6 Conformal Graphene Protection of Microwires

Graphene layers have potential for the conformal protection of Si microwire arrays against corrosion in solution. Graphene is an atomic monolayer of carbon consisting entirely of sp^2 hybridized bonds. This unusual structure gives rise to number of interesting properties, including high conductivity, strength, and chemical resistance. A single layer of graphene has been shown to protect planar Si surfaces against photocorrosion in aqueous, however typically graphene synthetic methods are only applicable for planar substrates. Three methods for the conformal preparation of graphene have been explored in order to extend this protection to structured Si microwire arrays. This will allow Si microwire arrays to be used in as electrodes in photosynthetic electrochemical cells.

6.1 Background and Introduction

Graphene is formed of a monolayer of unsaturated carbon atoms, or can also be described as a single layer exfoliated from bulk graphite. As a single layer it exhibits a 0 eV bandgap, with variable electronic properties as layers are stacked. Graphene is known for its high electron mobility, [68] as well as its high mechanical strength. [69] Graphene can be grown on a range of substrates, including insulators, [70–72] semiconductors, [73], and metals. [74,75] Despite being a single atomic layer, and therefore mostly transparent to visible light, graphene has good chemical resistance, making it a promising protecting layer for semiconductors against corrosion in solution.

A layer of graphene is layer of resonance stabilized carbon that is relatively resistant to chemical attack and is capable of shielding an underlying substrate from oxidation by water or polar solvents. It has been shown that while bare n-Si electrodes are only stable for approximately 30 s in the light under aqueous conditions, that by protecting the same electrode with a layer of graphene it can support current densities of over 10 mA cm^{-2} for > 1000 s. [76] Current methods for graphene protection of Si however rely on planar fabrication techniques and are therefore not applicable to structured Si microwire array electrodes. New methods for the protection of such electrodes need to be developed in order to use Si microwire arrays in aqueous solution for extended periods of time.

Three methods are presented here for the preparation of graphene or graphitic layers on structured Si electrodes. The first method involves the alkylation of a Si surface to prepare a single monolayer of short chain carbon species bound to the surface *via* Si–C bonds. Two transformations are subsequently performed at high temperatures, first converting the alkyl layer into a silicon carbide layer, and finally sublimating Si from the surface, leaving behind a layer of carbon atoms that reorganize into graphene.

The second method uses a layer of Ni as a catalyst to seed bilayer graphene growth on the Si surface, whereupon etching away the Ni the graphene is exposed. The final method is for the preparation of few-layer graphitic carbon, functional similar to graphene, *via* direct growth on the Si surface at elevated temperatures using a carbon precursor gas.

6.2 Characterization Methods

6.2.1 X-ray Photoelectron Spectroscopy

XPS is an X-ray technique where a sample is illuminated with monochromatic light which causes photoemission of electrons from near the sample surface. The photoemitted electrons carry information that can be correlated with elemental identity as well as binding environment. In this case, a scan of the energy region corresponding the C 1s orbital allows for identification between aliphatic C–C species, surface bound Si–C species, and carbide-based Si–C species.

6.2.2 Raman Spectroscopy

Raman spectroscopy is used for the characterization of all graphene samples. In Figure 27 the salient features of an example layer of graphene can be seen.

