Modification of the electronic properties of fluorinated epitaxial graphene with an electric bias

Kelly Denise McAllister
Clark Atlanta University

Follow this and additional works at: http://digitalcommons.auctr.edu/dissertations
Part of the Physics Commons

Recommended Citation

This Thesis is brought to you for free and open access by DigitalCommons@Robert W. Woodruff Library, Atlanta University Center. It has been accepted for inclusion in ETD Collection for AUC Robert W. Woodruff Library by an authorized administrator of DigitalCommons@Robert W. Woodruff Library, Atlanta University Center. For more information, please contact cwiseman@aubc.edu.
MODIFICATIONS OF THE ELECTRONIC STATES OF FLUORINATED EPITAXIAL
GRAPHENE WITH AN ELECTRONIC BIAS

A THESIS
SUBMITTED TO THE FACULTY OF CLARK ATLANTA UNIVERSITY
IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR
THE DEGREE MASTER OF SCIENCE

BY
KELLY DENISE MCALLISTER

DEPARTMENT OF PHYSICS

ATLANTA, GEORGIA
MAY 2014
ABSTRACT

DEPARTMENT OF PHYSICS

MCALLISTER, KELLY D. B.S. CLARK ATLANTA UNIVERSITY, 2012

MODIFICATIONS OF THE ELECTRONIC PROPERTIES OF FLUORINATED
EPITAXIAL GRAPHENE WITH AN ELECTRONIC BIAS

Committee Chair: Michael D. Williams, Ph.D.

Thesis dated May 2014

Ultraviolet photoemission spectroscopy measurements reveal that there is notable
variation of the electron density of states in valence bands near the Fermi level.
Evolution of the electronic structure of fluorinated graphene as a function of the applied
electric bias is investigated. The experimental results demonstrate that the tailoring of
electronic band structure correlates with the interlayer coupling tuned by the applied bias.
The change in the work function of fluorinated graphene demonstrates the ability of
fluorination to modify electron emissions characteristics of graphene.
ACKNOWLEDGMENTS

The work presented here has been a long time coming. I am thankful and forever grateful to the support system that I have been lucky enough to have around me. Firstly, I would like to thank my advisor and mentor Dr. Michael D. Williams. You took a gamble on me in 2008. I, for one, had no idea what I was doing, but your patience, insight, and guidance kept me going and motivated. You are undoubtedly the largest driving force which got me where I am today. So thank you.

I would also like to acknowledge my professors who have been on this journey with me, Dr. Ronald E. Mickens, Dr. Randal Mandock, Dr. Alfred Z. Msezane, Dr. Xiao-Qian Wang, Dr. Niranjan K. Talukder, Professor Terry Harrington, and the academic staff of Clark Atlanta University Department of Physics. Thank you so much for your guidance over these last years. I would like to also thank my classmates and colleagues. It's good to know that we were all in this together. My wish for all of us is that we become the best at what we do.

This research project was supported in part by the National Science Foundation PREM Program DMR-0934142 and the National Science Foundation CREST Program HRD-1137751.

