Noncovalent Chemical Modification of Graphene

by

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B.Sc., University of Victoria, 2010

A Thesis Submitted in Partial Fulfillment
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Low dimensional carbon allotropes presently provide an unparalleled platform to explore novel electronic properties, and with tremendous progress may one day supplant entrenched materials within the semiconductor industry. In order for graphene to continue on its extraordinary scientific and technological trajectories, many hurdles must be overcome such as reliable bandgap engineering, advances in processability, removal or mitigation of defects and so on. Noncovalent chemical modification of graphene offers a pathway to address many of these concerns and furthermore provides an opportunity to graft new functionality onto this unique material.

In this work, the effects of noncovalent modification of graphene by simple polyaromatic molecules – rubrene and tetracene – are investigated. By exploiting $\pi$-$\pi$ interactions between the two highly conjugated systems, a simple approach to functionalize graphene devices has been developed. Optical and electron-beam lithography are used to fabricate graphene field effect transistors, which can be subsequently modified either in their entirety or in a site specific manner.

In order to better understand the resulting graphene/rubrene structure, a suite of analytical tools has been employed. Raman spectroscopy and microscopy confirm
the presence of the rubrene and spatially correlate observed electronic changes with 
surface modification while polarized Raman spectroscopy is used to investigate any 
long range order of rubrene on the graphene surface. Photoluminescence 
measurements show that rubrene emission is not quenched, and spectral analysis 
offers insight into rubrene film characteristics. Atomic force microscopy provides 
detailed information as to film thickness, and suggests that rubrene film morphology 
is largely disordered. Due to the simplicity of this functionalization procedure, a 
rubrene-based motif could be widely expanded allowing researchers to explore 
grafting new chemical moieties onto graphene and enabling new device 
opportunities.

Transport measurements reveal the effects of rubrene on the graphene 
electronic properties. Modified devices display increased conductivity, a substantial 
shift in Dirac point and a moderate decrease in carrier mobility, all of which are 
consistent with an electronic doping mechanism whereby the rubrene acts as a hole 
dopant. Preliminary photoresponse measurements suggest that this graphene-
molecular hybrid could act as a potential photodetector.
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List of Abbreviations

2D two dimensional
AFM atomic force microscopy
CAD computer aided design
CCD charge coupled device
CVD chemical vapour deposition
DNA deoxyribonucleic acid
e-beam electron beam
FET field effect transistor
GS gate-source
HeNe helium-neon
HOMO highest occupied molecular orbital
HOPG highly ordered pyrolytic graphite
IPA isopropyl alcohol
LUMO lowest unoccupied molecular orbital
MIBK methyl isobutylketone
MOSFET metal-oxide-semiconductor field effect transistor
n negative
NIR near infrared
p positive
Ph phenyl
PL photoluminescence
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Full Form</th>
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<tr>
<td>PMMA</td>
<td>poly(methyl methacrylate)</td>
</tr>
<tr>
<td>RCA</td>
<td>Radio Corporation of America</td>
</tr>
<tr>
<td>redox</td>
<td>reduction-oxidation</td>
</tr>
<tr>
<td>SD</td>
<td>source-drain</td>
</tr>
<tr>
<td>SEM</td>
<td>scanning electron microscope</td>
</tr>
<tr>
<td>UV</td>
<td>ultraviolet</td>
</tr>
<tr>
<td>Vis</td>
<td>visible</td>
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Dedication

To my Uncle Sunny, a lifelong academic;

I wish you were here to see me finish this.
Chapter 1
Background and Introduction

The purpose of chapter one is to cover the pertinent background information and introduce the concepts relevant to the present research. First, Section 1.1 will discuss graphene’s recent discovery and the unusual band structure which has driven the initial rapid growth in the field. Next, graphene isolation and characterization will be covered, with an emphasis on the importance of Raman spectroscopy. Section 1.2 looks at atomic force microscopy as applied to graphene and its structure on silicon dioxide. Graphene field effect devices will then be outlined in Section 1.3 including their structure, operation, and characterization. Section 1.4 describes possibilities for the chemical functionalization of graphene in two broad categories – covalent and noncovalent modification. Lastly, in Section 1.5, there is a brief description of the potential of graphene – both chemically modified and pristine – as a photodetector. The chapter concludes with an overview of the thesis.

1.1 Graphene

Graphene is a two-dimensional sheet of sp²-hybridized carbon atoms in a honeycomb crystal lattice. It is often described as the “mother” of all graphitic materials as it can be stacked into graphite, rolled into carbon nanotubes or curled up into fullerenes. Graphene’s structure yields incredible thermal, electrical and mechanical properties, primarily arising from long distance \(\pi\)-conjugation.¹ Theoretical physicists have been exploring graphene for some time, both as a model for graphite and as a novel material in its own right, but it was not until Geim, Novoselov and coworkers first
isolated single layer graphene in a ground breaking 2004 paper\(^2\) that experimentalists took notice. In the ensuing years, the field has exploded with new graphene applications, ranging from high speed electronics\(^3\) to flexible touch screens\(^4\) to DNA sequencing\(^5\). In 2010, Geim and Novoselov were awarded the Nobel Prize in Physics for their discovery.

One reason that graphene has been so attractive to physicists is its unique band structure\(^6\) shown in Figure 1.1.

![Graphene band structure](image)

**Figure 1.1** (a) Graphene band structure and (b) band structure near the K points displaying unique linearity. Adapted with permission from reference 6.

Unusually, graphene has a linear dispersion relation near the band edges,

\[
E = \hbar v_f k
\]  

(1.1)

where \(E\) is the energy, \(\hbar\) is the reduced Planck constant, \(v_f\) is the Fermi velocity, which in this case is approximately equal to one three-hundredth the speed of light, and \(k\) is the wavevector. Because the effective mass of carriers is related to the curvature of the dispersion relation, the linear relation yields an effective mass of essentially zero for both electrons and holes. This phenomenon is responsible for many of graphene’s important electronic properties including its remarkably high mobility. The bandstructure also hints
at a second feature of graphene’s electronic performance; graphene is termed a “zero-bandgap semiconductor” meaning that the valence and conduction bands meet – in graphene’s case at six equivalent k-points, termed the Dirac points. This differs from common bandgap semiconductor materials like silicon and puts a limitation on graphene applications because, although a graphene transistor will experience a current minimum, the relatively high off currents make it difficult to discriminate between on or off (1 or 0). This makes graphene transistors impractical for digital logic operations. This limitation requires that graphene researchers tailor their devices to those applications for which graphene is particularly well suited such as high speed electronics and transparent electrodes. The first step in the fabrication of these devices is the production of graphene.

1.1.1 Production and visualization of graphene

Geim and Novoselov reported two major breakthroughs in their 2004 paper, the first of which was the production of graphene via micromechanical cleavage. Prior to this result, it was thought that two-dimensional materials would be too thermodynamically unstable to exist in a free-standing format. Prior examples of two-dimensional crystals had always been grown epitaxially, with the substrate acting as a crucial stabilizer while simultaneously making it difficult to access the intrinsic properties of the 2D material.

Micromechanical cleavage is also known as the “Scotch tape method”. This technique involves taking a piece of Scotch tape and adhering it to a highly oriented pyrolytic graphite (HOPG) substrate, which is a scientific grade of graphite in which the angular spread between the graphite layers is less than 1°. The tape removes the top several layers of the HOPG. The tape is subsequently folded onto itself repeatedly to produce ever thinner layers of graphite. Eventually the tape is then stuck face down onto
a substrate where it randomly deposits graphene and graphite of a variety of number of layers. The main advantage of this technique is the extremely high quality graphene produced, and this has led to its wide adoption at the research scale.

The second breakthrough reported in 2004, and arguably the more important of the two, was the ability to locate graphene using an optical microscope. Before this discovery, randomly depositing graphene over a substrate would be of limited use as time intensive techniques like atomic force microscopy (AFM) would be needed to locate it among all the graphitic material. In 2004, it was found that when graphene is deposited on a silicon wafer with a very specific thickness of silicon dioxide on the surface, the thin flakes can be distinguished from the background of a bare wafer. This was demonstrated initially with a 300 nm layer of SiO$_2$ as this is a dielectric thickness often chosen for the fabrication of back-gate field effect transistors. In 2007, a follow-up paper$^9$ in which they investigated optical contrast as a function of oxide thickness and wavelength of the illumination source, explored this phenomenon further. Using a simple model based on the Fresnel law describing the behaviour of light at the interface of two media with different refractive indices, they derived a theory which captured most of the experimentally observed results, and clarified the ideal oxide thickness to visualize graphene at a variety of wavelengths. Figure 1.2 shows the results of the paper in which it was concluded that with white light, either 90 nm or 280 nm of oxide offered optimal contrast. For electronic devices, the thicker oxide is preferred due to the high gate voltages applied and the resultant concern of gate leakage.
Figure 1.2 Calculated colour plot of optical contrast as a function of wavelength and SiO\textsubscript{2} thickness. Reprinted with permission from Blake, P. et al. Appl. Phys. Lett. 2007, 91, 063124. Copyright 2007, American Institute of Physics. Red line shows the oxide thickness used in this research.

Although micromechanical cleavage was the first technique used to produce graphene, it is not ideal if one hopes to eventually incorporate this material into industrial scale electronics. The main downsides of this technique are the relatively small size of the graphene flakes produced and their random distribution on the substrate. To produce graphene on a larger scale, chemical vapour deposition is the methodology of choice.\textsuperscript{10,11} In this technique, a metal foil – most often copper or nickel – serves as a catalyst for graphene growth. Copper in particular is popular as it is self-limiting – the catalytic reaction largely ceases after the formation of a monolayer. The metal foil is heated in a furnace under either vacuum or a reducing atmosphere before a carbon feedstock, usually methane or ethane, is flowed through the furnace chamber where it reacts with the metal surface generating a layer of graphene. Following this step, an additional challenge is the transfer of graphene to a substrate suitable for electrical experiments. To do this, the graphene is coated with PMMA and the copper foil is then dissolved away in iron nitrate.
solution. The graphene on a PMMA support is left floating on the surface of the solution where it can be “scooped up” with any desired substrate.

The obvious advantage to this technique is that the graphene can be produced reliably on a large scale, determined only by the size of metal foil. Thus far, this technique has yielded poorer quality graphene than that of micromechanical cleavage, but because it is the only method which allows for the production of graphene on a scale applicable for industrial applications, it is the subject of intense research focus and will likely improve rapidly.\textsuperscript{12} Already procedures have been established to create graphene sheets on a large scale and these sheets have been applied towards the fabrication of flexible touch screens.\textsuperscript{4} Although the present research uses entirely graphene from micromechanical cleavage, the chemical modification approaches discussed in this thesis are applicable regardless of the graphene production method.

1.1.2 Identification of graphene using Raman spectroscopy

As previously mentioned, the ability to find graphene using an optical microscope was a tremendous step forward; however, it is also useful to have a spectroscopic method to confirm findings by eye and gather further information on a particular sample. For graphene, Raman spectroscopy is a remarkable asset. It was Ferrari and colleagues\textsuperscript{13,14} at Cambridge University who first revealed the utility of Raman spectroscopy in 2007. It was found that the Raman spectrum of graphene was distinct for single, double and multilayer graphene allowing for an unequivocal determination of number of layers (Figure 1.3).
Figure 1.3 Representative Raman spectra of the 2D peak of (a) single layer, (b) double layer and (c) multilayer graphene. Green lines are individual Lorentzian fits and red lines are combined Lorentzian fits.

The graphene Raman spectrum, shown in Figure 1.4, consists of two main peaks – the G band is found at \(~1580\ \text{cm}^{-1}\) and the 2D band at \(~2650\ \text{cm}^{-1}\).

Figure 1.4 Raman spectrum of single layer graphene displaying two main features – the G band at \(1580\ \text{cm}^{-1}\) and the 2D band at \(2650\ \text{cm}^{-1}\). Spectrum was acquired with a 633 nm HeNe laser.
The G band is due to the doubly degenerate zone centre $E_{2g}$ optical mode in which the carbon atoms vibrate in the graphene plane.\textsuperscript{15} Zone centre refers to the Brillouin zone, the unit cell in the reciprocal lattice. Phonons at the zone centre correspond to simple vibrations of the entire lattice. The 2D band was historically (in graphite) termed the G’ band as it is the second most prominent feature in the spectrum, but this nomenclature was revised following improved interpretation of the spectrum. In fact, the 2D band is the second order of zone-boundary phonons, which correspond to a localized vibration in the lattice, and arises from the breathing mode of the graphene rings. Because zone-boundary phonons do not satisfy the Raman fundamental selection rule, the first order peak – the D peak at $\sim 1350 \text{ cm}^{-1}$ – is only seen in defected or edge graphene and graphite. This dependence on defects is a result of the mechanism through which the peak is formed. It requires a scattering event prior to electron-hole recombination and the defect or edge provides such a site. The D peak provides a useful way to determine the extent of defects in a graphene sample.

The 2D peak arises from a double resonance process which means that it will shift position with excitation wavelength and also evolve in shape with number of graphene layers. It is this second feature which makes this band so useful for graphene identification. The double resonance process links the phonon wave vectors to the electronic band structure, and involves four virtual transitions. It is shown schematically in Figure 1.5 in the case of graphene, bilayer graphene and bulk graphite.
Figure 1.5 Schematic describing the double resonance process which produces the Raman 2D peak in (a) single layer graphene, (b) double layer graphene, and (c) bulk graphite. Reprinted with permission from Graf, D. et al. *Nano letters*. 2007, 7, 238. Copyright 2007, American Chemical Society.

The first transition is the promotion of an electron due to the excitation laser, the second is an electron-phonon scattering event with exchanged momentum $\mathbf{q}$, the third is a second electron-phonon scattering with momentum $-\mathbf{q}$ and finally electron hole recombination. Within double resonance, energy should be conserved for these transitions. This explains the shift observed in the 2D peak position with change in excitation wavelength as the 2D frequency is dependent on $\mathbf{q}$ which, within double resonance, is dependent on the first transition. To understand the evolution of the 2D peak with number of layers, one must consider the band structure of bilayer graphene (Figure 1.5b) in which the $\pi$ and $\pi^*$ bands split into two bands each due to interlayer coupling. In this case, a single excitation wavelength can result in two differing states.
for the excited electron. From each of these cases, there are then two possible values of $q$ within double resonance. This leads to a total of four possible $q$ values and thus a convolution of four peaks makes up the 2D band in double layer graphene.

In bulk graphite (Figure 1.5c), the $\pi$ and $\pi^*$ split into a continuum of bands and the observed 2D band is in fact a superposition of numerous transitions.\textsuperscript{16} However, the theoretical model of double resonance does not explain the existence of two peaks or the intensity differences between them. It is postulated that some factors such as the role of excitonic effects are poorly accounted for in the double resonance model.