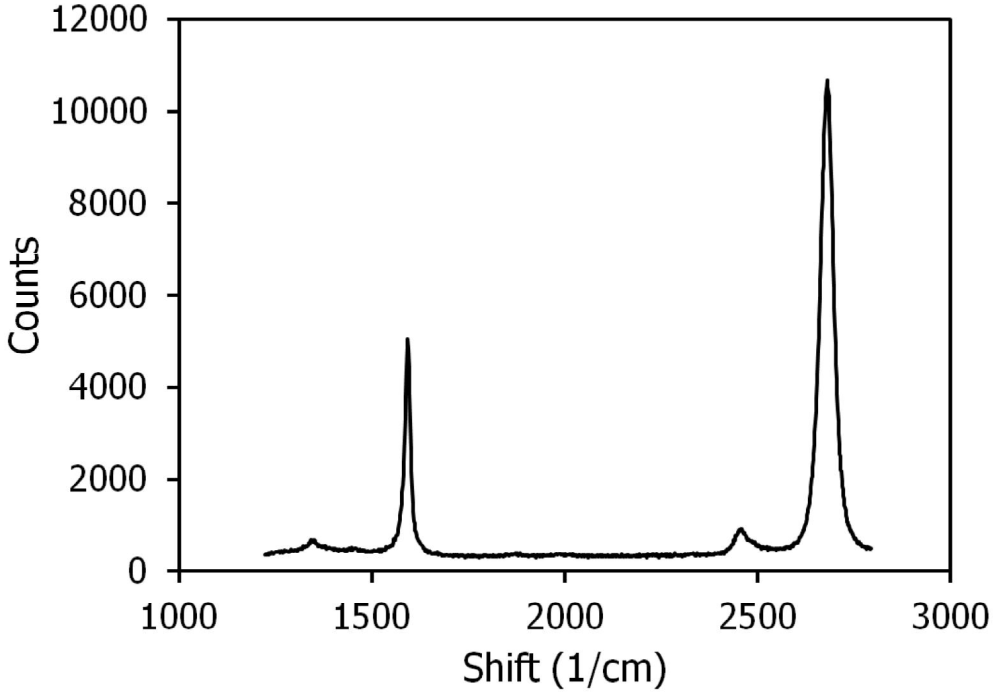

Figure 27: Raman spectrum of high quality graphene on SiO_2, with sharp peaks and 2:1 2D:G ratio.

Figure 27 shows a control sample with good quality growth. This sample was grown on a 300 nm layer of SiO_2, providing a resonant optical enhancement effect. [77] The peaks observed at approximately 1595 and 2680 cm^{-1} are known as the G and 2D peaks, respectively, and correspond to phonon modes. In single layer graphene the 2D/G ratio will be approximately 2, as is shown in this spectrum. [77] In bilayer graphene the ratio will be 1, with a ratio of < 1 for multilayer graphene. The small peak at 1345 cm^{-1} is known as the D peak and corresponds to the defect density of the graphene layer. This peak should be small to nonexistant for high quality graphene. In addition, the G and 2D peaks should be sharp, as both peak broadening and peak shift can carry information about the quality of the graphene.

6.2.3 Photoelectrochemical Stability Testing

Photoelectrochemical cells can be used to test the duration of aqueous stability provided to the underlying silicon by a graphene coating. A procedure adapted from Nielander et al. was used as follows. [76] Control Si samples and graphene or graphite coated Si samples are made into electrodes using an InGa eutectic mixture as the ohmic back contact. Following the application of InGa, silver print is used to attach the sample chip to a coil of wire. The wire is threaded through a $^1/_4$" glass tube, which is sealed to the sample using epoxy (Hysol 9460). The epoxy is applied to cover the rear and edges of the sample, leaving no contact to the solution other than through the sample front surface. Electrodes are submerged in a stirred, aqueous solution of ferri/ferrocyanide ($Fe(CN)_6^{3-/4-}$). Current voltage plots are swept from -0.5 to 0.5 V repeatedly at a rate of 50 mV s^{-1}.

Samples are exposed to $^1/_3$ sun illumination and the decay in photocurrent is observed. Samples with high current passage are desirable, as well as ones with stable performance with respect to time. For samples with insufficient protection, water from the solution will photocorrode or photopassivate exposed silicon sites, leading to degraded performance. These measurements can be made for p- or n-type semiconductors operating anodically or cathodically.

6.3 Growth of Graphene on Alkylated Silicon Through a Silicon Carbide Intermediate

6.3.1 Fabrication Scheme

A scheme for the fabrication of graphene layers using alkylated Si and SiC intermediates is shown below in Figure 28. In the first step PCl_5 is used to chlorinate a bare Si surface. In the second step a Grignard reagent is used to convert the chlorinated surface to an alkylated surface. Different Grignard reagents can be used, resulting in different alkyl monolayers. [56] Low temperature STM data of sample prepared using this process indicates that the methyl surface coverage is approximately 100%, with long alkyl chain derivatives having lower surface coverage. [78] In the third step, application of heat in vacuum causes the formation of a Si carbide layer. Finally, further heating *in vacuo* or under argon yields the desired graphene layer, as the top layer of Si sublimates off, leaving behind a layer of carbon atoms which restructure into graphene. This SiC to graphene process is highly dependent on the crystal face of the SiC intermediate and has been well characterized in the literature. [71, 72] All steps in this process are completely conformal and are well-suited to use with microstructured samples.