Last but not the least; I would like to thank my family; my mother, father, sister, niece and nephew for giving me a purpose and additional thanks to my friends; Andrea, Mai, P’Be, Dexandro, Toon, and Thai; who showed me the importance of an adventure.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>ACKNOWLEDGEMENTS</th>
<th>ii</th>
</tr>
</thead>
<tbody>
<tr>
<td>TABLE OF CONTENTS</td>
<td>iii</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td>v</td>
</tr>
<tr>
<td>LIST OF ABBREVIATIONS</td>
<td>vi</td>
</tr>
<tr>
<td><strong>CHAPTERS</strong></td>
<td></td>
</tr>
<tr>
<td>1. AN INTRODUCTION TO THE WORLD OF GRAPHENE</td>
<td>1</td>
</tr>
<tr>
<td>1.2 Structure and Properties</td>
<td>4</td>
</tr>
<tr>
<td>1.3 Applications of Graphene</td>
<td>7</td>
</tr>
<tr>
<td>1.31 Transparent Devices</td>
<td>7</td>
</tr>
<tr>
<td>1.32 Circuits</td>
<td>9</td>
</tr>
<tr>
<td>1.33 Supercapicitors</td>
<td>10</td>
</tr>
<tr>
<td>1.34 Flexibility</td>
<td>11</td>
</tr>
<tr>
<td>1.35 Sensors</td>
<td>11</td>
</tr>
<tr>
<td>1.4 Functionalization of Graphene</td>
<td>12</td>
</tr>
<tr>
<td>1.41 Covalent Interactions</td>
<td>12</td>
</tr>
<tr>
<td>1.42 Noncovalent Interactions</td>
<td>14</td>
</tr>
<tr>
<td>2. EXPERIMENT</td>
<td>16</td>
</tr>
<tr>
<td>2.1 Growth of Graphene</td>
<td>16</td>
</tr>
<tr>
<td>2.2 Graphene Properties</td>
<td>18</td>
</tr>
<tr>
<td>2.3 Fluorinated Graphene</td>
<td>18</td>
</tr>
</tbody>
</table>
TABLE OF CONTENTS

PAGE

2.4 Work Function Modifications .................................................................20
2.5 Material .....................................................................................................21
2.6 Characterization ........................................................................................22
2.7 Fluorinated Epitaxial Graphene with an electronic bias .........................23
2.8 Ultraviolet photoemission spectroscopy .................................................23
3. RESULTS .....................................................................................................25
4. CONCLUSION ..............................................................................................31
5. FUTURE WORK ............................................................................................35

REFERENCES ................................................................................................36
LIST OF FIGURES

1.1 Structure of graphite ................................................................. 1
1.2 Graphene as a 2D building block for other graphitic material .... 2
1.3 Graphene crystal on oxidized Si wafer by transparent tape method ... 3
1.4 H bonding system in graphene .................................................. 5
1.5 Semiconductor vs. Graphene ...................................................... 6
1.6 Polytron Technologies Transparent phone .................................... 8
1.7 Moore’s Law: Decrease in feature size and increase in CPU ......... 9
1.7 Fermi Surface of Graphene ....................................................... 27
2.1 Schematic of RIE system ........................................................... 21
3.1 UPS of MEG ........................................................................... 26
3.2 UPS of FEG ........................................................................... 27
3.3 Sample mounted on SiC with voltage ....................................... 28
3.4 Change in valence band width vs. bias ...................................... 29
3.5 Difference in shift vs. bias ......................................................... 30
LIST OF ABBREVIATIONS

C  Carbon
F  Fluorine
CNT  Carbon Nano Tubes
GNR  Graphene Nano Ribbons
MEG  Multilayer Epitaxial Graphene
FEG  Fluorinated Epitaxial Graphene
SiC  Silican Carbide
EDC  Electron Distribution Curve
CVD  Chemical Vapor Deposition
CCS  Confinement Controlled Sublimation
LEED  Low energy electron diffraction
UPS  Ultraviolet photoemission spectroscopy
RIE  Reactive Ion Etching
Graphene is a particularly wonderful and useful material that has the potential to revamp the future. It comes from humble beginnings by a material that has been sitting under the noses of countless people for many years. Most of us have been familiar with graphite, but only as the substance in our pencil and not as a material with a lot of interesting properties. The word graphite comes from the Greek word which means "to write" [1], a fitting definition. In most cases, Graphite is greyish-black, opaque, with a lustrous black sheen. It is an allotrope of carbon that has unique properties due to its crystalline structure [2-3]. The carbon atoms in graphite are aligned hexagonally in a plane, and layers of carbon are stacked parallel to each other forming the structure. There is a planar condensed ring system where the layers of atoms within this ring are bonded covalently and the top layers are bonded together through Van der Waals forces.

Figure 1. structure of graphite

1
It has high electrical conductivity as well as high thermal conductivity. In its crystal structure, the carbon atoms are bonded by three sigma ($\sigma$) bonds and one pi ($\pi$) bond. The $\pi$ bonds are weaker than the $\sigma$ bond, which means there is a free electron available for conduction. The $\pi$ bonds also preserve the carbon structure\[4\].