1.2 Atomic force microscopy of graphene

Atomic force microscopy (AFM) is a commonly used technique to measure the thickness of graphene layers. AFM imaging of graphene is always undertaken in tapping mode, as contact mode can easily tear or drag graphene sheets. In this mode, a piezoelectric element mounted in the tip holder drives the tip to oscillate at a frequency near its resonance frequency. The amplitude of the oscillation varies, but is generally greater than 10 nm, with the tip contacting the sample during each oscillation. This is distinct from noncontact mode in which the oscillations are much smaller and the tip never contacts the surface. Tapping mode is preferred for graphene imaging as it is less sensitive to tip-sample attractive forces and more likely to convey strictly topographical information. As the tip approaches the sample, various interactions – Van der Waals, dipole-dipole, electrostatics, etc. – cause the oscillation amplitude to change, thereby giving information regarding the topography of the sample.\textsuperscript{18} What complicates this measurement is that the information obtained is not strictly that of topography, but rather that of tip-sample interaction which is assumed, in tapping mode, to be primarily
influenced by topography. While this assumption holds true for many samples, it cannot be taken for granted when measuring a single atomic layer. The difference in interaction between tip and SiO₂ and tip and graphene can have a significant influence on the measured step height from substrate to sample. Furthermore, the interpretation can be clouded as different labs with different tip material, moisture content, mechanical exfoliation techniques, graphene annealing procedures and so on will observe different results. For this reason, the reported step height from SiO₂ to graphene has varied from 0.35 to 1.6 nm. Gupta et al. quantified this error by extracting an “instrumental offset” of 0.33 ± 0.5 nm, a significant value when considering a single atomic layer. A second study revealed that this offset itself is strongly dependent on the oscillation amplitude of the tip. Additionally, graphene does not sit perfectly flush against the SiO₂ substrate, resulting in a gap below the graphene that further increases the step height. The most reliable method to measure the thickness of a single layer of graphene is to find a monolayer-bilayer interface and measure the step edge. This minimizes any errors due to change of material as well as height added due to the imperfect SiO₂-graphene interface.

Aside from layer counting and thickness determinations, AFM has also been used to investigate the surface morphology of graphene. Despite being regularly described as a “flat monolayer” of sp² carbon atoms, graphene films are actually rippled. Figure 1.6 demonstrates the extent of this corrugation, which unsurprisingly can have a significant effect on the material properties.
Careful AFM studies in high vacuum have revealed that graphene will undergo an extrinsic rippling effect, with period on the order of 25 nm, due to the SiO$_2$ substrate and a simultaneous intrinsic rippling with a slightly smaller period of 15 nm. The implications of these results are twofold. First, by imaging both the intrinsic and extrinsic ripples at once, it was concluded that graphene on a silicon dioxide surface is partially suspended and only contacts the surface at the troughs of the ripples. This confirms the theory discussed above about the step height of graphene partially owing to a gap between graphene and the substrate. Second, the measurement of intrinsic ripples provides a thermodynamic justification for graphene’s existence. It was long postulated that 2D crystalline materials could not exist as thermal fluctuations should destroy long range order; however, a more detailed analysis led to the conclusion that three dimensional
deformations could potentially stabilize these materials and AFM imaging has since shown this hypothesis to be correct.\textsuperscript{22}

1.3 Graphene field effect transistors

A field effect transistor (FET) relies on an electric field to control the conductivity of the device channel. The transistor effect was first discovered in 1947 at Bell Labs by Shockley, Bardeen and Brattain\textsuperscript{23} with a bipolar junction transistor and was of sufficient importance to garner them a Nobel Prize in Physics in 1956. Currently, the most common type of FET is the metal-oxide-semiconductor FET (MOSFET) with silicon as the semiconductor. These devices form the basis for modern digital integrated circuits.

1.3.1 Structure of a graphene FET

A simple graphene FET is shown in Figure 1.7 with important components labeled.

![Graphene FET Diagram](image)

**Figure 1.7 Schematic of a simple back-gated graphene field effect transistor with important features labeled.**
On the top surface are two electrodes, source and drain, and a graphene channel running between them. A voltage is applied between the source and drain and a current is simultaneously measured. The measured current is proportional to the conductivity of the graphene channel. The graphene rests on a layer of dielectric, silicon dioxide (SiO$_2$); this is to separate it from the gate electrode, which is the heavily doped silicon substrate below. By applying a voltage between the gate and source electrodes, an electric field is generated which influences the conductivity of the graphene channel by varying the Fermi level of the graphene. This style of graphene FET is termed “back-gated” because the gate electrode lies below the graphene channel. Back gated graphene devices are very common for proof-of-concept experiments as they are easy to fabricate. The gate and dielectric are established simply by purchasing the correct substrate. However, these devices can suffer from large parasitic capacitances and cannot be integrated with other components prompting the need for top-gated transistors. In a top gate structure, a layer of dielectric material is deposited on top of the graphene channel, and a metal electrode is then fabricated on the dielectric. These FETs can be integrated together and offer improved performance, but require two additional fabrication steps. In this research, back-gated FETs are used to ensure that changes observed due to surface modification result solely from the interaction of graphene and molecules and are not a feature of dielectric or electrode deposition.

1.3.2 Operation of a graphene FET

Understanding the operation of a graphene FET entails understanding the graphene band structure. In pristine graphene (without defects, dopants or an applied gate voltage), the Fermi level – the topmost state occupied with electrons – falls at the point
where the valence and conduction bands meet. This point is called the Dirac point and corresponds to a current minimum as it has the fewest charge carriers at the Fermi level. Applying a positive gate voltage causes negative charge to build up in the graphene due to attraction toward the positive charge in the gate electrode. The Fermi level will therefore exceed the Dirac point and an increased conductivity will be observed. Conversely, applying a negative gate voltage immobilizes the electrons causing the Fermi level to fall below the Dirac point. This too leads to an increase in conductivity. Figure 1.8 shows the expected FET curve of pristine graphene which is symmetric and in the shape of a “V” with the minimum conductivity Dirac point falling at $V_{GS} = 0$.

In reality, no graphene is pristine due to processing, air exposure and the silicon dioxide substrate, all of which can act as dopants in addition to ever-present intrinsic defects. The dopants inject either electrons or holes, and can therefore also shift the Fermi

\[ I_{SD} (A) \]

\[ V_{GS} (V) \]

Figure 1.8 Expected pristine graphene FET curve has a current minimum at 0 gate voltage. Hourglass shapes show the graphene bandstructure with the change in Fermi level resulting from the application of positive and negative gate voltages. Adapted from reference 8.
level. This is seen in the FET curves as a shift in the Dirac point to $V_{GS} \neq 0$. Annealing either in vacuum or a reducing atmosphere is commonly used to mitigate these effects.\textsuperscript{24}

Two measurements are generally conducted on FETs to obtain two separate pieces of information. First, a simple IV curve, in which a voltage is applied to the source electrode and current is monitored at the drain. At room temperature, graphene is an Ohmic material, meaning it obeys Ohm’s Law,

$$V = IR$$ \hspace{1cm} (1.2)

where $V$ is the applied voltage, $I$ is the measured current and $R$ is the resistance. Therefore the plot of current vs. voltage is linear with the inverse of the slope giving the resistance. To normalize the result between devices, the resistivity is calculated to remove the influence of device size,

$$\rho = R \left( \frac{W}{L} \right)$$ \hspace{1cm} (1.3)

where $W$ and $L$ are the width and length of the device, respectively. Graphene is distinct from other materials in that it is strictly two dimensional. Its resistivity is termed “sheet resistivity” and has units of $\Omega$ as opposed to $\Omega \cdot \text{cm}$ in a standard three-dimensional device. Contact resistance between the graphene and chromium is also a significant factor and has, in fact, been shown to be the major contributor to resistance in these devices.\textsuperscript{25}

Four point probe measurements, in which the current and voltage electrodes are kept separate, can be used to determine the true resistance of graphene samples.

The second measurement is an FET curve. In this case a constant source voltage is applied while a second voltage, applied to the back gate, is varied. The slopes of the linear portions of the curve to the left and right of the Dirac point are related to the hole and electron mobility, respectively, by the following equation,\textsuperscript{26,27}
\[ \mu = m_{\text{lin}} \left( \frac{L}{W} \right) \left( \frac{1}{V_{\text{SD}}} \right) \left( \frac{1}{C_i} \right) \]  

(1.4)

where \( m_{\text{lin}} \) is the slope of the linear portion, \( V_{\text{SD}} \) is the constant source drain bias and \( C_i \) is the capacitance of the gate dielectric. The equation is derived from standard MOSFET model in the linear regime and relies on two assumptions: (a) the gradual channel approximation assumes that the voltage varies gradually along the channel, but rapidly perpendicular to the channel – this allows the gate voltage and source-drain voltages to be treated separately, and (b) the mobility is assumed to be a constant, independent of applied field. These assumptions generally hold provided \( V_{\text{SD}} \) is kept low relative to \( V_{\text{GS}} \).

In the literature, the mobility of graphene on silicon dioxide has been measured \(^7\) as high as 10,000 – 15,000 cm\(^2\)/V·s and is theorized to have an upper limit of 40,000 cm\(^2\)/V·s at room temperature. \(^28\) This limitation results from extrinsic scattering by surface phonons at the SiO\(_2\) substrate and can thus be overcome by creating suspended graphene devices. A suspended graphene device has recently been reported with electron mobility exceeding 1,000,000 cm\(^2\)/V·s. \(^29\) These values far exceed those of silicon, the industry standard (\(~1,400\) cm\(^2\)/V·s), InSb, the inorganic semiconductor with the highest mobility (\(~77,000\) cm\(^2\)/V·s) \(^30\) and carbon nanotubes (\(~100,000\) cm\(^2\)/V·s) \(^31\). This remarkable mobility is one of the primary reasons that graphene electronics show such promise as it can dictate the speed of electronic devices and the sensitivity of sensors.

### 1.4 Chemical modification of graphene

Chemical modification of graphene opens up a number of new possibilities for applications of this novel material. Modifications are used to dissolve graphene into
aqueous or organic solutions, to improve processability, to activate new optical functionality or to serve as dopants when engineering electronic properties. This area can be divided into two main categories: covalent and noncovalent modifications, both of which find their roots in the carbon nanotube literature of the preceding decade.32

1.4.1 Covalent modification of graphene

In 1991, Sumio Iijima published his findings33 on “helical microtubules of graphitic carbon” in the journal Nature setting off an explosion in the field of nanocarbon research. It was quickly realized that the utility of these new structures could be greatly enhanced if they could be dispersed in solution and much research into the covalent chemical modification of carbon nanotubes ensued with considerable success.34 However, covalent modification also yielded a notable downside; the addition of new functional groups disrupted the extended π system which was responsible for the nanotubes’ remarkable electronic properties.

Because of the previous research into carbon nanotubes, upon the first isolation of graphene, materials scientists were already primed with the tools to covalently modify graphene. Many of the reactions already shown to be effective with nanotubes translated easily to this new graphitic material. This time, however, researchers were a little more wary, knowing the danger that covalent chemical modification posed to electronic properties. For this reason, the covalently modified graphene literature is less robust than that of carbon nanotubes and very few studies have investigated the result of these modifications on electronic properties.

There are a variety of synthetic methodologies for covalently modifying graphene including directly adding atoms into the graphene lattice, modifying residual
functionalities (from a graphene oxide starting material), and direct modifications to the surface which disrupt the \( \pi \) structure.\(^{35} \) In all cases, one of the major advantages of the methodology is the ability to work in solution and produce graphene on a large scale, albeit in small pieces; however, while some authors propose that the resultant functionalized graphene might be a useful additive for electronic materials, none have studied the electronic effects of the modification on the graphene.\(^{36} \) It is also notable that the type of graphene commonly used for covalent modifications of graphene is reduced graphene oxide micrographenes. These graphitic materials are generated from small pieces of exfoliated graphene oxide which are then treated with a reducing agent to yield graphene.\(^{37} \) Although reduction treatments can remove most of the oxygen groups from these materials, they still have conductivity several orders of magnitude lower than exfoliated graphene.\(^{38} \) In cases where pristine graphene is used, the sonication and filtration steps required to get them into solution yields functionalized graphene pieces on the 500 nm – 1 \( \mu \)m length scale.\(^{39} \) The most feasible application of these products is likely for incorporation into composites to improve mechanical and electronic properties.

An exception to the research discussed above is the work of Colin Nuckolls et al.\(^{40} \) in 2009 where photochemistry was used to react benzoyl peroxide and graphene yielding benzene decorated graphene sheets. Unlike other examples, in this study the modification was carried out on pristine exfoliated graphene in a device architecture allowing for an investigation of the electronic effects of the modification. As anticipated, the functionalization resulted in poorer electronic performance as can be seen in Figure 1.9. Panel A displays a 50% decrease in conductivity which stemmed from the
introduction of sp\textsuperscript{3} defect centres and panel B shows a marked decline in mobility as evidenced by the shallower slope of the FET curve of the modified graphene.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure19.png}
\caption{The effect of covalent modification by photochemistry on the (A) I-V curve and (B) FET curve of a graphene device. Reprinted with permission from Liu, H. \textit{et al.} \textit{J. Am. Chem. Soc.} 2009, \textit{131}, 17099. Copyright 2009 American Chemical Society.}
\end{figure}

They also observed a large shift of the Dirac point to higher positive voltage due to hole doping from the benzoyl peroxide. Their methodology involved using a focused laser spot to induce the reaction, resulting in localized defect areas. It is thus reasonable to conclude that the other reactions discussed above, where the entire graphene surface was functionalized, would lead to further electronic deterioration.

Although covalent modifications of graphene can produce interesting new materials with a variety of potential applications, an alternative strategy is needed if one wishes to modify the graphene for use in an electronic device. In this case, noncovalent modifications should be a superior option.

\subsection*{1.4.2 Noncovalent modification of graphene}

In contrast with the reaction schemes discussed above, noncovalent modifications take advantage of the graphene \(\pi\) structure rather than disrupting it. These
functionalization schemes rely on π-π, CH-π, or hydrophobic interactions to graft new functionality onto the surface without introducing sp^3 carbon defect centres. It is worthwhile to consider both of these interactions in greater depth as they have considerable implications in the outcome of this research and are more complex than one might initially assume.

Despite having been recognized for decades due to their prevalence in biological systems, it was only in 1990 that Hunter and Sanders proposed an actual model\textsuperscript{41} to explain π-π interactions. Surprisingly, they postulated that the interactions arose not due to electronic attraction of the π systems, but rather when the favourable interaction between the π-electrons and the σ-framework outweigh the electron repulsion interactions. This model, derived from experiments on porphyrin stacking, explains the strong geometrical requirements of these interactions – the aromatic rings nearly always stack offset to one another or exist in a T-shape with one ring lying perpendicular to the other. However, later studies on substituted benzene molecules have cast a shadow of doubt on these results.\textsuperscript{42} The ongoing scientific debate is evidence in itself for the complexity of these interactions.

CH-π interactions are comparably simple being weak hydrogen bonding interactions where the C-H is the hydrogen donor and the aromatic ring acts as the acceptor. Figure 1.10 exhibits diagrams of the varying geometry of π interactions.
Figure 1.10 Different types of π interactions. (a) sandwich conformation π-π stacking, (b) offset conformation π-π stacking, (c) T-shaped π-π stacking and (d) CH-π binding. (b) and (c) represent the preferred geometry of π-π interactions.

Again, this area of research has its roots in carbon nanotubes. A general and highly adaptable approach, reported by Hongjie Dai and coworkers, is to react a molecule with the desired functionality with N-succinimidyl-1-pyrenebutanoate. The pyrene component of this molecule, which consists of four benzene molecules joined in a planar edge sharing configuration, binds irreversibly to the nanotube using π-stacking interactions while the functional component remains free for further chemistry. This technique has been used for a variety of applications including solubilisation, creating quantum dot nanotube-hybrids, and biosensing devices. This type of noncovalent interaction has been directly studied by Zhang et al. using single molecule force spectroscopy. In their experiment, a pyrene molecule was tethered to an AFM tip by means of a poly(ethylene glycol) linker before being lowered onto an HOPG surface. The strength of the π-π interaction, quantified as the force required to pull the pyrene away from the HOPG surface, was found to be ~55 pN in aqueous solution.
Theoretically, the same functionalization methodology can be applied to graphene, although it is unexpectedly underreported thus far. Three early mentions of graphene functionalization have been reported in the past several years.\textsuperscript{45-47} In two of these studies\textsuperscript{45,47}, the authors utilized pyrene derivatives to decorate graphite sheets in solution. Their proposal was that the pyrene molecules were able to infiltrate between the layers and eventually exfoliate aqueous single layer graphene. Although an interesting result, neither group performed any sort of electronic characterization of their exfoliated graphene. Because preserving electronic structure is one of the major advantages of the noncovalent technique, this was a surprising omission.