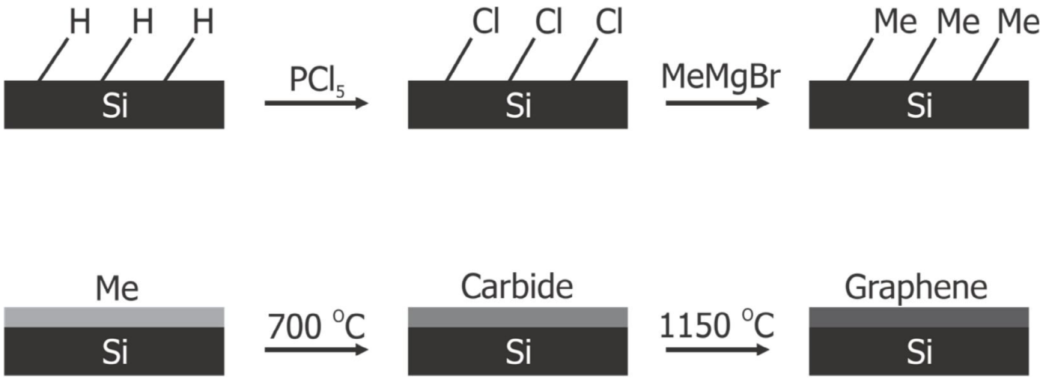

Figure 28: Scheme of a process for the fabrication of graphene from alkyl-Si *via* a carbide intermediate.

6.3.2 Results and Characterization

Methyl, ethyl, and octyl derivatized Si samples were obtained used the procedure described above. The samples were annealed *in vacuo* using a Kratos Axis Ultra X-ray photoelectron spectrometer (XPS) with a base pressure of $< 1 \times 10^{-9}$ torr. XPS scans were obtained for the C 1s region at room temperature and from 100 to 800 °C in increments of 100 °C.

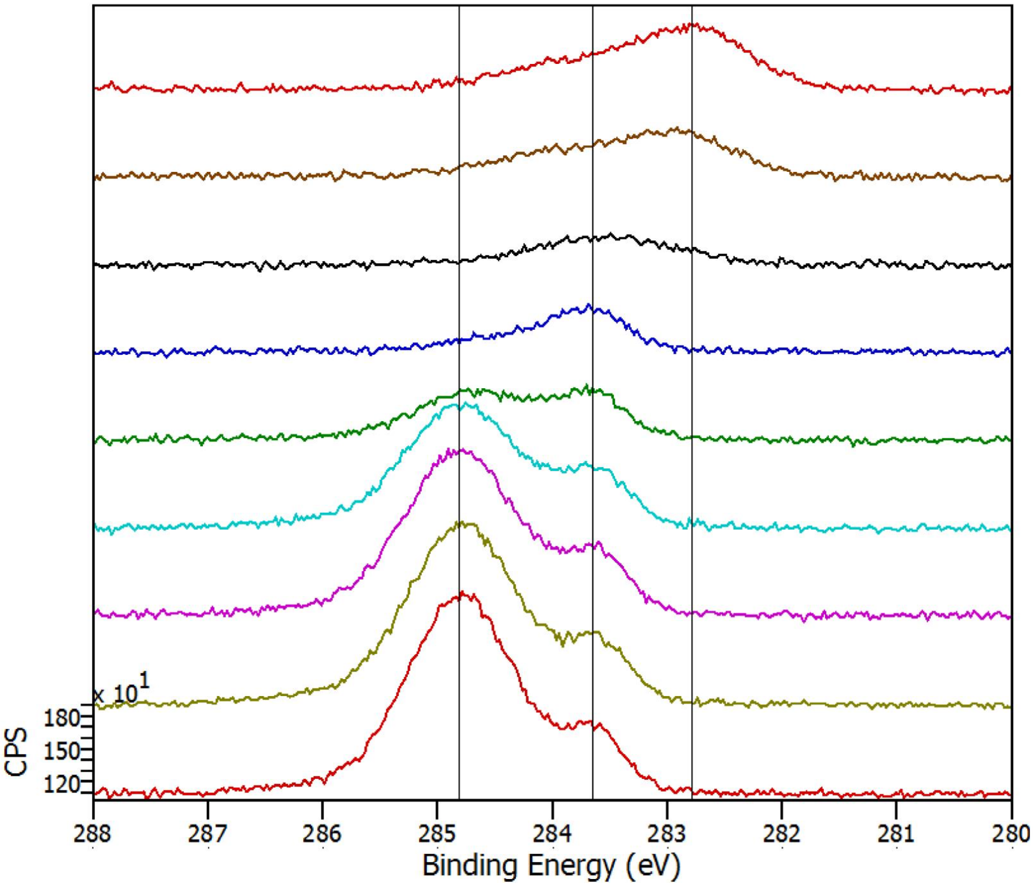

Figure 29: X-ray photoelectron spectrum showing the C 1s region of octyl-Si annealed from room temperature to 800 °C, with room temperature as the lowest trace.

