $Q_{\text{Gr, eq-a}} = \Delta Q$ and $Q_{\text{electrolyte, eq}} = -\Delta Q$. The energy of the Fermi levels at equilibrium implies that the graphene is positively charged and the liquid phase is negatively charged.

To determine the charge distribution for the three-phase Si/Gr/electrolyte system, the two-phase Si/Gr system was modeled by the following equation:

$$\phi_{sc} - \phi_{Gr} = V_{bi} - V_{Gr} \tag{4}$$

where

$$V_{bi} = \frac{(Q_{sc} + \Delta Q)^2}{2qN_D \varepsilon_0 \kappa_{sc}}$$
(5)

and

$$V_{Gr} = \pm \sqrt{\frac{|Q_{Gr} - \Delta Q|}{0.5 * \frac{dDOS}{dE_{F,Gr}}}} \tag{6}$$

where $Q_{sc} = 0$, $Q_{Gr} = Q_{Gr, eq-a}$ from above, ΔQ is the change in charge required to reach equilibrium, q is the elementary charge, N_D is the dopant density, ε_0 is the permittivity of free space, and κ_{sc} is the relative permittivity of the semiconductor phase.⁸ The sign convention on ΔQ was chosen to reflect the decrease in positive charge on the graphene phase and the increase in positive charge on the semiconductor. The graphene phase "loses" charge because it was previously positively charged from equilibration with the liquid phase, and the relative Fermi levels of the semiconductor and graphene phases dictate that the semiconductor transfers negative charge to the graphene. The solution to this system of equations results in four values for ΔQ because of its quartic dependence; however, only one of the results is physical. The equilibrium charge distributions for the two-phase Si/Gr system are $Q_{sc, eq} = \Delta Q$ and $Q_{Gr, eq-b} = (Q_{Gr, eq-a} - \Delta Q)$. The energy of the Fermi levels at equilibrium implies that the semiconductor is positively charged and that the graphene remains positively charged.

Equilibration of the two-phase Si/Gr system resulted in non-equilibrium conditions for the two-phase Gr/liquid system as the graphene charge density, and thus potential drop, changed. Thus, the first set of equations was re-solved with the initial conditions, $Q_{Gr} = Q_{Gr, eq-b}$ and $Q_{electrolyte} = Q_{electrolyte, eq}$. The solutions were then used as initial conditions in the second set of equations as $Q_{sc} = Q_{sc}$, eq and $Q_{Gr} = Q_{Gr, eq-a}$, resolved, and the process was iterated until $|Q_{Gr, eq-a} - Q_{Gr, eq-b}| < Q_{Gr, eq-a} \times 10^{-5}$. The converged values of the charges were determined to be $Q_{sc, eq} = (+) 2.30 \times 10^{-8} \text{ C}$, $Q_{Gr, eq-a} = Q_{Gr, eq-b} = (+) 9.67 \times 10^{-7} \text{ C}$, and $Q_{electrolyte, eq} = (-) 9.97 \times 10^{-7} \text{ C}$. These were used to calculate the potential drops: $V_{bi} \approx 0.65 \text{ V}$, $V_{Gr} \approx 0.35$ and $V_{H} \approx 0.15 \text{ V}$. For comparison, for the two-phase Si/liquid electrolyte system $Q_{sc, eq} = (+) 1.64 \times 10^{-8} \text{ C}$, $Q_{electrolyte, eq} = (-)$

1.64 x 10⁻⁸ C, $V_{bi} = 0.797$ V, and $V_{H} = 0.0030$ V. These trends are consistent with the experimentally observed V_{oc} values (Figure 4.1).