In the third example\textsuperscript{46}, the authors tested a small assortment of large aromatic molecules for their interaction with graphene. Though the functionalization was carried out in solution, in this case the resultant graphene composites were integrated into electronics and partially characterized as a function of temperature. The conductivity of the material was found to increase upon functionalization provided the device was thermally annealed. Again the authors were using reduced graphene oxide and thus had relatively low conductivities to begin with. They did not incorporate the material into a field effect device and there is therefore no information as to the effect of the aromatic molecules on the charge carrier density or mobility of the graphene.

Few examples\textsuperscript{48,49} have been presented with the electronic characteristics of the modified system fully characterized. In one study\textsuperscript{48}, graphene was functionalized with an azobenzene chromophore that had been synthesized with a pyrene group at one end to allow noncovalent tethering to the graphene. This structure allowed for light modulated doping dependent on the conformation of the azobenzene. They found that the hybrid
devices were p-doped relative to pristine graphene. In a separate study\textsuperscript{49}, a series of four aromatic molecules were tested to determine their electronic effects on graphene. It was found that aromatic molecules with electron donating groups tended to act as n-dopants while those with electron withdrawing groups were likely to be p-dopants.

A more common approach to noncovalently functionalizing graphene is the use of small molecules as dopants.\textsuperscript{35} Indeed, this occurs naturally through processing as water, oxygen and/or photoresist adsorb to the graphene surface. Water and oxygen are both p-dopants which inject holes into the graphene. Another common p-dopant is nitrogen dioxide. Common n-type dopants are ethanol and ammonia. The charge transfer involved in these interactions is dictated by energetic level of the HOMO and LUMO of the dopant molecule relative to the Fermi level of the graphene. If the HOMO of a dopant is above the Fermi level of graphene, electrons flow from the dopant to the graphene layer, and the dopant acts as a donor (n-type); if the LUMO is below the Fermi level of graphene, the opposite occurs, with charge flowing from the graphene to the dopant (p-type).\textsuperscript{35}

The advantages to this type of doping are twofold – they allow for the tailoring of electronic behavior and they also lend the devices some stability. The stability is enhanced by doping because the presence of dopants prevents any further surface functionalization. Perfectly undoped graphene must be stored under vacuum or an inert atmosphere lest it be contaminated by water vapor or oxygen in the air. It is worth distinguishing between this model of small molecule doping, which is well studied and can quite readily be used to modify the electronic characteristics of a graphene device, and chemical functionalization via π-π stacking which can be used to graft an almost
limitless variety of new functionalities to the device in addition to acting as a chemical dopant.

1.5 Photodetection using graphene

One example of a new functionality which can be obtained through noncovalent functionalization is that of photodetection. Although most graphene research so far has focused on exploiting its remarkable electronic properties, graphene also shows great promise as a photodetector. It can absorb approximately 2% of light over a broad wavelength range which is quite impressive for a material of just one atomic layer. Furthermore, graphene’s high carrier mobility could lead to photodetectors of an unprecedented speed.\(^{50}\)

Graphene does not require chemical functionalization to act as a photodetector, but must overcome one major hurdle. In order for a photodetector to operate, the incoming radiation must promote an electron from the valence to the conduction band. This promotion generates an electron-hole pair termed an exciton. Once the promotion occurs, the carriers are now free to move about the material, but they must reach an electrode in order to be detected. If the electron recombines with the hole prior to detection, there is no observed photocurrent.

In a zero bandgap material like graphene, electron-hole recombination is extremely rapid, on the order of tens of picoseconds\(^{50}\), meaning that excited electrons travel only hundreds of nanometers in an average mobility sample before falling back to the valence band. This phenomenon makes photodetection extremely difficult when not dealing with suspended, high mobility graphene devices. However, an important discovery has boosted this research area – the presence of an internal or external field can
allow for longer separation of the charge carriers and a measured photocurrent. Such fields arise either by the application of a large gate voltage (external) or near the graphene-metal contacts (internal). It has been reported that multilayer graphene FETs display a photoresponse as high as 0.4 mA/W when illumination occurs near the metal contact and a gate voltage of 80 V is applied. However, at 0 gate voltage, this drops to approximately -0.1 mA/W. The authors did not report the photoresponse of single layer graphene without an applied external field.

A simple device geometry modification can be employed to improve the performance of these intrinsic detectors; the device is fabricated with interdigitated electrodes of differing metals. The differing metals are used to ensure the presence of the internal field and by using an interdigitated structure, the entire surface area of the graphene falls under the category of “near an electrode” so the carriers don’t need to travel far to avoid recombination. This setup dramatically enhances photodetection yielding a photoresponse of 1.5 mA/W at a gate bias of -15 V or approximately 1 mA/W without a gate bias. Again, these results were from a bilayer graphene device and no single-layer device results were reported.

Noncovalent chemical modification offers another potential route to high speed graphene photodetectors with the potential for tailored spectral response. Thus far, only one demonstration of this functionality has appeared in the scientific literature, but this is unsurprising given the very few demonstrations of noncovalent chemical modification with large molecules thus far. It has been much more thoroughly studied in carbon nanotube systems and this suggests that, given time, the graphene research will head in the same direction. In this experiment, there are two potential mechanisms for
photoresponse. In one, the excitation occurs from the HOMO to the LUMO of the functionalizing molecule. If the LUMO of the molecule is at a higher energy than the Fermi level of the graphene (or nanotube), then the excited electron can easily drop to the conduction band of the graphene (or nanotube); this charge transfer leads to an increase in the conductivity of the graphene. In a second, the photoexcited molecule has a dipole which causes it to act like a gate thereby changing the conductivity of the channel. Graphene photodetectors made via chemical modification will not have the same broad wavelength operation as pure graphene, but will have a “tunable” detection range which depends on the molecule used.

For carbon nanotubes, this has been demonstrating using a Zn porphyrin derivative as the optically active molecular dopant. Upon illumination, the measured “off” point of the SWCNT device shifts toward less positive gate voltage, suggesting a charge transfer from nanotube to porphyrin. The graphene example works on the same principle but involves a much more complex molecule shown in Figure 1.11a. In that result, a ruthenium complex, known to be electrochemiluminescent, is synthesized with a pyrene tail which allows it to bind to a graphene substrate. The synthesis, binding and electrical characterization, shown in Figure 1.11b, were all carried out in solution without the need for complicated electrode structures or large external fields. In measuring the photoelectrical response, the authors used a potentiostat/galvanostat and a three electrode system of glassy carbon (working electrode), platinum wire (counter electrode) and Ag/AgCl reference electrode. The graphene-ruthenium hybrid was deposited in solution on the glassy carbon electrode which was then dried prior to experimentation. In contrast to the nanotube example, the proposed mechanism in this case is a charge transfer from
complex to graphene. They deduced the mechanism from cyclic voltammetry rather than FET measurements.

Figure 1.11 (a) Structure of a ruthenium complex with the pyrene tail anchored to graphene and the proposed charge transfer mechanism upon exposure to radiation (b) Photoelectrical response in aqueous solution of the graphene-ruthenium hybrids (red) and pure ruthenium complexes (black) at 20mV bias. Adapted with permission from reference 52.

Similar electrochemical experiments using noncovalently functionalized graphene oxide have also shown promising results, although they suffer from the poor conductivity inherent to oxidized graphene.

1.6 Thesis outline and scope of research

The following thesis will document current research into the fabrication and characterization of chemically modified graphene field effect transistors with a demonstration of their potential application as photodetectors.

Chapter 2 discusses the fabrication of graphene field effect transistors. First, a combination of optical and electron beam lithography is used to produce a patterned platform on thermally oxidized p-doped silicon wafers. The platform serves as a substrate
upon which graphene is randomly deposited. The graphene is then identified optically and verified by Raman spectroscopy. Electron beam lithography is used to wire the graphene candidates to large pre-patterned electrodes to yield completed devices. The devices are then fully characterized by electronic transport measurements and atomic force microscopy.

Chapter 3 outlines the noncovalent chemical modification and subsequent characterization of the hybrid device surface morphology. The modification is carried out with the polyaromatic hydrocarbon rubrene which shows a strong affinity for graphene. The modified devices are investigated optically, using Raman and fluorescence spectroscopy, and structurally by atomic force microscopy. Conclusions are proposed regarding the thickness and ordering of the rubrene film.

Chapter 4 looks at the electronic characteristics of the modified devices using two- and three-point transport measurements including an analysis of how the transport properties vary over time. Additionally, the potential of the rubrene-graphene devices as photodetectors is investigated.

Chapter 5 provides a summary of the research and major conclusions as well as a discussion of proposed future work on this project.
Chapter 2

Fabrication and Characterization of Graphene Field Effect Transistors

Chapter two discusses the fabrication of graphene field effect transistors (FETs) and their subsequent electronic, structural and optical characterization. Obtaining properly functioning graphene electronics was one of the major hurdles to overcome in this project, and required a number of trials and adjustments to arrive at the procedure described below. Section 2.1 describes the design and production of a platform for the efficient fabrication of graphene devices. With the platform in hand, graphene must then be deposited on the surface and located using optical microscopy and Raman spectroscopy and these steps are covered in Sections 2.2 and 2.3. The final transistor fabrication using electron beam lithography is then laid out in Section 2.4. The fabrication of a graphene FET, from start to finish, was a 3-4 day procedure, although several could be run in parallel during this time. Proper characterization using a variety of techniques was essential for optimizing procedures, confirming successful fabrication and readying the devices for chemical modification. Electronic transport measurements and atomic force microscopy were the primary characterization tools and are discussed in Section 2.5.

2.1 Platform design and fabrication

In order to fabricate graphene devices in a reproducible manner, a substrate with particular characteristics was required. Large electrodes for making electronic connections in a probe station along with a finer alignment grid were crucial to accurately
locate graphene specimens. It was important to also take into account both ease of use and material waste to set upon an optimal platform size. Lastly, the platform needed to be compatible with all current instrumentation and any future project directions.

2.1.1 Platform design

The requirements listed above resulted in the following platform design, with the CAD design and completed platform shown Figure 2.1.

Figure 2.1 (a) CAD drawing of device fabrication platform. (b) Optical image of completed device platform.

Eight external pads measuring $1 \times 1$ mm made up a $5 \times 5$ mm total patterned area. One of the squares was altered to be an “L” shape, as a unique corner is necessary to ensure proper orientation over repeated steps. Inside these large electrodes, a $20 \times 20$ grid of $10 \, \mu$m squares was used as finer alignment for locating graphene. Experimentation over the course of the project revealed that graphene was less likely to adhere to the substrate if there was too high a density of alignment squares. The $20 \times 20$ grid was chosen to have the minimum number of squares while still being dense enough to locate
any graphene piece relative to a square at 500× magnification. This grid also contained a unique shape at the centre and within each quadrant. Lastly, ‘plus’ shapes were designed to fall between the large electrodes, allowing for repeated lithographic steps without disrupting the graphene samples within the fine grid. The design was created using Raith50 CAD software.

### 2.1.2 Fabricating an optical mask

The platform design was then translated to an optical mask using electron beam (e-beam) lithography. Figure 2.2 shows a schematic flow chart of the e-beam lithography process.

![Flow chart demonstrating the fabrication of the optical mask using electron beam lithography.](image)

In this technique, the surface of a substrate is coated in a layer of electron beam resist. This resist is a polymer whose solubility changes upon exposure to a beam of
electrons. The beam of electrons is guided by computer software which traces out the pattern from a CAD design. After exposure, the substrate can then be placed in a specially formulated developer which allows one to wash away only the exposed resist, thereby transferring the pattern to the substrate. It is a very powerful technique as it allows for unique patterns to be designed and transferred with extremely highly resolution, down to tens of nanometers. However, it is a slow and costly procedure which requires highly specialized instrumentation in a clean room.

For the fabrication of the optical mask, a 1” × 1” glass slide was carefully cleaned in piranha solution (Appendix) before being coated with 100 nm of chromium using an Angstrom Engineering e-beam evaporator. The cleaning and relatively thick layer of metal ensured a minimum of pinholes in the final mask. The chromium was then coated with a layer of e-beam resist, poly(methylmethacrylate) with a molecular weight of 950 kDa (PMMA 950), using a spin coater at 4000 rpm and baked on a hotplate at 220 °C for one minute. A Raith50 electron beam lithography writer was used to transfer the pattern of the CAD design to the resist and 1:3 methyl isobutyl ketone (MIBK) to isopropyl alcohol (IPA) was used as a developer to wash away the exposed polymer. The exposed layer of chromium was subsequently etched away using a proprietary acidic chromium etchant (Aldrich – Chromium Etchant Standard) to reveal the glass below. Lastly, the remaining resist was washed off with acetone. The whole procedure took approximately 24 hours.

Although this technique for optical mask fabrication was more time consuming and costly than simply having a CAD drawing printed commercially, it allowed for greater accuracy and smaller feature sizes. Also, because the same pattern was used
throughout the project, the mask only needed to be made once, which further justified the complex procedure.

### 2.1.3 Optical lithography

As in e-beam lithography, the first step of optical lithography is to coat the substrate with a resist (Figure 2.3).

![Flow chart demonstrating the fabrication of the device platform using optical lithography.](image)

**Figure 2.3** Flow chart demonstrating the fabrication of the device platform using optical lithography.

In this case, a photoresist, which changes solubility on exposure to ultraviolet radiation, is used. Instead of writing a unique pattern with a beam of radiation, the prefabricated optical mask is placed over the coated substrate to create the pattern. The entire wafer is simultaneously exposed to UV light, solubilising only the resist exposed through the mask. Again the sample is then developed to reveal the pattern. Optical lithography is much higher throughput than e-beam as it generates all of the features in
parallel rather than in series. It is for this reason that it is widely used in industry for fabrication of electronic components.

In the present work, optical lithography was used to generate patterned platforms for the fabrication of graphene devices. The substrate purchased was 500 μm thick (100) silicon wafer p-doped with boron (resistivity of 0.005-0.020 Ω·cm) with a 300 nm thick SiO₂ coating (University Wafer, Boston, MA). The oxide thickness was etched down to 280 ± 4 nm using CF₄/O₂ plasma etch at a 1:1 ratio for 11 seconds and at a pressure of 301 mtorr (Plasmatherm Etcher, Ampel Nanofabrication Facility, University of British Columbia) as this was found to offer better contrast when searching for graphene pieces optically while still providing a sufficiently thick oxide layer for electronic isolation from the substrate. Oxide thickness was then measured with a Filmetrix F20 thin film measurement system (Ampel Nanofabrication Facility, University of British Columbia).