An example spectrum for octyl-Si is shown in Figure 29. Spectra for the methyl and ethyl surfaces look functionally identical. In Figure 29 the peak at approximately 284.8 eV corresponds to aliphatic carbon species, in which in this case is a combination of the 7 aliphatic carbons in the octyl chain and any carbon deposited on the surface adventitiously during the sample transfer process. The peak at approximately 283.65 eV corresponds to the Si–C bond of the octyl chain to the Si substrate. These carbons are not incorporated into a crystal lattice in the form of silicon carbide. The peak at approximately 282.75 eV corresponds to the carbon incorporated into the desired SiC phase. It can be seen through these data that the aliphatic signal slowly decreases, a result of adventitious carbon being desorbed from the surface. The alkyl Si peak remains constant up until approximately 500 °C, past the point where the weaker bonded material has volatilized, until after which point it is converted to SiC. At approximately 600 °C this effect can be seen as the SiC peak increases in intensity, and is the only major signal remaining, indicating a largely SiC surface within the top several nm of the sample.

This sample is now suitable for further annealing and conversion to graphene *via* either conventional heating [71, 72] or microwave-induced heating. [79] SiC samples created from methylated Si were heated to temperatures $> 1000°$C using an electron beam heater in vacuum. Raman characterization of these samples before and after annealing is shown in Figure 30. This sample was characterized on Si without the optical resonance enhancement effect of SiO_2, so a rising background makes quantitative characterization difficult. Nonetheless, peaks are observed around 1595 and 2680 cm^{-1}, which indicate the growth of graphitic carbon. A low 2D/G ratio suggest that this sample is comprised of graphite rather than single of few layer graphene, and the broad peaks indicate a randomized and defective film. Further samples run at more controlled temperatures, or using microwave-induced heating [79] are necessary to properly quantify the viability of this growth method.

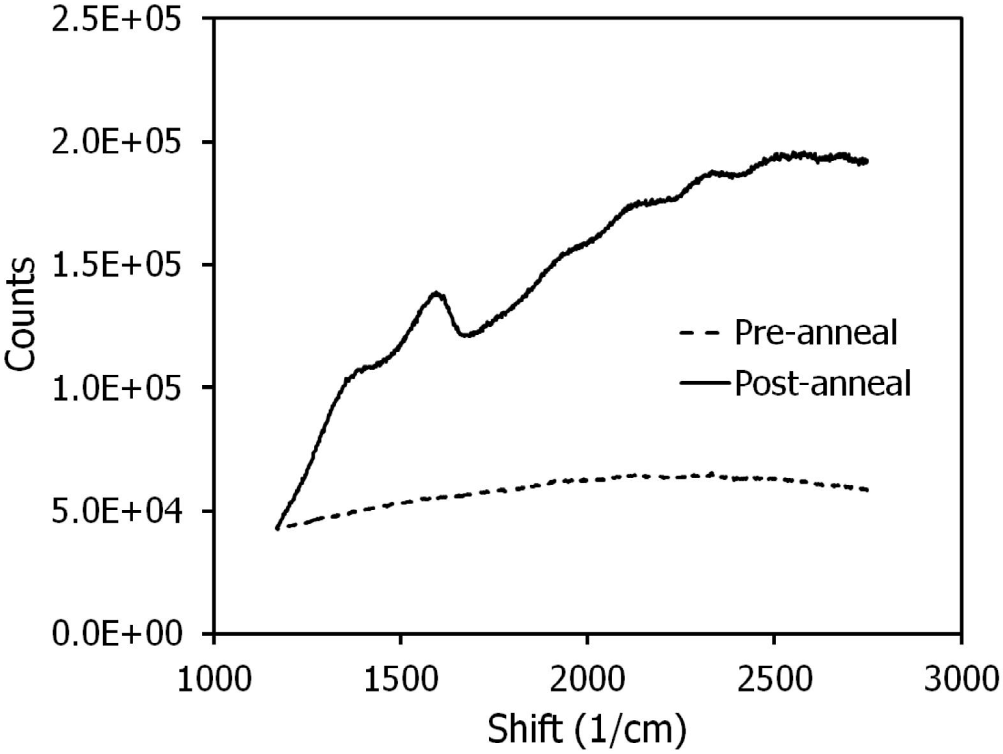

Figure 30: Raman spectrum of a SiC layer, before and after annealing *via* electron beam heating.