4.6.4 XPS Analysis

XPS analysis was performed in order to determine the effect of graphenecovering procedure on the n-Si surface. No silicon oxide was detected on freshly HFetched silicon surfaces (Figure 4A.4). Silicon oxide was detected on the graphenecovered sample (Figure 4A.5) and quantified using a simple substrate—overlayer model described by equation 7¹⁴:

$$d = \lambda_{ov} \sin \theta \left\{ \ln \left[1 + \frac{I_{Si}^0}{I_{ov}^0} * \frac{I_{ov}}{I_{Si}} \right] \right\}$$
(7)

where d is the overlayer thickness, λ_{ov} is the attenuation factor through the oxide overlayer (assumed to be 2.6 nm)¹⁵, θ the angle from the surface of the sample to the detector (90°), $\frac{I_{Si}^{0}}{I_{ov}^{0}}$ is an instrument normalization factor related to the expected signal for a pure Si and a pure SiO₂ sample (taken to be 1.3 for this instrument), I_{ov} is the measured intensity of the silicon, and I_{ov} is the measured intensity of the silicon oxide overlayer. The thickness of a monolayer of oxide was taken to be 0.35 nm.¹⁶ Using the data in figure 4A.5, equation 7 indicates that the oxide thickness was approximately 0.41 nm, or 1-2 monolayers of oxide.



Figure 4A.4. Representative high resolution XP spectrum of the Si 2p region of a silicon wafer that had been etched in HF_{aq} just prior to XPS analysis. The lack of a peak in the 102-104 eV region indicates that there was not silicon oxide present at the Si surface prior to covering the wafer with graphene.



Figure 4A.5. Representative high resolution XP spectrum of the Si 2p region of a silicon wafer covered by graphene. Peak fitting gave peak areas of 80, 239, and 369 for the SiOx, Si $2p^{1/2}$, and Si $2p^{3/2}$ peaks, respectively.



Figure 4A.6. Representative high resolution XP spectrum of the copper region of a silicon wafer covered by graphene. Spectrum indicated copper impurities below the detection limit of the XPS instrument used.

4.6.5 Methylated n-Si stability versus graphene-covered n-Si stability

It is interesting to compare the electrochemical stability imparted by the presence of a graphene layer to the stability imparted by methyl-termination of the silicon surface since both entail a single layer of carbon atoms covering a silicon lattice. As seen in figure 4A.7, at lower light intensities, the n-Si-Me electrode performance is comparable to that of the n-Si/Gr electrode performance. However, as seen in figure 4A.8, at higher light intensities, the n-Si/Gr electrode yielded more stable performance than the n-Si-Me electrode. Future studies will evaluate the stability when these protection techniques are used in tandem.



Figure 4A.7. *J-E* behavior (5 cycles at 30 mV s⁻¹) of the n-Si/Gr, n-Si-Me and n-Si-H electrodes $Fe(CN)_6^{3-/4-}_{(aq)}$ under ELH lamp illumination necessary to give ~3 mA cm⁻² light-limited current density.



Figure 4A.8. *J*–*t* behavior of an n-Si/Gr and a n-Si-Me electrode in $Fe(CN)_6^{3-/4}$ (aq) under illumination required to produce a short-circuit photocurrent density of 10-11 mA cm⁻² over 1000 s (E = 0 V vs. solution).

4.6.6 PMMA/Cu Control electrodes

Bare n-Si electrodes were fabricated analogously to graphene-covered electrodes except that PMMA/Cu stacks were used instead of PMMA/Gr/Cu stacks. As shown in figure 4A.9, such PMMA/Cu coated Si electrodes were unstable under our test conditions and exhibited rapid photopassivation due to oxide formation.



Figure 4A.9. *J-E* behavior (5 cycles at 50 mV s⁻¹) of a bare n-Si electrode exposed to the graphene transfer procedure in $Fe(CN)_6^{3-/4-}$ under approximately $1/10^{th}$ sun illumination provided by an ELH lamp.

4.6.7 n-Si/Gr and n-Si-H Electrode stability at ~100 mW/cm²

As seen in figure 4A.10, both the n-Si/Gr and n-Si–H electrodes showed degradation of performance under approximately 1 sun illumination, albeit at reduced rates for the n-Si/Gr electrode. This underscores the need for further strategies, such as methyl termination combined with graphene multiple layers of graphene in order to address the challenging issue of obtaining long-term protection of Si in aqueous solution while evolving oxygen from water.



Figure 4A.10. *J*–*t* behavior of an n-Si/Gr and a n-Si–H electrode in $Fe(CN)_6^{3-/4-}$ (aq) under approximately ~100 mW/cm² light intensity (ELH lamp) over 1000 s (E = 0 V vs. solution).

4.6.8 Appendix References

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