The wafers were diced into 1 cm squares then thoroughly cleaned using RCA1 (Appendix) to remove organic contaminants and RCA2 (Appendix) to remove metal and alkaline contaminants, including the embedded ions from the plasma etch, and leave the surface hydrophobic. Just prior to lithography, a layer of hexamethyldisilazane was evaporated onto the wafers. This step was found to be crucial to prevent cracks in the resist during subsequent processing. A spin coater was run at 5000 rpm to apply an approximately 1.4 μm layer of AZ5214e photoresist (MicroChemicals GmbH) to the wafers after which they were baked on a hotplate at 85 °C for one minute. The wafers were then positioned on a mask aligner with the optical mask placed on top and exposed to ultraviolet light for 13 s. After exposure the wafers were soaked in AZ 300MIF (AZ Electronic Materials) developer for 100 s. The exposure and development times were
varied widely in search of the optimal combination as they were crucial to achieve the sharp features necessary for further alignment steps. The wafer was then rinsed in distilled water to stop development and blown dry with nitrogen gas.

The e-beam evaporator was used to deposit 5 nm of chromium, which served as an adhesion layer, followed by 50 nm of gold. The system remained under vacuum for both evaporations so no oxide layer could form on the chromium. The remaining unexposed photoresist, as well as the gold on top of it, was rinsed away with acetone leaving the pattern transferred in gold on the silicon wafer. At this stage, the wafers were thoroughly cleaned by sonicating in acetone followed by IPA for 15 minutes each. This was found to be necessary in order to remove all traces of photoresist around the edges of the pattern, which was important for eventual electrical contacts. This procedure allowed for the fabrication of 20 patterned chips over the course of a half day.

**2.2 Graphene transfer**

Having fabricated the platform, the next step was to add the graphene. Both micromechanical cleavage and CVD growth were attempted,\(^2,57\) but the Scotch tape technique proved preferable as it gave more reliable single layers of graphene. Prior to transfer, it proved important to clean the wafers briefly using RCA1 to leave the surface hydrophilic. The quality of HOPG was also found to be a crucial variable and for this research the top grade (ZYA) was used (Momentive Performance, Materials Quartz, Inc).

As previously described, Scotch tape was used to remove several layers from the HOPG and then repeatedly folded on *itself* until it achieved the correct appearance, a uniform gray which was no longer shiny. Initially, the graphitic material was folded repeatedly onto clean tape resulting in very thin layers; however, high graphitic coverage
was eventually deemed preferable to the thin layers. It was pressed firmly onto a patterned wafer and left to sit for 10 minutes. The tape was removed very slowly from the wafer which was then soaked in hot acetone for 5 minutes. This served to remove most of the tape residue and the weakly surface bound graphitic sheets.

2.3 Locating and identifying graphene

To locate graphene candidates on the wafer and confirm their structure, two techniques were used. Optical microscopy was used to locate possible graphene pieces on the wafer and to accurately determine their position within the alignment grid. Raman spectroscopy was subsequently used to confirm that the graphene was single layer. Conveniently, the two instruments were coupled allowing for rapid analysis of graphene candidates.

2.3.1 Optical microscopy

Because the oxide layer on the silicon substrate was carefully chosen to maximize contrast, single layer graphene was visible optically. In early trials using a thicker 300 nm oxide layer, the graphene proved indistinguishable from tape residue and often nearly invisible, as in Figure 2.4b, and thus spectra had to be relied upon to distinguish the two. This method dramatically reduced throughput. On the 280 nm oxide, the graphene revealed itself as a very faint purple colour – distinct from the darker purple of the multi-layer and the bright blue of the tape (Figure 2.4a). The colours arise from the resonance of the optical frequencies within the cavity of silicon dioxide resulting from the silicon below and the graphene above.
Figure 2.4 (a) Optical microscopy image of a typical device platform on 280 nm SiO$_2$ after graphene transfer. Regular features include a. single layer graphene, b. multilayer graphene, c. bilayer graphene, d. gold alignment marker, e. tape residue and f. laser spot. (b) Optical image of graphene on a 300 nm oxide layer. The graphene is circled to highlight its location.

The microscope was equipped with a CCD camera so each graphene piece, once identified, was photographed relative to a particular alignment mark in order to be accurately positioned for later patterning. In a batch of 20 wafers, the majority would have 1 – 5 graphene candidates, with some containing up to 10 or 15. It was rare to have a wafer with no graphene at all. The graphene pieces were generally on the order of 5 to 40 microns in diameter.

2.3.2 Raman spectroscopy

As discussed in Chapter 1, Raman is an extremely useful tool for characterizing graphene as the spectrum is unique for single, double and multilayer graphene. Raman spectra were acquired using a Renishaw Raman Microscope equipped with three lasers – 514 nm, 633 nm and 785 nm. Although the 514 nm wavelength resulted in a more intense graphene signal, the 633 nm HeNe was used for all spectra because it warmed up faster,
easier to operate and less likely to generate fluorescence in future chemically modified samples. A 1200 lines/mm grating was used and identification spectra were taken with a 9 second exposure time at maximum laser power, approximately 5 mW. Repeated Raman spectra showed no signs of laser damage at this power.

In order to confirm the monolayer structure of a candidate graphitic material, four criteria were employed, as demonstrated in Figure 2.5: (i) the graphene G peak intensity must be smaller than the graphene 2D peak intensity; (ii) the graphene 2D peak centre must fall at or below 2640 cm\(^{-1}\); (iii) the 2D peak width must be 30 cm\(^{-1}\) or less; and (iv) the 2D peak must be fit with a single Lorentzian. Lorentzian fits are used when the lifetime of the vibration exceeds the lifetime of coherence and there is exponential vibrational population relaxation. These criteria stem from the work of Ferrari et al.\textsuperscript{13,14} who monitored the evolution of Raman spectra with number of graphene layers.

![Figure 2.5](image)

*Figure 2.5* (a) Typical Raman spectrum of graphene displaying all four characteristics of single layer graphene, (b) characteristics of the 2D peak.
In order to improve throughput in practice, generally only criteria (ii) - (iv) were employed to allowed for a short scan covering just the 2D peak area to be used for graphene identification.

2.4 Field effect transistor fabrication

In order to make electrical contact with the graphene, gold wires were added joining each end of the graphene to one of the large electrodes on the platform. By wiring the graphene to the outer pads, the device could be electrically interrogated using a probe station. The wires were created using the same e-beam writer employed in mask fabrication. This technique was necessary since each chip contained randomly distributed graphene pieces and required a unique wiring pattern.

Using the optical microscopy images and position data, wiring patterns were designed using Raith50 CAD software. These leads were written with “T” shapes at the end to maximize the chance of contacting the graphene. Although the positioning of the e-beam system was designed to be accurate down to tens of nanometers, in practice it was found that alignment could be off by as much as a few microns when operating at the millimeter scale. It was discovered that this was due to the size and stitching of the write fields. Because the wires could be as long as several millimeters, it was determined that 1000 µm write fields should be used to save time. However, the instrument was set up to work on a much smaller scale and was thus optimized for 100 µm write fields. The 1000 µm fields also tended to yield gaps in the wires at the edges of the write field. This problem was surmounted by employing a second write to add “patches” at the field edges. Eventually, it proved necessary to use the 100 µm write fields to improve alignment accuracy, at the cost of approximately 10 minutes per write.
The wafers were spin-coated with a dual-layer of PMMA of differing average molecular weights – 495 kDa and 950 kDa. The bottom layer was a roughly 350 nm layer of 6% PMMA 495 spun on at 2500 rpm while the top layer was a thinner 200 nm layer of 4% PMMA 950 spun on at 4000 rpm. The thickness of each layer is a function of both the viscosity of the polymeric solutions and the spin speeds. The wafer was baked for one minute after the first layer and five minutes after the second to set the PMMA. Although the mask required only a single layer of PMMA, early trials with the wires showed that the heat generated during the subsequent gold evaporation caused the single layer to bond to the wafer. Using two layers of PMMA eliminates this problem in two ways. First, by yielding undercut features after development – the bottom layers dissolves away more than the upper layer. As a result, the gold evaporated onto the wafer surface is kept isolated from the gold above on the e-beam resist promoting proper lift-off. Second, the lower layer of PMMA is protected from the hot gold by the upper layer and is less likely to bond to the wafer.

Initially, dose testing was carried out in order to determine the maximum speed at which wires could be written without sacrificing resolution. It was concluded that the optimal conditions were an accelerating voltage of 30 keV and a beam current of 1.3 nA, resulting in approximately 20 minute writes for an average chip. After the write, the pattern was developed by soaking for 50 s in 1:3 MIBK:IPA, rinsing with IPA and blowing dry. E-beam evaporation was used to deposit 5 nm of chromium and 100 nm of gold on the wafer. One hundred nanometers of gold was chosen in this case as it was found that the thickness of the wire had to exceed the thickness of the gold pattern or poor contact was made between the contact pads and the wires. To remove the PMMA
and excess gold after evaporation, the wafers were soaked in acetone for several hours followed by a 2 second sonication in acetone. A set of completed devices on a platform is shown in Figure 2.6b, with the red box displaying a scanning electron image of a single device. Figure 2.6a shows a schematic of device with labeled electrodes.

Figure 2.6 (a) Schematic of the graphene devices fabricated in this research. Top electrodes are 100 nm Au with 5 nm Cr for adhesion. Connection to the back gate was made using silver paint. (b) Optical image of platform holding four completed devices with an SEM image of one device.
While it was not ideal to have to sonicate the graphene devices, topographic imaging by atomic force microscopy, displayed in Figure 2.7, showed that it was crucial in order to remove all traces of PMMA from the surface of the device. The change due to sonication can be quantified by calculating the root mean squared roughness on the graphene surface which was found to be 0.025 nm before sonication and 0.012 nm afterwards.

![AFM images](a) before and (b) after 5 seconds sonication in acetone. Colour scale is identical for both images.

**Figure 2.7** Tapping AFM images of the same graphene device (a) before and (b) after 5 seconds sonication in acetone. Colour scale is identical for both images.

### 2.5 Device characterization

After fabrication, a number of characterization steps were carried out to ensure that processing had not negatively affected the graphene, to determine device quality and reproducibility and to serve as “before” measurements for comparison with future chemically modified devices. Graphene quality was tested first by a simple repeat of the Raman scan, and then more conclusively with electronic transport measurements. The samples were also imaged using an atomic force microscope (AFM) to get a measure of the step height from the silicon dioxide layer to the graphene.
2.5.1 Electronic characterization

Two separate measurements were carried out in order to extract information on the transport properties of the graphene FETs. Both were carried out in ambient conditions using a standard 3-pin probe station setup with a Keithley 4200 Source Measure Unit. The first was a simple IV curve (Figure 2.8).

![Figure 2.8 Current vs. voltage response of a typical graphene device with calculated resistance (R) and resistivity (ρ).](image)

In this measurement, a voltage is between the electrodes at either end of the graphene device (the “source” and the “drain”) while the current through the graphene is measured. The source voltage is then varied and the change in drain current is plotted. A LabView program was written to carry out this function, making the process fully automated. Graphene is an Ohmic material, meaning it obeys Ohm’s Law, \( V = IR \).
Therefore the plot of current vs. voltage is linear with the inverse of the slope giving the resistance. In this research, it was reasonable to conclude that a significant portion of the measured resistance is a result of the contacts as contact resistances have been measured from 800 – 10,000 Ω,\textsuperscript{25,58} and no recent 4-point measurements have been done to confirm or dispute this. However, the resistance calculation is used to monitor the consistency between devices. To normalize result across varying devices, the resistivity can be calculated from the resistance by estimating the size of the device and using equation 1.3. Most devices had a resistivity of between 1 and 10 kΩ with the distribution shown in Figure 2.9. As discussed in the introduction, this equation is unique to 2D materials as those with 3 dimensions must account for device area rather than width and their resistivity would be measured in units of Ω·cm.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{resistivity_histogram.png}
\caption{Histogram showing the distribution of resistivity values for fabricated graphene devices.}
\end{figure}
The second, and more informative, measurement is an FET curve (Figure 2.10). In this case a voltage is again applied at the source and a current is measured at the drain, but the source voltage is kept constant while a second voltage, applied to the back gate, is varied.

![Graph of an FET curve](image)

**Figure 2.10** Gate response of a graphene device prior to functionalization. This device had a conductivity minimum (Dirac point) at 9.6 V. Red and green lines are fits to the linear regime of the electron and hole portions of the curve, respectively. Electron mobility was calculated to be 2028 cm²/V·s and hole mobility was 2634 cm²/V·s.

In order to make good contact to the back gate, it was found that the back of the wafer had to be vigorously scratched with a diamond scribe to remove any native oxide and then glued with silver paint to a glass slide. In earlier methods, the wafer simply sat on the brass plate of the probe station, but this was determined to be too inconsistent.
The resultant curve is a “V” shape with the Dirac point, the curve minimum, falling anywhere from 9 to 27 V. As discussed in Chapter 1, pristine graphene should yield a Dirac point at 0 V, so these results suggest dopants are present on the graphene. The most likely sources of this are air and water vapour as well as the SiO₂ substrate. It has been shown previously⁵⁹ that these moieties act as p-dopants, resulting in the shift of the Dirac point towards positive voltages. Given that these FETs were stored in air and no annealing was undertaken, it was unsurprising to find the Dirac points falling at high positive voltages.

The slopes of the linear portions of the curve to the left and right of the Dirac point are related to the hole and electron mobility, respectively, by equation 1.4. Values for the mobility varied from 1000 - 2700 cm²/V∙s. In pristine graphene, the hole and electron mobility should be equal and that was generally observed in these experiments. This provides further proof of the high quality of the graphene samples. The observed mobility values were on par with many of those reported in the literature among those researchers whose focus was not on maximizing mobility.²,⁶⁰

2.5.2 Atomic force microscopy characterization

An Agilent 5500 atomic force microscope was used to gather more structural information on the graphene devices. It was operated in tapping mode with a silicon tip of radius < 10 nm (Ted Pella, TAP190-G-50) vibrating at approximately 170 kHz. In order to image the graphene devices, the approximate location of the device was found using the built-in CCD camera and then a 50 μm × 50 μm area was imaged initially at high speed. Although the graphene was not readily visible at this scan rate, it was easy to locate the gold T-shaped wires, which were 105 nm high. The scan area was then zoomed
in to the region between the electrodes and improved images were obtained using a scan speed of 0.5 or 0.25 lines per second and 512 pixels per line. Rotating the sample such that the graphene edge was perpendicular to the fast axis of the scanner aided in obtaining high contrast images. An example image of single layer graphene is shown in Figure 2.11a. The height of single layer graphene as measured by the atomic force microscope was found to be 1.3 nm as calculated from the step height profile in Figure 2.11b.

![Tapping AFM image of single layer graphene.](image)

**Figure 2.11** (a) Tapping AFM image of single layer graphene. (b) Profile of step from SiO$_2$ to graphene averaged over 128 lines.

As discussed previously, the discrepancy between this measured height and what one might expect of a single atomic layer is likely due to a gap between the silicon dioxide substrate and the graphene or an instrumental offset which was not accounted for.\textsuperscript{19,20} This was confirmed by imaging the edge of a single layer-bilayer graphene junction in which case the measured height difference was on the order of 5 Å. AFM images were processed and analyzed using Gwyddion software to flatten the image and improve contrast.
AFM analysis revealed that directly after lift-off, the graphene devices were still contaminated with some surface particulates, likely remnants of PMMA. It was found that a few seconds of sonication in acetone removed the vast majority of the contaminants and this extra step was subsequently added to the standard procedure.