6.4 Nickel-Catalyzed Bilayer Growth of Graphene on Silicon

6.4.1 Fabrication Scheme

The process proposed for conformal nickel-catalyzed growth of graphene is shown below in Figure 31. In this process a 400 nm film of Ni is deposited *via* evaporation, sputter deposition, or electrochemical deposition. The latter two techniques have been described previously (Section 3) and are suitable for structured surfaces. Carbon has a high diffusivity in Ni and therefore during annealing at temperatures in the range of 400 to 1000 °C can transit through the Ni film and nucleate a graphene bilayer at the substrate-Ni interface. Following growth the Ni is etched off using Marble's reagent (1:5:5 $CuSO_4$:HCl:H_2O w/v/v).

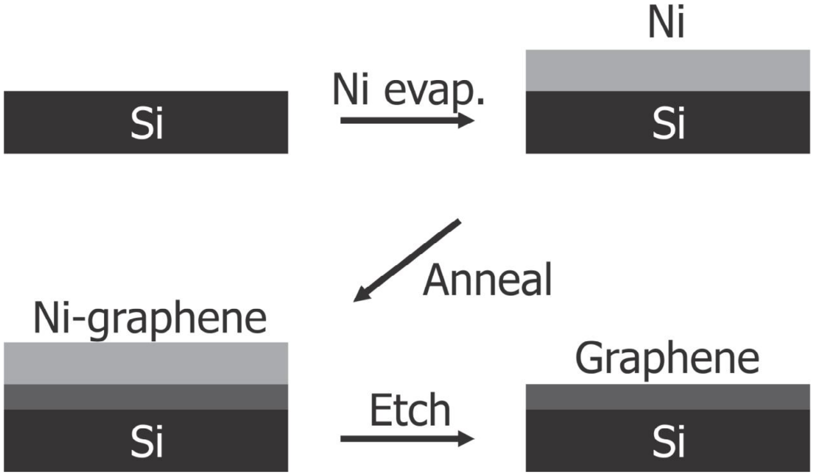

Figure 31: Schematic of the process of Ni-promoted bilayer growth of graphene *via* an annealing step and subsequent removal of the Ni catalyst.

This process has been demonstrated previously using SiO_2 substrates, [75] however a thick oxide layer would be detrimental to photoelectrochemical device performance. Therefore a Si substrate with a 2 nm oxide layer is used here, to form a metal-insulator-semiconductor (MIS) junction between the graphene, oxide, and Si. The SiO_2 buffer layer is still necessary in order to prevent the formation of a bulk nickel silicide which would prevent growth. Lower temperatures (∼ 400°C) were used in an attempt to preserve this separation. This process is conformal and has the distinct advantage that it is easily incorporated into the magnetic alignment process described in previous sections, by leveraging the ferromagnetic alignment handle as the graphene growth catalyst.

6.4.2 Results and Characterization

A Raman spectrum of the above process carried out on Si with a 300 nm oxide is show in Figure 32. This sample was grown at 1000 °C and etched with Marble's reagent.