This brings us to the topic of this thesis, graphene. Graphene is a single layer planar sheet of $sp^2$- hybridized carbon atoms arranged in a hexagonal lattice and is one of the crystalline forms of carbon alongside diamonds, carbon nanotubes, fullerenes, and graphite [5-6, 7]. It is currently one of the great finds of the 20th century and may impact our quality of life through its various applications. One may call the process of graphene discovery serendipitous or plain dumb luck, but this fascinating material, a 2D building block for graphitic material, described as a one-atom thick layer of graphite; may change the world. Stacked graphene monolayers makes up 3D graphite. Graphene can be visualized as an atomic-scale chicken wire made out of carbon atoms. Its inherent 2D nature produces unique properties.

![Graphene as a 2D building block for other graphitic materials](image)

Figure 2. Graphene as a 2D building block for other graphitic materials\[5\]
Isolated by University of Manchester scientists in 2004, Andrei Geim and Kostya Novoselov as an accidental discovery, graphene has since become a groundbreaking material. On a day just like any other day, they were attempting to investigate the electrical properties of graphite and wanted to see if the material could be made thinner. Using a piece of pressure sensitive tape, they peeled off layers of graphite until the material was to the thickness of only a few atoms (5-6,8). For most, playing with transparent tape would lead to a day of fun, filled with ripped skin and hair; but not for these seasoned scientists. They were on a mission, and that mission would lead to greatness. It was discovered that this new material is permeated with incredibly interesting properties. Once Geim and Novoselov had the thin flakes, they needed a way to transfer the material to a silicon wafer so that it could be further studied. Silicon (Si) is an important material because it is at the heart of most semiconductors used today ie. microprocessors and transistors.

Figure 3. Large graphene crystal prepared on an oxidized Si wafer by the transparent tape technique

5
1.2 Structure and Properties

Lighter than a feather and stronger than most materials on this planet, graphene is a fascinating material. It is the subject of much discussion due to its strength; graphene has a tensile strength 200 times greater than steel [7,9], its high carrier mobility[10], and transparency[11], just to name a few. The possibilities for graphene are endless.

One of the more interesting properties of graphene is that it is a zero-overlap semi-metal, with charge carriers being played by both holes and electrons. This gives way to its high electrical conductivity. Although graphene is essentially carbon, the valence electrons act differently. Carbon has an atomic number of 6, which would indicate that it has 2 electrons in its inner shell and 4 electrons in its outer shell, which is a carbon atom available for bonding. In graphene, each carbon atom is attached to 3 other carbon atoms. Although graphene is a 2D material, there is one electron available in the third dimension for electrical conduction. These electrons are called \( \pi \) electrons and are located in the third dimension above and below graphene's 2D plane. These \( \pi \) electrons have an incredible high mobility and their orbitals overlaps. This aids in the improvement of the carbon to carbon bonds in the graphene sheets. The incredible electronic properties of graphene are essentially decided by the bonding and anti-bonding of these orbitals.
A property witnessed was that the electrons began to behave as though it had no mass loosely called a “ghostly” quantum state. Electrons in graphene behave as quasi-particles called “Dirac fermions” [12]. This happens when electrons in graphene mimic relativistic particles at speed of $10^6$ m/s with a zero rest mass. Dirac-fermions are described by a Dirac-like equation, which includes the speed of light as a constant rather than the Schrodinger equation, which includes Planck’s constant. The Dirac equation also makes use of multiple complex values and a relativistic generalization of the Schrodinger’s equation. This is an important factor in the application of graphene giving it an edge over other electronics in the market in the realm of speed.