2.6 Device failure analysis

Despite the presumed simplicity of graphene FET fabrication, there were in fact a number of hurdles to overcome and failure analysis became a crucial component of the research. Initially, a number of devices seemed to spontaneously stop working following gate measurements. To determine the cause, scanning electron microscopy (SEM) was employed to see if there was any visible damage to the devices. Figure 2.12 shows the resultant image of the graphene device completely shattered and the gold wires peeled away. This led to the conclusion that a wiring mistake was causing the gate voltage to be applied across the source-drain channel and rewiring was required.

![Figure 2.12 SEM image showing the consequences of applying too much voltage across a graphene device.](image)
Later, a new problem arose when the devices looked fine and appeared to be connected to the contact pads, but showed minimal conductivity. SEM, AFM and an e-beam write with contact pads wired to each other, were employed in this case to demonstrate that poor contact was arising not between the graphene and the leads, but between the leads and the large pads. The solution was to use a thicker gold layer on the wires (100 nm) than the pads (50 nm) as well as to intensify the cleaning procedure after optical lithography.

Having solved the above two problems, a new dilemma arose when devices displayed anomalous gate behaviour. Two main problems occurred when attempting to make three point measurements on the graphene devices. In some cases, there was leaking between the gate and drain. This rendered the devices essentially useless for further experimentation and often led to devices being destroyed by the high gate voltages applied. Scanning electron microscopy revealed that a particular batch of wafers seemed to have a network of cracks throughout the silicon dioxide suggesting a possible systematic cause of this failure. A second issue was difficulty in making good contact with the back gate. While it was initially thought that the wafers could simply sit on a metal surface and make contact, it was eventually found that vigorous scratching coupled with silver paint was necessary for reliable gate contact due to the native oxide on the back surface of the wafer. Figure 2.13 presents the data obtained from both difficulties with panel (a) showing the curve obtained when gate leakage was a problem and panel (b) being an example of poor gate contact.
Figure 2.13 Examples of poor gate response: (a) Leakage pathway between gate and drain, and (b) poor contact to the gate electrode.

This careful analysis of each step improved device yields from approximately 10% in the early portion of the research to 90% by the final batch of devices. Furthermore, device resistivity became more consistent in the latter half of the research, with most devices falling in the range of 1-3 kΩ.
Chapter 3

Chemical modification of graphene

Although graphene FETs are an interesting area of study in their own right, the ability to chemically functionalize the graphene surface opens up a wide variety of new applications. Because graphene consists of a single atomic layer, it is entirely surface, making it ripe for surface modifications. By choosing noncovalent modifications, one can access these new applications with minimal disruptions to the impressive transport characteristics of pristine graphene.

Chapter 3 will cover two such noncovalent modifications. In Section 3.1 and 3.2 the criteria for selecting an appropriate functionalization molecule are discussed and rubrene is selected as a suitable candidate. The previous applications of rubrene in electronic and optical devices are outlined and Section 3.3 covers the pertinent optical and electronic spectra. Section 3.4 describes the functionalization procedure and how it was monitored by Raman spectroscopy and atomic force microscopy. Section 3.5 presents the data gathered on the modified devices by Raman, polarization dependent Raman, photoluminescence spectroscopy, and atomic force microscopy. Section 3.6 offers a demonstration of site specific modification with rubrene, a methodology which can expand the applicability of this research. Lastly, Section 3.7 discusses the effects when the procedure is carried out with tetracene instead of rubrene. The results are used to further clarify the interaction between rubrene and graphene.

Although this research demonstrates only two examples of molecular modification, it is proposed that this methodology could readily be extended to a variety
of molecules in order to tailor the optical and/or electronic properties of graphene devices.

3.1 Selecting a candidate molecule for functionalization

When selecting an appropriate modifying molecule, a number of factors need to be considered. Noncovalent modification was necessary to minimize disruption of the transport properties of the underlying FET, so it was important to choose a molecule which could interact with graphene via the $\pi$, rather than the $\sigma$, system. Therefore, the primary criterion was that the candidate molecule be highly conjugated and thus able to form $\pi$-$\pi$ stacking interactions with the graphene. It was also important that the molecule be commercially available and inexpensive to make the procedure easily adoptable by other researchers in the field. Finally, it was vital that the molecule, once bound to the graphene, be readily identifiable using common techniques – Raman spectroscopy, fluorescence spectroscopy, and atomic force microscopy. Conveniently, most highly conjugated molecules have identifying optical spectra that can be used to confirm their presence as graphene has no inherent photoluminescence, provided the fluorescence is not fully quenched by the binding of the fluorophore to graphene.

3.2 Rubrene

Rubrene was selected as a promising candidate. Its structure (Figure 3.1) is four benzene rings fused in a linear fashion with four phenyl groups, one attached to either side of the centre two benzene rings.
In its lowest energy conformation, the benzene backbone is twisted with a 42° twist angle due to the presence of the side phenyl groups. The phenyl groups themselves are also rotated relative to the backbone. As desired, it is highly conjugated and fluorescent, and commercially available from Sigma Aldrich. Additionally, both its optical and electronic properties can vary based on structural conformation and these variations have been previously characterized. Aside from matching the criteria listed above, it is also an organic semiconductor with a variety of interesting optical and electronic device applications.

### 3.2.1 Rubrene electronic devices

Over the past several decades, as materials and manufacturing costs for traditional semiconductor devices have increased along with the environmental awareness of consumers, the field of organic electronics has emerged and flourished. At the forefront of this field is rubrene, which holds the distinction of having the highest field effect mobility of any organic semiconductor.
The first rubrene organic field effect transistor (OFET) was reported in 2003. It was fabricated from single crystal rubrene with a top gate separated from the rubrene channel by a parylene dielectric. This early example exhibited p-type conductivity and a field effect mobility of $0.1 - 1 \text{ cm}^2/\text{V} \cdot \text{s}$. One year later, the same group revealed a unique device structure in which a back gate was used in conjunction with air as a dielectric. This technique allowed for intrinsic device mobilities as high as $20 \text{ cm}^2/\text{V} \cdot \text{s}$. In 2006, the first ambipolar rubrene OFETs were reported based on both single crystal and thin films of rubrene. The single crystal devices displayed much higher mobilities as compared with the thin films, as would be expected. Although these mobility values seem small when compared with graphene ($\mu_{\text{electron}} > 200,000 \text{ cm}^2/\text{V} \cdot \text{s}$) and doped silicon ($\mu_{\text{electron}} > 1500 \text{ cm}^2/\text{V} \cdot \text{s}$), they represent a considerable achievement for organic electronics and have led to rubrene being broadly adopted in this field.

3.2.2 Rubrene optical devices

The major optical application of rubrene is as an emitter in organic light emitting diodes (OLEDs). OLEDs are increasingly used in flat panel displays and solid state lighting thanks to their low power consumption, high contrast and wide viewing angle, low cost and fast response. Doping of emitting layers is generally used in the fabrication of these devices to improve performance or change emission colour. Rubrene has emerged as an effective yellow-orange dopant because it possesses an unusually high photoluminescence quantum yield which can enhance efficiency and improve stability of an OLED.

A second optical application of rubrene is as a laser dye, the lasing medium of a dye laser. Because dye lasers tend to have liquid lasing media, they can be used for
broader range of wavelengths and are thus frequently used as tunable lasers. In the case of rubrene, it is again its high quantum efficiency that makes it such a useful molecule for this application. Furthermore, it is able to emit at wavelengths from 554 – 575 nm and also 585 – 600 nm, a tuning range much broader than those of other polyaromatic hydrocarbons.\textsuperscript{69}

3.3 Characterization of rubrene

In order to understand and detect the effect of the rubrene on the graphene, it was important to first fully characterize the commercial rubrene.

3.3.1 Raman spectrum

The Raman spectrum of rubrene has been well characterized with each peak assigned a particular vibration that is consistent with theoretical calculations.\textsuperscript{70} Unfortunately, many of the rubrene diagnostic peaks fall below 500 cm\textsuperscript{-1} and are either incompatible with available instrumentation or overlapped by the significant silicon peak present at 520 cm\textsuperscript{-1}. There were, however, several peaks of interest that were used for analysis in the present research. These peaks fell at 1432 cm\textsuperscript{-1}, 1519 cm\textsuperscript{-1} and 1540 cm\textsuperscript{-1} and are interpreted as follows with reference to Figure 3.2.
Figure 3.2 Rubrene molecule with carbon atoms labeled to interpret molecular vibrations corresponding to Raman peaks. Hydrogen atoms omitted for clarity.

The mode at 1432 cm\(^{-1}\) arises from an in-plane vibration where C3 and C6 vibrate vertically while C1, 2, 4 and 5 vibrate horizontally. The 1519 cm\(^{-1}\) peak occurs when C1 and C2 vibrate vertically in opposite directions while C3 and C7 while C3 vibrate vertically in concert yielding a rocking motion. The motion of C7 is much greater than that of C3. Finally, the peak at 1540 cm\(^{-1}\) is due to a horizontal vibration in which C1 and C2 approach while C2 and C3 get further apart, and vice versa. Again, this is an in-plane vibration. Although the Raman spectrum of pure rubrene proved difficult to obtain, a noisy spectrum was acquired using short (6 s) exposure time coupled with low laser power and the summation of multiple spectra. The result was found to be consistent with the single crystal spectrum found in the literature.\(^7\)
3.3.2 Absorbance and emission spectra of rubrene

The rubrene absorption spectrum (Figure 3.2) was acquired on a Cary 5 UV-Vis-NIR Spectrophotometer using a saturated solution of rubrene in hexanes. Hexanes was chosen as the solvent with an eye to future experimentation in which a solvent compatible with PMMA would be desired. Rubrene is not highly soluble in hexanes and therefore a saturated solution was the appropriate concentration for UV-Vis absorption spectrometry. The spectrum was taken from 400 to 650 nm, which eliminated the major UV absorption peak at 299 nm. The primary peaks in the spectrum were found at 459 nm, 489 nm and 523 nm.

The importance of this data was to determine which wavelength could be used to look at a Raman spectrum of rubrene on graphene without exciting fluorescence, i.e. anything greater than 550 nm, and also which wavelength would be optimal for looking at the fluorescence of rubrene on graphene, i.e. anything between 450 and 525 nm. Knowing that the Raman spectrometer was equipped with 785 nm, 633 nm and 514 nm lasers, it was decided that 514 nm would be used for fluorescence spectra while 633 nm would be used for Raman spectra.
Figure 3.3 Absorbance and emission spectra of rubrene. The absorbance spectrum was taken in hexanes solution using a UV-Vis spectrometer while the emission spectra was taken in the solid state on silicon oxide using a Raman spectrometer with 514 nm excitation. Maximum absorbance at 459, 489, and 523; and maximum emission at 580 nm.

The emission spectrum of rubrene (Figure 3.3) was taken in the solid state using the Raman spectrometer with the 514 nm laser. A solution of rubrene in hexanes was drop cast on a glass slide and a spectrum was gathered using a long exposure time with very low power. This minimized the appearance of actual Raman peaks by enabling the background fluorescence to dominate the spectrum. The result was a single broad emission peak centered at 580 nm. The relatively small range of the emission spectrum relative to absorption is a limitation of the instrument.
3.4 Modification procedure

The functionalization procedure was simple and could be easily adapted to a variety of molecules, solvents and laboratory environments, as no specialized equipment was required. A solution of red rubrene crystals and hexanes was made up in a small dedicated vial. The rubrene was not very soluble in the hexanes, and thus a saturated solution was made up each time in order to maintain consistency. Ten seconds in the ultrasonicator aided greatly in dissolution of the rubrene and yielded a bright red-orange transparent solution, with some undissolved rubrene powder remaining. A chip with one or more graphene FETs was then submerged in solution for a minimum of 18 hours, and a maximum of 24 hours. It was noted that the solution colour became decreasingly red over this time, presumably as the rubrene crystallized to the wafer surface and beaker walls.

The effect of different soaking times was investigated using Raman spectroscopy which showed the steady growth of peaks in the 1100 – 1550 cm\(^{-1}\) region of the spectrum, the strongest of which was found at 1530 cm\(^{-1}\) (Figure 3.4). Over the course of a day, the 1530 cm\(^{-1}\) peak grew steadily larger in relation to the graphene 1580 cm\(^{-1}\) G peak, eventually overtaking it after an overnight soak. Soaks over 18 hours led to no further appreciable change in the 1530 cm\(^{-1}\):1580 cm\(^{-1}\) peak ratio and it was proposed that either this time scale led to the formation of a monolayer and no further reaction occurred, or that after this time there was no further thermodynamic incentive for the rubrene remaining in solution to bind to the surface.
After being removed from the rubrene solution, the wafer was blown dry with compressed air before being placed in a solution of pure solvent for 2 more hours of soaking. Atomic force microscopy analysis showed that the soak in solvent eliminated any large pieces of rubrene that had crystallized on the wafer surface and left only the thin film of rubrene which was bound to the graphene surface (Figure 3.5).
Figure 3.5 Tapping mode AFM images of the same rubrene functionalized device (a) before and (b) after 2 hours soaking in acetone. Dashed line in (a) is a guide to highlight the edge of the graphene device.

3.5 Characterization of modified graphene

Following the functionalization procedure, the graphene-rubrene hybrid was characterized using a variety of techniques in order to confirm the presence of the rubrene and gauge its influence on the underlying graphene device. Raman and photoluminescence spectroscopy are used to study the optical properties of the modified device while atomic force microscopy was used to structurally characterize the thin film.

3.5.1 Raman spectroscopy

Raman spectra of rubrene on graphene were obtained using a 633 nm excitation source, to minimize rubrene fluorescence, and at high laser power to maximize signal intensity. It was found that after repeated spectra, the intensity of the rubrene peaks would decrease suggesting that the high power laser was damaging the rubrene film. For this reason, the power was lowered and exposure time increased in cases where multiple spectra were acquired in the same location.
Rubrene on graphene displays three distinct Raman peaks which are not present in the spectrum of graphene (Figure 3.6).

Figure 3.6 Raman spectrum of a graphene device functionalized with rubrene. Peaks circled in grey are from graphene while those circled red are attributed to the rubrene.

These peaks fall at approximately 1340 cm\(^{-1}\), 1450 cm\(^{-1}\) and 1530 cm\(^{-1}\). The peak at 1340 cm\(^{-1}\) is the most ambiguous of the three as it falls at a frequency which could correspond to a vibration\(^{70}\) in rubrene moved to slightly higher frequency due to \(\pi\)-interactions or could arise from the aforementioned graphene D peak. The D peak is only present in defected graphene or along graphene edges, but it is likely that presence of the rubrene results in defects on the graphene surface. Often, the intensity ratio of the D peak to the G peak is used as an indicator for the level of chemical modification.\(^{52}\) In this case, the ratio
before modification was 0.24 and after was 0.79 consistent with increased disorder due to the rubrene.

The peaks at 1450 cm\(^{-1}\) and 1530 cm\(^{-1}\) are concluded to arise only from the rubrene and are thought to be due to the molecular modes discussed previously, shifted to slightly higher frequency than expected due to the binding interaction. The peaks in the graphene spectrum at 1580 cm\(^{-1}\) and 2650 cm\(^{-1}\) do not shift consistently upon rubrene binding suggesting that the presence of the rubrene does not affect the phonons of the graphene in the same way the graphene affects the molecular vibrations of the rubrene.

It was also noted that, as would be predicted, no peaks other than those of silicon dioxide were observed outside the graphene devices, proving that the rubrene binds strongly to the graphene and not to the substrate. This is consistent with the model of π interactions anchoring the rubrene to the graphene, as opposed to rubrene simply crashing out of hexanes solution and coating the surface.