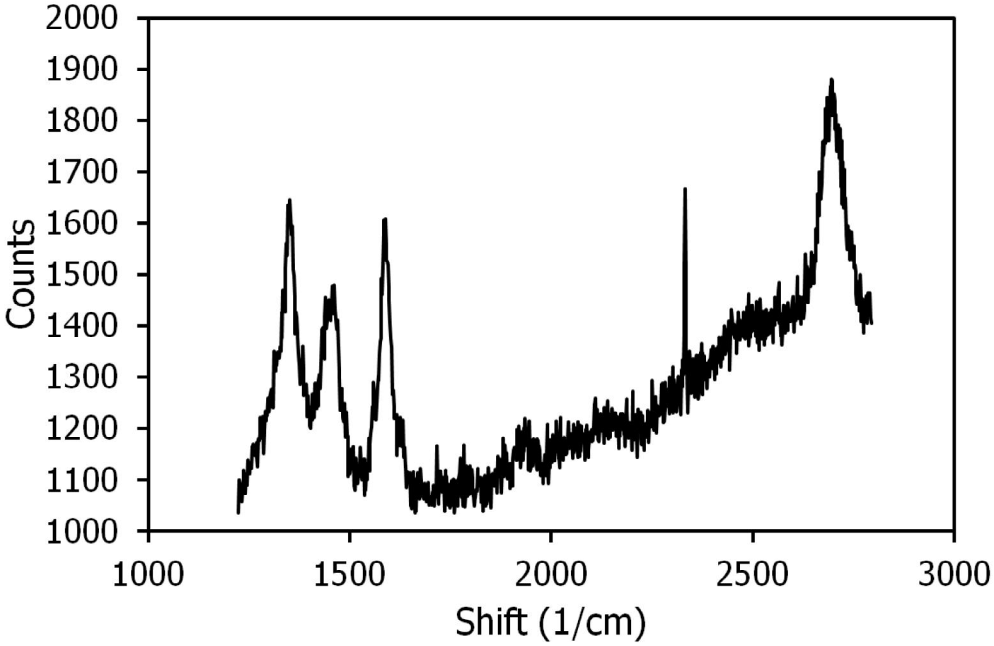

Figure 32: Raman spectrum of Ni-catalyzed bilayer graphene growth, with an approximately 1:1 G:2D ratio and a large D defect peak.

This Raman spectrum shows a 2D/G ratio of 1 indicating that bilayer growth has been achieved. However, a large defect peak is still present. All attempts to grow graphene at these conditions using thin oxide buffer layers (2 nm SiO_2 and 10 nm

SiO_2 grown *via* dry oxidation, and 2 nm Al_2O_3 grown *via* atomic layer deposition and evaporation) were unsuccessful and resulted in formation of bulk nickel silicide.

Figure 33 shows a Raman spectrum for the growth of graphene at 400 °C on a Si sample with a 2 nm thermal oxide buffer layer grown by dry oxidation. A 400 nm layer of Ni was used as the catalyst and removed after growth using Marble's reagent for 10 min. A spin-coated layer of poly(methylmethacrylate) was used as a carbon source. Flow rates were 50:100 sccm H_2:Ar for 20 min with a base pressure $< 1\times10^{-4}$ Torr and a run pressure of $\sim$250 Torr. This sample shows the characteristic G and 2D peaks, though they are shifted, likely by sample overheating during Raman acquisition. This process will need to be tuned in order to maintain the lower temperatures necessary for preventing silicide formation, while increasing the quality of the graphene film produced to that seen on bulk SiO_2.

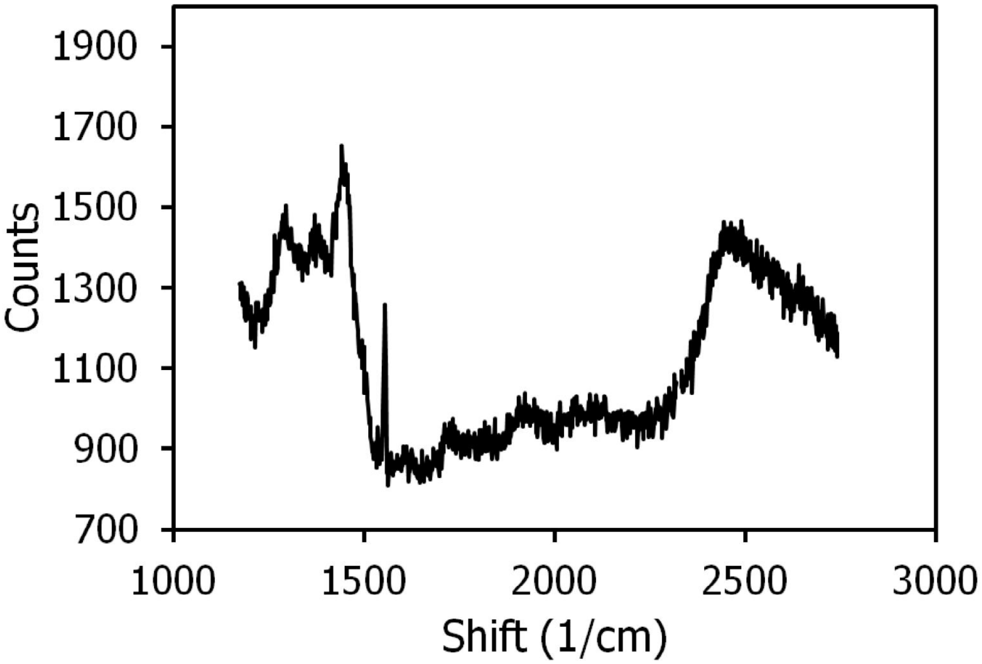

Figure 33: Raman spectrum of Ni-catalyzed bilayer graphene growth on a Si surface with a 2 nm oxide buffer layer.