A suspended sheet of pure graphene- a plane layer of C atoms bonded together in a honeycomb lattice- is a two dimensional system. Graphene is a zero-gap semimetal.
Functionalizing graphene is of critical importance for future applications. Chemically functionalized graphene have displayed a band gap of approximately 2.8 eV\textsuperscript{14} which may be a result from doping. This method allows the tailoring of the graphene’s electronic, chemical, and physical properties. The conventional way of functionalizing graphene includes the addition of oxygen, hydrogen, and fluorine for band gap opening; with graphene sheets produced by the reduction of graphite oxide. Graphene can be chemically functionalized via either covalent or non-covalent interactions. Covalent interactions usually result in the re-hybridization of carbon atoms from sp\textsuperscript{2} to sp\textsuperscript{3} thereby disrupting the lattice while the non-covalent interactions preserve the planarity of graphene layers.
1.3 Application of Graphene

Scientists and engineers are continuously looking into making a product better, faster, and stronger. Improving the efficiency of current electronics is the current focus and graphene may be the answer. The properties of graphene make it potentially a viable successor to silicon in a new generation of microchips. This is a practicable application because of its single atom thickness and its transparency (it only absorbs 2.3% of light's intensity); electrodes for LEDs could be in its future. Furthermore, graphene also looks to be the successor for copper in electronic devices due to its low resistance, high carrier mobility, and its generation of less heat. A current problem with electronics is the ability to increase the speed of the device without increasing the heat load.

1.31 Transparent devices

Currently, Indium tin oxide (ITO) is most abundantly used in transparent electrode materials, with a work function approximately 4.8 eV and a transparency greater than 90% at a wavelength of 550 nm. Nevertheless, the cost of indium is increasing due to its scarcity [15]. Additionally, the processing requirements are complicated, it’s sensitive to both acidic and basic environments, and there is high surface roughness. The general roughness of the surface makes it brittle; not suitable for flexible displays and touch screens. Due to the Indium shortage, surrogate materials were considered. Metallic nanowires, Carbon Nanotube (CNT) films and conductive polymers were examined. Out of these materials, CNT displays meaningful transparency across the visible light spectrum. A necessary requirement for CNT films is that the density of nanotubes be greater than the percolation network. Furthermore, the nanotube-nanotube
junctions have a high electrical resistance; this limits the conductive pathway inside the films even though the CNTs are highly conductive.

Graphene has shown to be a possible contender to replace ITO as a transparent electrode material in electronic devices such as solar cells, touch-screens, organic field-effect transistors and liquid crystal devices; to name a few. Graphene has a tensile strain of approximately 6.5% and the electrical resistance is not subject to any significant change with bending. It has a bending radius of 2.3 mm and the resistance can be recovered after unbending. Graphene displays incredible mechanical stability in contrast to the common materials used in flexible electronics. Additionally, both the longitudinal and transverse resistance seems to retain its stability up to 11% stretching. Furthermore, there seemed to be only one order of magnitude change at 25% stretching. Graphene appears to be an excellent successor based on various graphene-based electronic devices.

The transparency and conductivity of graphene could make it an awesome contender for future cellular phones. Currently, a Taiwanese company, Polytron Technologies, is in the process of patenting the first “see through” phone[16].

Figure 6. The Taiwan division of U.S. Polytron Technologies has spent six years researching and developing this transparent mobile phone[16].
Transparent electronics such as touch screens can be incredible in limiting the amount of space needed in an office building or home, due to their multilateral functions. Imagine a transparent computer, tablet, or television set that is embedded into the windows of your house or office.

1.32 Circuits

Negligible electrical resistivity of the charge carriers in graphene at room temperature suggests the possibility of ultra-fast field effect transistors (FETs) without consuming high power and without going down the avenue of ordinary scaling dictated by Moore’s law [17].

Figure 8. Moore’s Law: Decrease in feature size and increase in CPU
Moore’s law states that approximately every two years the number of transistors on integrated circuits doubles over the history of computing hardware.

Graphene has an ultra-high carrier mobility which makes it a desirable material for switching devices as well as transistors for interconnected layers. In the future, systems may not be architecturally separated components but all interwoven, creating less space, making it faster, and possibly easier to use. Graphene nanoribbons (GNR) may be a possible successor to copper for interconnected metals in integrated circuits. Studies have shown that the average GNR has a resistivity 3x that of Cu. However, the best GNR has approximately the same resistivity of Cu [18].