To investigate the ordering, or lack thereof, of rubrene on the graphene surface, a polarized Raman experiment was performed. In this experiment a waveplate was placed in the path of the excitation source and turned 20 degrees between each spectrum. The spectra were gathered over a frequency range which captured the rubrene 1450 and 1350 cm\(^{-1}\) peaks as well as the graphene G peak. The graphene G peak has been previously shown to be polarization independent and was thus used as a normalization constant in order to eliminate any polarization dependence of the optics. Both the rubrene peaks yielded polar plots which were essentially circular, with a slight decay from the first to last point (Figure 3.7a).
Figure 3.7 (a) Polar plot of the intensity of the rubrene 1530 cm$^{-1}$ peak vs. polarization angle. Peak intensity was normalized to the graphene G peak which is known to be polarization independent. (b) Polar plot of the graphene D peak vs. polarization angle normalized to the graphene G peak. The D peak is known to be polarization dependent.

The circular plots are evidence of the rubrene being disordered, at least on the scale of the excitation laser spot size which was about 1µm. The slight decay is attributed to the damage to the rubrene caused by the laser. Although the laser power was lowered to mitigate this problem, it could not be entirely avoided when taking 19 spectra in the same location.

To validate this result, the experiment was repeated using the graphene D peak. The D peak has been previously demonstrated to be polarization dependent$^{71}$ and was expected to yield a polar plot with two lobes 180° apart. This experiment was more difficult as the D peak is only present at graphene edges and thus tends to have fairly weak intensity. Nevertheless, it was clearly demonstrated that the graphene D peak did display polarization dependence using an identical experimental setup (Figure 3.7b).
Although the polar plot does not illustrate the well-defined lobes published in the literature, it is clearly distinct from the circular plot corresponding to the rubrene peaks.

3.5.2 Photoluminescence

The photoluminescence (PL) spectrum of rubrene on graphene can be a useful diagnostic tool for a number of reasons. The occurrence of PL can absolutely confirm the presence of rubrene as graphene does not fluoresce. Furthermore, the presence of PL would demonstrate a relatively weak binding between the graphene and rubrene as one would expect a strongly bound rubrene to undergo charge transfer and be quenched by the graphene as has been seen before with pyrene.\textsuperscript{45,72} Additionally, the shape of the PL spectrum can give information regarding the quality of the rubrene film. An absence of PL would be a more difficult interpretation as it could arise from an absence of rubrene or strong quenching due to the graphene. Conveniently, PL was observed from the graphene-rubrene hybrid device.

Four PL spectra were gathered and compared to better understand the graphene-rubrene interaction (Figure 3.8).
Figure 3.8 Photoluminescence spectrum of graphene (purple), rubrene on graphene after 1 day soaking time (maroon), rubrene on graphene after 4 days soaking time (green) and pure rubrene (blue). Spectra taken with 514 nm excitation source.

All were taken in the solid state using a 514 nm excitation source at low power, long exposure and with a spot size of 1 µm, allowing for the spectrum to be generated from a very specific area. The first, shown in teal in Figure 3.8, is of pure rubrene and was discussed earlier. The second, shown in purple, is of pure graphene. As expected, the baseline of this spectrum is totally flat. The two peaks observed around 560 nm and 595 nm are the G and 2D peaks of graphene, and the broad bump at 540 nm is from the silicon dioxide substrate. Interestingly, the graphene G and 2D bands are much more intense when excited with 514 nm light and this is why they show up in the PL spectrum despite the extremely low power used.
With this background data established, a PL spectrum of rubrene on graphene after 1 day of soaking, shown in maroon (Figure 3.8), was taken. This spectrum clearly displays fluorescence with two peaks in the spectrum – one at 552 nm and a second around 586 nm. These results differ from the spectrum of drop cast rubrene which had a single peak centered at 580 nm and a much greater intensity. This data is consistent with a previous study\textsuperscript{73} in which the PL spectrum of an amorphous rubrene film was shown to consist of one broad peak whereas a 90% crystalline film gave two separate peaks. In that work, the peak at lower wavelength was attributed to the amorphous material while the higher wavelength peak was thought to be from the crystalline rubrene. This suggested that in the present research there could be some crystalline character in the film of rubrene molecules, perhaps due to a ‘templating’ by the graphene; however, the ordering must be on a length scale below 1 micron or it would have been observed in the polarized Raman experiment.

A final PL spectrum, shown in green (Figure 3.8), was gathered after soaking the graphene in rubrene solution for 4 days. It should be noted that this required adding additional rubrene to the solution after the second day; it had gone essentially clear as the rubrene adsorbed to the graphene surface and crystallized out of solution. The result looked much like the drop-cast rubrene spectrum, although with lower intensity. It is thought that by adding additional rubrene to the solution, additional layers eventually formed on the rubrene surface due to rubrene-rubrene interactions. The single peak was shifted to lower energy compared with the amorphous peak suggesting a greater degree of crystallinity in the new layers.
3.5.3 Atomic force microscopy

Atomic force microscopy (AFM) is a very powerful tool in the field of surface characterization in that it allows one to measure height differences down to the angstrom length scale. To establish the thickness of the rubrene film, AFM images were acquired of the same device before and after functionalization. The images were taken at the edge of the devices because, as was proven in the Raman experiment, the rubrene exists solely on the graphene surfaces and thus by looking at the edges, the additional step height should correspond to the thickness of the rubrene layer.

The images were acquired with the instrument in tapping mode with a silicon tip and a frequency of approximately 170 kHz. As with the unfunctionalized devices, large and fast images were first gathered in order to pinpoint the correct location before increasingly small and slow images were subsequently acquired. The resulting images clearly display a difference between the modified and unmodified devices (Figure 3.9a and b), but it is useful to quantify this data by taking an average of the step edge height over 128 lines. The resultant profiles (Figure 3.9c and d) show that the rubrene film is approximately 1 nm thick.
Unfortunately, this result is a bit ambiguous as it leads to two possible conclusions regarding the morphology of the film. Previous studies have proposed that rubrene lying flat on HOPG, with its tetracene backbone parallel to the surface, has a height of approximately 0.3 nm. However, other researchers have used two-photon photoemission spectroscopy to define a monolayer of rubrene coverage on HOPG as 10 Å in thickness, without discussing the structure of the monolayer. Because rubrene’s natural inclination is to exist in a twisted conformation with the phenyl side groups rotated relative to the backbone, there needs to be a strong interaction with the surface in order to encourage a flat-lying interaction. It is possible that graphene provides such an
interaction via π-π stacking and that the observed 1 nm film is the result of 3 layers of flat-lying rubrene molecules.

A second possibility is that a monolayer of rubrene molecules is lying diagonally on the surface. The distance across a rubrene molecule, determined from its crystal structure, is ~1.7 nm. So a single layer of rubrene molecules, all lying at an angle would yield a film thickness of 1 nm. In this case the interactions would be a mix of π-π stacking (in a cross between a T and offset flat geometry) and CH-π interactions between rubrene and graphene, as well as π-π interactions between rubrene and rubrene.

This second scenario was judged the more plausible of the two given rubrene’s preferred structure, the energetically favourable conformations of π-π stacked molecules and the PL evidence already discussed suggesting that the binding is not strong between the rubrene and graphene. Previous work has shown that rubrene deposited on HOPG by vacuum sublimation adopts both planar and twisted geometry, but behaviour will not necessarily be identical in the solution deposited rubrene discussed here.

To further clarify the structure of the rubrene film and the nature of the interaction, a series of AFM images were gathered at different soaking times (Figure 3.10). After only 30 minutes of soaking, the average profile height had increased by the anticipated 1 nm and subsequent profiles showed no further step height increase. Instead, the images seemed to show a more uniform rubrene film on the surface. These results again suggest that the rubrene exists as a monolayer on the surface, although further analysis at even shorter soak times could prove more conclusive.
Figure 3.10 (a) Step-edge profiles, averaged over 128 pixels and (b) AFM images acquired of the same single layer graphene device after different times soaking in rubrene solution.

3.6 Site-specific device modification

In the manufacture of electronic components, it is often useful to modify only a portion of a device. One example of this is the fabrication of p-n junctions in which one
side must be p-doped and the other n-doped. Therefore, any chemical modification scheme can have its value greatly enhanced if it can be adapted for patterned modification.

To carry this out, an entire wafer, which supported one or more graphene devices, was coated with a dual layer of PMMA. E-beam lithography was then used to open a small window in the PMMA over a portion of a graphene FET (Figure 3.11a). The most challenging portion of this experiment was finding a solvent which would dissolve the rubrene but would not also dissolve away the PMMA. Hexanes proved amenable to the task. As with the un-patterned samples, acetone was used to wash away excess rubrene and, in this case, also dissolve away the remaining PMMA (Figure 3.11b).

To analyze the results, a Raman map scan was carried out. A series of Raman spectra, spaced 800 nm apart, were taken over the whole device – both the portion that had been exposed to rubrene and that which had been protected by the PMMA. The scans were taken in the region of the spectrum containing both the graphene G peak and the main rubrene peaks at 1450 cm\(^{-1}\) and 1530 cm\(^{-1}\), an example of which is shown in Figure 3.11c. For each spectrum a ratio was taken between the peak intensity of the rubrene 1530 cm\(^{-1}\) peak and the graphene G peak. The ratio was then plotted in a 3D plot with the X and Y axes representing position and the colour corresponding to the value of the ratio (Figure 3.11d).
Figure 3.11 Patterned chemical modification (a) Graphene FET coated in PMMA with half of the device exposed (graphene added with Photoshop as a guide for the eye). (b) Graphene FET following rubrene functionalization and removal of PMMA. Dashed lines show area of Raman map. (c) Representative Raman spectrum from the modified portion of the device. Coloured circles correspond with colours of the Raman map. (d) Raman map of the device with colour corresponding to the intensity ratio between the rubrene 1530 cm\(^{-1}\) peak and the graphene G peak.

The resultant plot clearly demonstrates the success of the experiment. The portion of the device that had been exposed to rubrene is coloured red on the plot, meaning the peak ratio is greater than one (rubrene peak > graphene peak). The unexposed side of the device is a blue colour in the plot meaning the peak ratio is less than one (graphene peak
rubrene peak). It is worth noting that the white areas are where the ratio is equal to one, but there are two distinct types of white. Outside the dotted lines are spectra taken on the silicon; in this case neither peak is present making the ratio equal to one. Conversely, within the dotted lines, both peaks are present and of equal intensity leading to a ratio of one. The success of this experiment makes this methodology much more widely applicable for complex device structures such as complementary logic gates.

3.7 Tetracene

Tetracene can be described as the ‘parent molecule’ of rubrene as it is identical in structure but lacks the four phenyl side groups (Figure 3.12).

Figure 3.12 Molecular structure of tetracene.

As a result of the missing phenyl groups, the fused benzene backbone is perfectly planar as there is no energetic reason for it to twist. It was hypothesized that the planar structure would allow it to form a stronger interaction with the graphene substrate in one of two ways. It could lie flat on the graphene, with π-stacking interactions between the tetracene and graphene keeping it anchored on the surface. This option is more likely with the tetracene than the rubrene due to its naturally planar backbone. Alternatively, it
could stack on its side with T shaped π-π interactions keeping the tetracene on the graphene and offset π-π interactions between individual tetracene molecules. By functionalizing graphene with tetracene and noting the differences in the Raman spectra and AFM images, it was hoped that more knowledge could be gained regarding the graphene-rubrene interaction. A photoluminescence study of tetracene on graphene would also have proven useful; however, upon obtaining the absorbance spectrum it became clear that the correct laser wavelength was not readily available for this experiment.

3.7.1 Raman characterization of tetracene-modified devices

Raman spectra were taken of four graphene devices before and after tetracene functionalization. A 633 nm HeNe laser was used as the excitation source and identical exposure parameters were used in each case. The spectra of the tetracene-modified devices were remarkably different than those seen for rubrene-modified devices and perhaps offer some insight into the difference in binding between rubrene and tetracene on a graphene surface.

The Raman spectra of tetracene functionalized devices showed just two peaks – the G and 2D peaks of graphene. There were no peaks visible that could be attributed to the tetracene. However, in all cases, the 2D peak of the graphene after modification was shifted towards higher wavenumber relative to the unmodified spectrum (Figure 3.13).
Figure 3.13 Effect of tetracene modification on the graphene 2D peak in the Raman spectrum. (a) 2D peak shifts to higher wavenumber upon functionalization. (b) Similar behavior was observed in all samples.

This is consistent with what is seen in the spectrum of bilayer graphene, with the exception of the division into four convoluted peaks. This data may suggest that the tetracene molecules form a much stronger bond to the graphene than does the rubrene, essentially acting as another layer on the surface akin to a second graphene layer. It is therefore proposed that the tetracene lies flat on the graphene surface with π-π interactions being the primary source of its stability. It is unsurprising that the peak splitting which is characteristic of double layer graphene is not observed as graphene and tetracene have wholly different bandstructures.

This data provides some evidence that the rubrene is not lying flat on the graphene surface because if it were, this sort of peak shift would also have been present in the Raman spectra of the rubrene devices. It is thus postulated that indeed the twisted backbone and phenyl side groups prevent the rubrene molecules from interacting more strongly with the graphene surface.
3.7.2 Atomic force microscopy of tetracene-modified devices

Atomic force microscopy was used to support the deductions made based on the Raman experiment. A piece of single layer graphene which had been functionalized with tetracene was imaged with the AFM microscope using tapping mode conditions identical to those of the analogous rubrene experiment. It was found that the tetracene forms a layer approximately 5 Å thick on the graphene surface (Figure 3.13). This is identical to the step height measured from single to double layer graphene. These results serve as further evidence for the flat-lying tetracene structure proposed above as well as supporting the theory that the twisted backbone and phenyl side groups of the rubrene prevent it from adopting a similar interaction.
Figure 3.13 AFM analysis of a tetracene-functionalized single layer graphene device: (a) comparison of step height profile between modified (orange) and unmodified (black) devices; (b) AFM image of unmodified single layer graphene; (c) AFM image of single layer graphene functionalized with tetracene. Colour scale applies to both.
Chapter 4

Electronic characterization of modified devices

With the tailoring of device characteristics being a major driving force behind research into chemically modified graphene, it was important that the rubrene-functionalized devices be fully electronically characterized. Understanding the modified device characteristics can give insight into both the mechanism of rubrene binding as well as the potential applications of the technique. For this reason, this chapter is broken down into three sections so the information gleaned from each type of measurement can be carefully analyzed. The data presented in this section stems from seven devices, all of which performed in a consistent manner.

In Section 4.1, two point current-voltage measurements are presented which display an increasing conductivity upon rubrene functionalization. To clarify the mechanism behind this observed increase, three point measurements were carried out and are discussed in Section 4.2. Similar measurements, covered in Section 4.3, were then conducted to determine the influence of different rubrene soaking times on device electronic characteristics. Lastly, Section 4.4 offers some preliminary data suggesting that the modified devices possess photodetection capabilities.

4.1 Two point characterization

The two point measurement, as previously discussed, is simply monitoring the change in current at the drain electrode while the voltage is varied at the source electrode. Graphene being an Ohmic material, a linear response is predicted from equation 1.2 as was indeed observed for both graphene and graphene-rubrene devices (Figure 4.1), but in
the case of the hybrid devices, all seven demonstrated a higher conductivity after functionalization (Table 4.1). Resistivity was calculated for each device from equation 1.3. Conductivity ($\sigma$) is simply the inverse of resistivity.

$$\sigma = \frac{1}{\rho} \quad (4.1)$$

Conductivity can equivalently be described by the equation

$$\sigma = ne\mu \quad (4.2)$$

where $n$ is the charge carrier density, $e$ is the elementary charge and $\mu$ is the mobility.