6.5 Direct Growth of Graphitic Carbon on Silicon

6.5.1 Fabrication Scheme

Graphitic layers can be grown directly on a range of materials, including Si, [80] by annealing in the presence of a carbon precursor gas such as CH_4 or C_2H_2. This method is shown schematically in Figure 34 and has the advantage that no catalyst materials are necessary, which prevents undesired contamination of any fabricated devices. However, films grown by this method lack the quality of single layer metal-catalyzed graphene results. Nonetheless, multilayer graphene films, or graphite, are a promising conductive layer that could still prevent underlying Si structures from oxidation in solution.

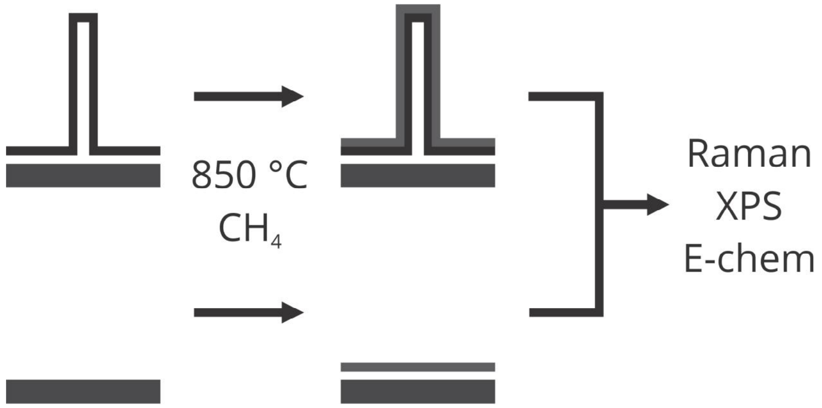

Figure 34: Schematic of the process for direct growth of graphite on Si and subsequent analytic methods used. This process is applicable for planar as well as structured samples.

6.5.2 Results and Characterization

Graphite films were grown on planar Si wafers as well as Si microwires using methane as the carbon precursor during a slow annealing process to 850 °C in a 50:100 sccm H_2:Ar mixture. A Raman spectrum is shown below in Figure 35 for the planar sample. This sample shows a large G peak but no 2D peak, indicating that there are many layers of graphitic carbon. Additionally, a range of high intensity defect peaks are present, centered around 1500 cm^{-1}.

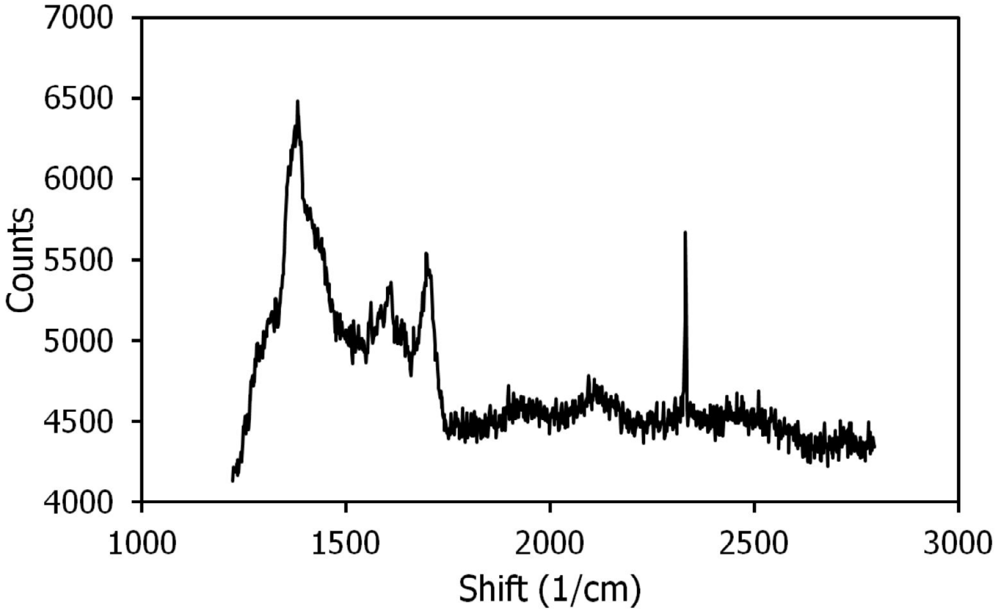

Figure 35: Raman spectrum of highly defective graphite grown on planar Si.