From this equation, it can be seen that an increase in conductivity can result from two distinct mechanisms – either an increase in the number of charge carriers or an increase in the mobility. In the context of the current experiment, the former would be due to a charge transfer from the rubrene to the graphene and the latter would occur if the rubrene acted to remove scattering sites from the graphene or reduce their cross-section. The two point measurement cannot distinguish between these mechanisms and thus a three point gate measurement is required.

An alternative explanation for the increased conductivity could be additional pathways for electron travel through the rubrene. However, previous work on rubrene single crystal transistors shows that under the conditions of this experiment ($V_{SD} = 100$ mV and $V_{GS} = 0$ V), the current through rubrene is on the order of picoamps. Rubrene polycrystalline thin film transistors, with a thickness of 80 nm, have shown conductivity several orders of magnitude poorer than their single crystal counterparts. Therefore it is concluded that the primarily amorphous 1 nm thick rubrene
film present here likely does not provide a pathway which would contribute significantly to the observed conductivity increase.

Figure 4.1 Two point measurement showing the increase in conductivity after rubrene functionalization.

4.2 Three point characterization

The three point FET characterization (Keithley SMU 4200) requires that the current again be measured at the drain, but the source voltage is held constant. Instead, the gate voltage is varied, which changes the carrier concentration in the graphene channel. To distinguish between the mechanisms above, one observes the shape of this curve. An increase in mobility (decrease in scattering) would display as an increase in the slope of the curve on either side of the minimum; an increase in charge carriers would appear as a shift in the location of the Dirac point, the minimum of the curve.

The data for all seven devices showed a shift in the Dirac point towards greater positive voltages as well as a moderate decrease in the slope (Figure 4.2a).
Figure 4.2 (a) FET measurement of a graphene device before and after rubrene functionalization. (b) control measurement in which a graphene device is soaked in hexanes without rubrene.

Therefore, it was concluded that the increased conductivity stemmed from an increase in charge carriers rather than an increase in mobility. An instrumental limitation prevented the gate voltage from being swept higher than 40 V. The result of this limitation was that an actual minimum current was only observed for two of the seven devices, those corresponding to the devices with the original Dirac point at the lowest positive voltages (8 - 9 V). The observed shift in the Dirac point for these devices was approximately 25 V which, if consistent across all devices, suggests that the minima of the remaining five should fall somewhere between 40 and 60 V. Despite this limitation, hole mobilities could still be calculated, using equation 1.4, for all seven devices (Figure 4.3) and conclusions drawn from the data.

By rearranging equation 4.1, the charge carrier density can be calculated,

\[ n = \frac{\sigma}{e\mu} \quad (4.3) \]

which is necessary to confirm the validity of the results. If indeed a charge transfer mechanism is responsible for the observed increase in conductivity, the charge carrier
density should increase upon functionalization with rubrene, and this increase should be sufficient to overcome the decrease in mobility. This was observed in all devices. The results can then be independently verified using a different equation for charge density,

\[ n = \frac{\varepsilon_{SiO_2} \varepsilon_0 V_{DP}}{te} \]  

where \( \varepsilon_0 \) is the permittivity of free space, \( \varepsilon_{SiO_2} \) is the relative permittivity of the silicon dioxide, \( V_{DP} \) is the Dirac point voltage, and \( t \) is the oxide thickness. By rearranging this equation and solving for \( V_{DP} \), a prediction of the Dirac point voltage is obtained based on the charge carrier density obtained from equation 4.3. This value can then be compared with the observed Dirac point. These calculations were carried out for all seven devices with the results presented in Table 4.1. Although not every Dirac point was calculated with a high level of accuracy, all the calculations predict a shift in Dirac point from a positive voltage to a higher positive voltage.

The discrepancy between the observed and calculated values of the Dirac point could stem from a number of reasons. The first to note is that the number of charge carriers calculated from the conductivity as determined by the IV measurement should not necessarily be equivalent to that calculated from the Dirac point using the parallel plate capacitor equation. This is a result of the former equation giving only the concentration of mobile carriers while the latter also takes fixed charges into account. Calculating the two values of \( n \) separately, it can be seen that the number of charge carriers derived from the location of the Dirac point is greater in 6 of the 7 cases. Fixed charges are likely present in defects, as well as on the rubrene molecules and in the silicon dioxide substrate.
Additionally, following binding, the rubrene exists in a negatively charged state having accepted electrons from the graphene. In this state, the rubrene molecules themselves can act as gating agents on the graphene surface. It is difficult to quantify the extent of this gating, but given graphene’s monolayer structure and the proximity of the rubrene to the surface it seems likely that this too could influence the position of the Dirac point without altering the number of mobile charge carriers. This is consistent with the observed Dirac points for functionalized devices falling at consistently higher positive voltages than the calculated Dirac points.

Finally, the contact resistance must be taken into account. As previously discussed, contact resistance is thought to contribute significantly to the overall resistance of these FETs. Therefore, the number of charge carriers as calculated from the conductivity may be misleading. An estimate of contact resistivity may be obtained by calculating charge carrier density using the capacitor model and then using this value to calculate the conductivity, and subsequently, the resistivity. A comparison between calculated and measured resistivity shows that the calculated result is lower than the measured result in 6 of 7 devices. The difference is on the order of 500 – 2500 Ω for pristine graphene and 0 – 2000 Ω for rubrene-graphene hybrids. These results suggest that contacts may also be affected by the presence of the rubrene, an unsurprising conclusion. However, at present it is difficult to separate the effects of contact resistivity from those of the mechanisms discussed in the preceding two paragraphs.
Table 4.1 Calculation of electronic properties of unmodified and rubrene-functionalized (pink background) graphene devices.

<table>
<thead>
<tr>
<th></th>
<th>Device 1</th>
<th>Device 2</th>
<th>Device 3</th>
<th>Device 4</th>
<th>Device 5</th>
<th>Device 6</th>
<th>Device 7</th>
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<tr>
<td>$\sigma \left(10^{-4} \ \Omega^{-1}\right)$</td>
<td>1.99</td>
<td>1.65</td>
<td>3.96</td>
<td>2.47</td>
<td>3.30</td>
<td>3.35</td>
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<tr>
<td></td>
<td>2.29</td>
<td>2.08</td>
<td>4.39</td>
<td>4.39</td>
<td>3.36</td>
<td>5.91</td>
<td>6.52</td>
</tr>
<tr>
<td>$\mu \left(10^{4} \ \text{cm}^2/\text{V} \cdot \text{s}\right)$</td>
<td>1.49</td>
<td>1.49</td>
<td>2.53</td>
<td>2.55</td>
<td>1.86</td>
<td>4.59</td>
<td>3.34</td>
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<td></td>
<td>0.875</td>
<td>0.809</td>
<td>1.08</td>
<td>0.873</td>
<td>0.807</td>
<td>2.45</td>
<td>1.81</td>
</tr>
<tr>
<td>$n \left(10^{11}/\text{cm}^2\right)$</td>
<td>8.36</td>
<td>6.88</td>
<td>9.38</td>
<td>4.82</td>
<td>11.1</td>
<td>4.56</td>
<td>6.05</td>
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<tr>
<td></td>
<td>16.3</td>
<td>16.0</td>
<td>25.4</td>
<td>17.7</td>
<td>26.0</td>
<td>15.1</td>
<td>22.4</td>
</tr>
<tr>
<td>Observed Dirac point (V)</td>
<td>16</td>
<td>16</td>
<td>10</td>
<td>23</td>
<td>21</td>
<td>8</td>
<td>12</td>
</tr>
<tr>
<td></td>
<td>&gt;40</td>
<td>&gt;40</td>
<td>34</td>
<td>&gt;40</td>
<td>&gt;40</td>
<td>33</td>
<td>38</td>
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<tr>
<td>Calculated Dirac point (V)</td>
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<td>9</td>
<td>12</td>
<td>6</td>
<td>14</td>
<td>6</td>
<td>8</td>
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<td>33</td>
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<td>20</td>
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The data clearly supports a charge transfer mechanism in which the rubrene acts as a hole dopant on the graphene. A control measurement (Figure 4.2b) was also conducted in which a graphene device was soaked in only hexanes for 24 hours. The result was a slight (2 V) shift in the Dirac point towards higher voltage as well as a minor decrease in conductivity and increase in mobility. All changes in transport properties were within the error expected when measuring a device repeatedly. These small sources of error arise for a variety of reasons including the shifting position of the contact pins and graphene’s strong sensitivity to environmental contaminants.

Two mechanisms have been developed to explain transport changes associated with the chemical doping of graphene. They have been termed electronic and
electrochemical. In the electronic mechanism, usually that ascribed to large-molecule dopants, the energies of the HOMO and LUMO of the molecule relative to the Fermi level of the graphene dictate the charge transfer. In the electrochemical model, redox reactions of graphene and adsorbates occurring in aqueous layers above and below the graphene make up the primary mechanism. This is the mechanism thought to be in action for small gaseous molecules such as NO$_2$ and NH$_3$. The main experimental difference between the two is that the former leads to a decrease in carrier mobility while the latter does not. In the electronic version, mobility decrease is observed due to Coulomb scattering whereas in the redox case, the reactions occur in an aqueous layer allowing charge transfer to the graphene without the addition of scattering sites.

The observed mobility decrease leads to the conclusion that it is the electronic mechanism in action in the present work. However, Schedin and coworkers$^{77}$ have also stated that unavoidable contaminants on the graphene surface, such as e-beam resist remnants, may also play a role – acting as adsorption sites and/or intermediaries in charge transfer and further complicating the scenario.

4.3 Change in transport as a function of soaking time

The effect of different times soaking in rubrene solution on the transport characteristics of the devices was measured in much the same way as with Raman and AFM. A single device was pulled out of solution after 30, 90, 180, 300 and 1380 minutes and both two and three point measurements were carried out (Figure 4.3).
Figure 4.3 Transport data as a function of soak time: (a) IV curves showing an increase in conductivity over time, and (b) FET curves showing a decrease in mobility and increase in charge carriers over time.

Similar to the AFM, the most dramatic change was seen after 30 minutes, with an approximately 17 V shift in the Dirac point towards higher positive voltage, a 40% increase in conductance and a 24% decrease in mobility. After longer times, the conductance continued to increase, but by lesser amounts with an eventual saturated increase after 23 hours of 61%. Likewise, the Dirac point continued to shift to the right, although the final two measurements at 300 and 1380 minutes had essentially identical points. The total shift was 24 V corresponding to an increase of $1.2 \times 10^{12}$ carriers/cm$^2$. 
Using this value for carrier density, an estimate can be made for the number of holes transferred per rubrene molecule assuming a monolayer coverage. Because the value depends strongly on rubrene packing density, it was calculated using two alternatives corresponding to flat-lying and standing rubrene to give an upper and lower bound for carrier transfer. In the case of flat-lying rubrene, it has been shown\textsuperscript{78} to close-pack on a gold surface at a coverage of 0.5-0.6 molecules/nm\textsuperscript{2}. This yields an upper bound for carrier transfer of 0.024-0.020 holes per rubrene molecule.

To determine the packing density of the vertically bound rubrene, the packing density of a rubrene crystal was used, recognizing that this would likely over-estimate the number of rubrene molecules on the surface. The crystalline packing density of rubrene has been reported\textsuperscript{79} as 2.2 molecules/nm\textsuperscript{2}, giving a lower bound for carrier transfer of 0.0055 holes per rubrene molecule. Because the photoluminescence spectra demonstrated that the rubrene possessed partial crystalline character, it is proposed that the true charge transfer per molecule falls within this range. The relatively small values calculated are consistent with the lack of quenching in the PL spectrum and the theory that the rubrene is weakly bound to the graphene surface.

The mobility continued to drop gradually as a function of soaking time, although again the later measurements had approximately the same value. Although these results seem to suggest a trend, the changes in mobility (and conductivity) as a function of soak time are so small that it cannot be conclusively stated that they are indeed decreasing (increasing) over time. What can be concluded is that the majority of the transport changes occur quite rapidly, after 30 to 90 minutes of soaking time. These results suggest the importance of repeating the measurements using shorter soak times. Previous research
into using graphene FETs as gas molecule detectors have shown that graphene transport properties can change extremely rapidly on exposure to dopants. This is unsurprising given that graphene is a single atomic layer and is thus highly susceptible to the effects of surface modification.\textsuperscript{77}

4.4 Modified graphene devices as photodetectors

Preliminary results in this area were obtained by affixing a green laser pointer inside the probe station and switching it on and off by hand while monitoring the current. The measurements showed promise with a moderate increase in current observed upon illumination. However, the high level of background noise and poor reproducibility left the results subject to doubt.

To improve upon the measurement, the laser pointer was affixed to a support with a chopper placed between the laser and modified graphene sample. The laser power at the sample was measured and found to be 21 mW. The chopper frequency was then used as reference for a lock-in amplifier (Signal Recovery 7265) which measured only the change in current as a result of illumination (Figure 3.14). By adding the chopper and the lock-in, the noise in the measurement was substantially reduced; and by affixing the laser to a support and setting up the measurement on a laser table rather than in a probe station, reproducibility issues were eliminated. The current was seen to increase by approximately 13 pA upon illumination and to do so reproducibly as the light was repeatedly turned on and off.
Figure 4.4 Photoelectric response of the chemically modified graphene FETs when excited with a 532 nm laser. A green background shows the data points for which the laser was on.

It is hypothesized that the laser radiation, which falls within the absorbance region of rubrene, excited an electron from the HOMO to the LUMO of the rubrene molecules. Following excitation, the hole in the HOMO could then drop into the valence band of the p-doped graphene generating the increase in current. This mechanism offers an advantage over using pristine graphene as a photodetector because the fluorescence lifetime of rubrene is on the order of 10 ns, three orders of magnitude higher than that of graphene. Several other experiments could further clarify the mechanism at work. Most importantly, a measurement of the gate response to laser excitation; a shift of the Dirac point to the left would be consistent with the transfer of electrons into the graphene.

Rough calculations can be done to determine the charge transfer taking place upon illumination, although without knowing the change in mobility, the value is simply an estimate. If a monolayer of coverage is assumed with a rubrene packing density of
2.2 nm$^2$ – 0.5 nm$^2$ on a device measuring 3 × 7 µm (2.1 × 10$^7$ nm$^2$), then there are 4.6 × 10$^7$ – 1.1 × 10$^7$ rubrene molecules on the device. A current increase of 13 pA corresponds to an increase of 8.1 × 10$^6$ carriers/s. Therefore, the estimated charge transfer per rubrene molecule is 0.18 - 0.74 holes/s.

A control measurement was also conducted in which a red 650 nm laser of roughly equivalent power (23 mW) was used as the excitation source (Figure 4.5). Although the device still showed a photoresponse, it was substantially lower than that observed with the green laser. The observed response is potentially due to the inherent photodetection of graphene devices. It is crucial that a second control, in which an unfunctionalized graphene device is tested with these two excitation sources, be conducted in order to determine the role of rubrene in the photodetection.