Photoelectrochemical stability measurements were taken in the form of repeated current-voltage sweeps, as shown in Figure 36. Samples shown in the plot are planar, 0.24 Ω cm resistivity, p-type Si samples. The dotted control trace shows a higher initial current which rapidly degrades over three sweeps, or approximately one minute under $^1/_3$ sun illumination. The graphite coated Si sample has a lower initial current, but is relatively stable at approximately 0.1 mA cm^{-2}. The treated samples are likely to be able to pass less current than bare Si due to the resistance of the added graphite coating. Graphene and graphite are both conductive in plane, but the through plane resistance, while minute for single layer graphene, can create significant resistive losses with thick coatings of graphite. Control over the layers deposited is therefore desirable.

These samples only show stability when passing low levels of current, not providing a significant advantage over bare Si. However, with further tuning of the graphitization process, it may be possible to deposit a thinner, more conductive layer, with a lower defect density in order to chemically protect Si photoelectrodes.

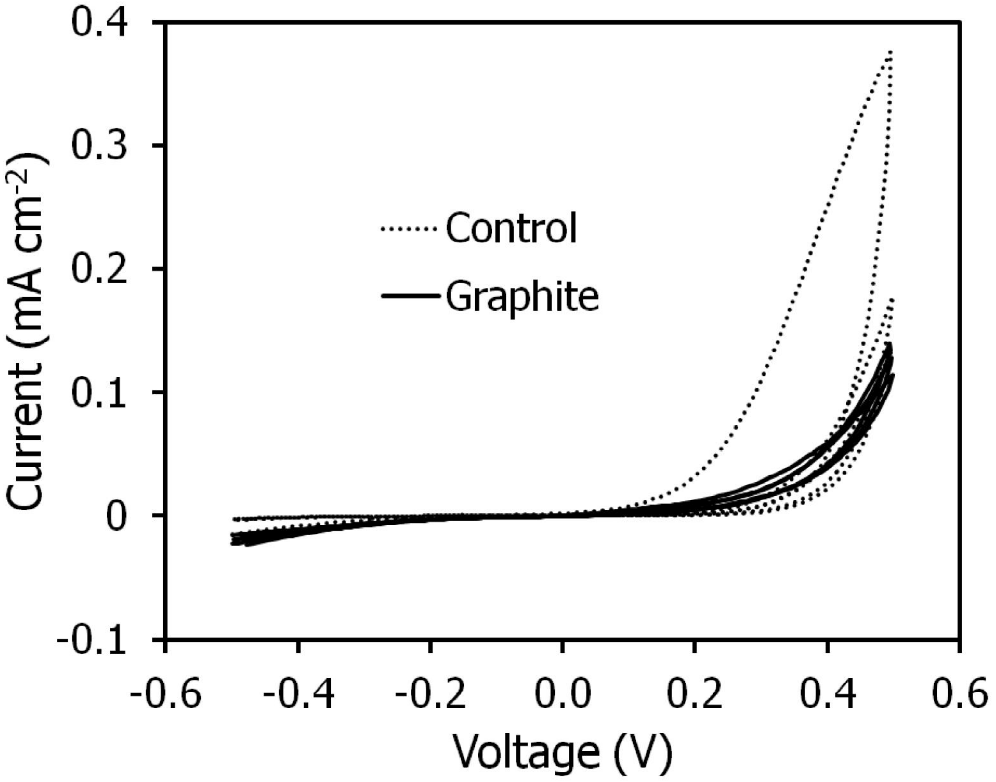

Figure 36: Photoelectrochemical stability data for a planar Si control as well as a graphite coated Si sample.

6.6 Conclusions

Graphene is a promising material for the aqueous protection of photoelectrodes, but current methods are largely restricted to planar systems. In order to enhance the performance of Si microwire array solar devices, new routes for the conformal preparation of graphene on Si are highly desirable. Three methods have been presented here, first, a method by which a covalently bound alkyl layer on a Si surface is converted into graphene through a Si carbide intermediate, second, a method by which a graphene bilayer is grown using a Ni catalyst, and finally, a method for the direct growth of graphite layers on Si using a gaseous carbon precursor. Each method has resulted in the synthesis of graphitic carbon, and while no enhanced photoelectrochemical performance has been observed as of yet, these methods are highly facile and scalable procedures that have promise for future growth of conformal graphene layers.