![Figure 4.5](image-url)

*Figure 4.5* Photoresponse of a rubrene-functionalized graphene device at two different wavelengths. Green light falls within the absorption spectrum of rubrene while red does not.
Chapter 5

Summary, conclusions and future work

Chapter five serves to emphasize the important lessons learned from this research and to place it in context within the field of graphene electronics. It begins, in Section 5.1, with a summary of the important results covered in chapters two, three and four concerning the fabrication of graphene field effect transistors and the influence of rubrene on these devices. The summary will touch on the rubrene film morphology, the influence of rubrene on electronic transport and the photodetection properties it bestows. Section 5.2 will consist of a brief discussion of potential future directions for this project and proposals for upcoming experiments. Finally, in Section 5.3, conclusions will be drawn regarding the novelty of this research and its utility in the broader scientific community.

5.1 Summary of important conclusions

5.1.1 Overview of graphene FET fabrication

One of the early lessons learned in this research was the importance of starting with the right platform. Crucially, the silicon dioxide layer must be of a very specific thickness in order to both see the graphene and distinguish it from other features on the wafer. An oxide coating of 280 nm was deemed optimal while on 300 nm oxide, just a 7% difference, graphene was essentially invisible. The patterning of the wafers was also of critical importance. In order to make use of the micromechanical cleavage technique for graphene transfer, which yields randomly distributed graphene pieces, an alignment grid was necessary. In order to then contact these graphene pieces using e-beam lithography, a second set of alignment marks was of equal importance. Additionally, the
spacing of the alignment grid and the thickness of gold from which it was fabricated were important parameters, with wider spacing and ‘thinner’ alignment marks being preferred.

The utility of Raman spectroscopy\textsuperscript{13,14} for graphene identification was a second important theme throughout this research as there was no other tool available (and indeed there are few other tools in existence) to conclusively determine number of layers. While atomic force microscopy can be useful in that regard, an unknown instrumental offset\textsuperscript{20} requires that calibrations be carried out before it can be applied to graphene. Furthermore, the slow operation of an AFM would preclude it from use in locating randomly distributed single layers over large areas. In contrast, the Raman spectrometer coupled with an optical microscope allowed the graphene to be visually located and spectroscopically confirmed in a matter of seconds.

Although back-gated FET fabrication is now a well-established procedure for graphene, and was indeed the first graphene device constructed in 2004,\textsuperscript{2} there was still much to be learned when carrying it out. Being just an atom thick, graphene is not a forgiving material and a number of parameters had to be varied to achieve success. The first such parameter was the height of the contact wires, as it was found that these must exceed the height of the contact pads in order to make reliable electronic connections.

A second widely tuned parameter was the cleaning methodology at each step. It was a constant balancing act to minimize surface contaminants – which would certainly skew the results of a surface functionalization project – without harming the graphene itself. It was determined using AFM that a few seconds of sonication after the final e-beam write, while not ideal for all devices, was necessary to ensure a relatively pristine graphene surface.
Once fabricated, the devices were electrically characterized using two point source-drain measurements as well as three terminal transistor experiments. It was observed that all devices behaved in an Ohmic fashion and had similar values of resistivity on the order of $1 – 10 \, \text{k}\Omega$, which is consistent with what has been reported in the literature.$^{2,81}$ The three point measurements allowed for the observation of the current minimum – Dirac point – as well as an estimation of the mobility. Here too, results were comparable with those in the literature$^{48}$ with Dirac points falling between 9 and 26 V and carrier mobilities ranging from 1500 to 3000 cm$^2$/V·s. The large deviation from the expected value of zero for the Dirac point in unmodified graphene has been regularly explained as being a consequence of surface doping by air and water vapor as well as the SiO$_2$ substrate.$^{2,49}$ The mobility values, while much lower than the maximum reported graphene mobility, are on par with what has been reported in other groups in which optimizing mobility is not a priority.$^{60}$ Finding a reliable procedure for annealing would likely both improve the mobility and shift the Dirac point toward zero.

5.1.2 Characterization of rubrene film morphology

Chapter three presented a wealth of data from different instruments, which each offering additional clues toward understanding the rubrene morphology and its interaction with a graphene substrate. Raman spectroscopy was the first technique utilized and one of the most fruitful as it provided a number of insights. First, Raman spectra were taken over time, revealing that binding of rubrene to graphene occurs over the course of approximately 24 hours. The final spectrum showed three new peaks attributable to the presence of the rubrene. One, the graphene D peak, emerges only when defects are present and suggests that the rubrene acts as a defect on the graphene surface.
The other two are thought to arise from molecular vibrations of rubrene, both of which were shifted to higher wavenumber as compared with pure rubrene. The graphene peaks, in comparison, did not shift at all suggesting that the binding was insufficiently strong to influence the graphene phonons. A polarized Raman experiment was also conducted to investigate potential ordering of the rubrene film. It revealed no polarization dependence and led to the conclusion that the rubrene molecules were unordered on the scale of the laser spot (1 µm).

Photoluminescence spectra were also enlightening. The presence of PL was itself quite revealing as it both established the presence of the rubrene on the graphene surface and confirmed the weak binding theory first proposed due to the lack of Raman shift in the graphene G and 2D peaks. A stronger interaction would be expected to result in the quenching of rubrene fluorescence. The PL spectrum had two peaks, a deviation from that of rubrene drop-cast on a silicon wafer, which had a single peak. This suggested a degree of crystallinity in the rubrene structure, although not one detectable by polarized Raman spectroscopy.

Atomic force microscopy was used to aid in clarification of the rubrene film structure. The film was found to be approximately 1 nm in thickness, consistent with either three ‘flat’ monolayers or a single ‘tilted’ monolayer. It was proposed that the ‘tilted’ monolayer was a more reasonable conclusion for three reasons. First, the fact that the Raman spectrum ceases changing after a day of soaking is suggestive of the formation of a monolayer; otherwise, one would anticipate the intensity of the rubrene peaks to the go on increasing relative to the graphene peaks as additional layers continued to form. Second, the structure of rubrene with both rotated phenyl side arms and a twisted
tetracene backbone is energetically disinclined to flatten to a surface if another pathway is possible. It has been shown that a T-shape is a favourable geometry for π-π interactions and this is potentially the arrangement adopted here. Lastly, previous work looking at rubrene sublimed on HOPG under vacuum using two-photon photoemission spectroscopy defined 10 Å as a monolayer of coverage.

A trial was also conducted to determine the feasibility of patterning rubrene molecules over the graphene surface. Raman mapping confirmed the success of this experiment. This achievement opens the technique up to a much broader range of applications including complex devices like complementary logic gates.

Experiments with tetracene allowed for further insights on the graphene-rubrene interaction. The Raman spectrum was particularly intriguing as it displayed the opposite behavior of the rubrene case. No new peaks emerged as a result of the tetracene functionalization, but the graphene 2D peak shifted consistently toward higher wavenumber, which is the same shift seen when a second graphitic layer is present. This has also been seen in previous experiments with graphene which have shown that aromatic p-dopants yield an upshift in the graphene 2D peak. This suggests that the tetracene is forming a much stronger interaction with the graphene.

These results were supported by AFM measurements in which the tetracene film thickness was measured to be just 0.5 nm – the same step height observed for single to double layer graphene. It is proposed that without the side phenyl groups and resultant backbone twist, the tetracene lies flat on the graphene surface. These results further support the postulated binding mechanism of the rubrene molecules.
5.1.3 Electronic characteristics of rubrene-graphene devices

In Chapter 4, the electronic characteristics of the rubrene modified devices were investigated by two and three point measurements and found to behave consistently across all devices. Functionalization with rubrene was found to increase the device conductivity, decrease the mobility and increase the number of charge carriers. The increase in charge carriers was sufficiently large to overcome the decreased mobility leading to the overall conductivity increase. A shift in the Dirac point towards higher positive voltages demonstrates that the rubrene acts as a hole dopant on the graphene with roughly $1.2 \times 10^{12}$ carriers/cm$^2$ transferred.

Investigation of these phenomena as a function of soaking time demonstrated that the majority of these electronic changes occur rapidly, on a time scale of less than 30 minutes. Further work is needed looking at even shorter time scales.

Preliminary results also suggest that rubrene functionalization allows the graphene devices to behave as photodetectors whose performance is enhanced when excited with a laser of wavelength within the absorption region of the rubrene molecule (450 - 550 nm). Rough calculations suggest that on the order of 0.18 – 0.74 holes/rubrene molecule is transferred upon illumination. However, more control measurements must be done to validate this conclusion.

5.2 Future work

Because one of the goals of this project was to provide a basis for other researchers to jump off from, there are a number of directions in which future work could progress. Listed below are just a few possibilities, either direct extensions of the original project or collaborations with another researcher in the lab.
To complete the project at hand, further experimentation needs to be done to clarify the photodetection properties of the rubrene-graphene hybrid. First, a control using unfunctionalized graphene to confirm that the photoresponse is indeed due to charge transfer from the rubrene. Second, photodetection can be measured as a function of wavelength, which should correlate with the absorption spectrum of rubrene. Photodetection could also be investigated as a function of laser power and gate voltage which would shed light on the mechanism involved in the observed current increase upon illumination.

An obvious continuation of this research is to begin functionalizing graphene with other molecules. There would be two purposes for this, either to learn more about graphene’s ability to interact with molecules or to graft new and more interesting functionality to the graphene. In the former case, molecules that consist of rubrene’s substructure, but which have been modified with electron donating and withdrawing groups on either the phenyl substituents or the tetracene backbone could be really interesting in that they would allow for a greater understanding of the mechanism behind graphene doping.\textsuperscript{49,83} Although the functionalization procedure is already established, the challenge in this work would be in the synthesis of the rubrene derivatives\textsuperscript{84,85} and analysis of the resultant data.

In the latter example, an option would be functionalization with metallorganic porphyrins which have already been shown to install photodetection properties in carbon nanotubes. Another possibility would be functionalization with magnetic molecules and analysis via magnetic force microscopy and magneto transport studies. An additional experiment which may provide interesting and useful results would be to functionalize
graphene with a strongly fluorescent molecule tethered to rubrene or tetracene. By not attaching the fluorophore directly to the graphene, presumably the fluorescence would remain unquenched. The modified graphene could then be imaged using a fluorescence microscope, rather than an optical microscope. This would allow for graphene to be visible on arbitrary substrates without the limitation of the necessary oxide thickness. A similar, but reverse, experiment has already been done using graphene oxide to quench fluorescence and thus reveal its position. It was found that by analysing brightness of the image, the number of graphene layers could be counted in this way.\textsuperscript{86}

Another straightforward step would be the investigation of the electronic properties of the tetracene modified graphene devices. Having already concluded by AFM imaging and Raman spectroscopy that the tetracene forms a stronger bond with the graphene, it would be interesting to see how this translates into its dopant properties. The ability to perform photoluminescence spectroscopy on these devices could also be beneficial because quenching of the tetracene fluorescence by the graphene would provide further support to the theory of weakly bound rubrene.

A more complex, but potentially more informative experiment would be to conduct photoelectron spectroscopy on the rubrene-modified graphene devices. It has already been shown that applying this technique to a vacuum-sublimed thin film of rubrene on HOPG can yield both the binding energy and the conformation of the rubrene molecules on the surface.\textsuperscript{62} This is possible as twisted rubrene and planar rubrene exhibit slightly different binding energies. Figure 5.1 shows the calculated energy differences between neutral and ionized rubrene in the planar and twisted conformation. The authors of the study used high resolution angle resolved ultraviolet photoelectron spectroscopy to
capture details of the rubrene molecules’ orientation; however, even the comparatively simple x-ray photoelectron spectroscopy could also provide useful information regarding binding energy.

Figure 5.1 Schematic of the energy differences of neutral and ionized rubrene in the planar (green) and twisted (blue) conformation. Reprinted with permission from reference 62.

Several collaborations could also be envisioned taking advantage of the focused ion beam system skills of co-worker Daniel Collins. As he has already had some success fabricating photonic cavities, which select and intensify particular wavelengths, a next step would be the placement of a cavity on a graphene-rubrene device. This could potentially yield significantly improved photodetection results as well as making photodetection possible with white light, provided the cavity was constructed in such a way as to allow only green light to pass through.
5.3 Relevance of this research to the broader scientific community

An important component of any scientific research is taking a step back to contemplate the novel aspects of the project and how they contribute to advancements in the field. In this research, noncovalent binding of large aromatic molecules to graphene was investigated. In most of the previous examples of noncovalent binding to graphene, the molecules used were small (NO$_2$, NH$_2$, O$_2$, H$_2$O)\textsuperscript{35} and served only to alter the electronic properties of the graphene by shifting the Dirac point or opening a band gap.

Examples in which graphene was noncovalently functionalized with larger molecules, are much rarer\textsuperscript{45-47,52}, are generally undertaken in solution, and usually rely on reduced graphene oxide – a more readily available material, but one of poorer electronic quality. This research provides the one of very few examples\textsuperscript{48,49} in which a graphene field effect transistor is noncovalently functionalized with a large aromatic molecule allowing for a thorough electronic characterization of the system. Further, this is the first investigation in which a non-planar molecule is used for functionalization of graphene, suggesting that more than just π-π interactions can be relied upon for the fabrication of graphene-molecule hybrids.

This research is useful to the broader scientific community in that it opens up a wide new selection of molecules for noncovalent graphene functionalization and thus allows for the creation of novel hybrid electronic devices. One example was demonstrated in the present research in the form of a graphene-rubrene photodetector of which the preliminary results showed considerable promise. By using a chemically functionalized graphene device as a photodetector, one avoids a pitfall of unmodified graphene photodetectors which is the rapid exciton recombination\textsuperscript{51} and gains a
substantial advantage in being able to tailor the optical response. Unlike small molecule functionalization which only adjusts the electronic properties, using large molecules provides an opportunity to graft new optical, magnetic or other properties onto the graphene surface, while still maintaining, to a large degree, its remarkable electronic performance.
Bibliography


Appendix: Cleaning procedures

A.1 Piranha clean

- 1 part 30% hydrogen peroxide
- 4 parts concentrated sulfuric acid
- Use 100 mL total volume (20 mL : 80 mL)

All done in a fume hood:

The $\text{H}_2\text{O}_2$ is put in a beaker to which the sulfuric acid is added. Samples are added to the mixture and left for 15 to 20 minutes. Upon removal, samples are rinsed with deionized water to remove the Piranha solution.

Piranha clean is used to remove organics from substrate surfaces and can also dissolve through metals.

A.2 RCA1 clean

- 5 parts water
- 1 part 30% hydrogen peroxide
- 1 part ammonium hydroxide
- Use 140 mL total volume (100 mL : 20 mL : 20 mL)

In a fume hood, the water is put in a beaker and heated to 60 °C on a hotplate. The $\text{NH}_4\text{OH}$ is then added followed by the $\text{H}_2\text{O}_2$. The reaction is exothermic and will bring the temperature up to ~ 70 °C. At this point the samples are added and left for 10 minutes. Upon removal, samples are rinsed with deionized water to remove the RCA1 solution.

RCA1 clean removes organics and dust and leaves the surface hydrophilic.

A.3 RCA2 clean

- 6 parts water
- 1 part 30% hydrogen peroxide
- 1 part concentrated hydrochloric acid
• Use 160 mL total volume (120 mL : 20 mL : 20 mL)

In a fume hood, the water is put in a beaker and heated to 60 °C on a hotplate. The HCl is then added followed by the H₂O₂. The reaction is exothermic and will bring the temperature up to ~ 70 °C. At this point the samples are added and left for 2 minutes. Upon removal, samples are rinsed with deionized water to remove the RCA2 solution. RCA2 clean removes organics and dust and leaves the surface hydrophilic.