1.33 Supercapacitors

Energy stored in electrochemical double layers storage devices is called Supercapacitors. Supercapacitors are unlike batteries who store their energy through electrochemical reactions. Due to the fast ion flow, Supercapacitors carry higher power densities than batteries which rely on redox reactions. However, batteries show high energy densities of 20 to 150 Wh kg⁻¹, whereas Supercapacitors are restricted to energy densities of 4 to 5 Wh kg⁻¹. Although Supercapacitors are extremely fast with accepting and releasing energy, they cannot hold the amount of energy that a battery can. Graphene can be the solution to this problem. An electrode that obtains a larger surface area than an ordinary supercapacitor electrode without forgoing the high electrical conductivity will grant a blend of power performance of a supercapacitor with the high energy density of a battery. Possibly in the near future, the battery charges on smart phones can last up to a week! Graphene possesses excellent mechanical and electrical properties and unusually
large specific surface area of 2630 m² g⁻¹. This is significantly higher than the surface area of carbon currently used in supercapacitors[19-20].

1.34 Flexibility

Graphene has properties that provide nearly weightless but incredibly strong composites. Graphene has a Young's modulus of ~2400 GPa versus Cu and Si which has a Young’s modulus of 110-128 and 130-185 GPa respectively. The surface to weight ratio is also exceptional. At approximately 2,700 m²/gram, graphene is remarkably strong for its weight. This could be useful in the production of airplanes and cars by subsequently cutting fuel costs and reduce our carbon footprint. It is known to move electrons 200 times faster than silicon with little interruption at room temperature[21-22]. Additionally, with its strong bonds between carbon atoms, Graphene remains the strongest material as well as one of the more flexible materials[23]. The carbon atoms can be twisted and pulled without breaking.

1.35 Sensors

Single gas molecules have been detected using graphene-based sensors[24]. Up until now, sensors have not been able to detect an entity at this level including solid state gas sensors which are known for their high sensitivity. The operating principle of both solid state gas sensors and graphene based sensors are generally the same[25]. In graphene based sensors it uses the change in the electrical conductivity of the graphene to detect to the adsorption of gas molecules which can act as acceptors or donors of electrons.
Solid state sensors have their limitations in that there are fluctuations due to thermal motions of charges and defects[25]. This leads to an intrinsic noise level that is over the necessary signal from the individual molecules. On the other hand, graphene is a low noise material and a few electrons can add noticeable changes within the carrier concentration. The high sensitivity of graphene makes it a viable contender for chemical detectors and sensitive probes where external charge, magnetic field, or mechanical strains are used.

1.4 Functionalization of Graphene

Introducing impurities to a semiconductor, known as doping, allows the modulation of its electronic properties and graphene can be functionalized through these means. Graphene does not have a band gap, and this greatly limits its uses in electronics[26]. Opening the band gap and having the ability to tune is an important aim for electronic applications.

Figure 7. Fermi surface showing zero-band gap nature of graphene.\textsuperscript{27}
1.41 Covalent interactions

Two types of interaction that may functionalize graphene are covalent and non-covalent interactions. Covalent interactions may result in the rehybridization of $sp^2$ to $sp^3$ disturbing the lattice. The carbon atoms in graphene are secured by the $\pi$-conjugation system and are inhibited from motion by the other surrounding carbon atoms. It is possible to alter the hybridization of carbon from $sp^2$ to $sp^3$ but there requires much more energy to overcome the barrier; therefore more reactive chemical groups are needed. Hydrogen, oxygen and aryl diazonium salt have been examined theoretically and experimentally.

Results have shown that with an addition of hydrogen, graphene shows different electronic properties. Rehybridization from $sp^2$ to $sp^3$ occurs which yields extended carbon-carbon (C-C) bonds in the graphene. If only one side is hydrogenated, it can be used for carbon nanotubes (CNTs) because of the difference in stress[28]. Semi-hydrogenated graphene yields ferromagnetic properties because some of the delocalized $\pi$-bonding is destroyed[29]. Full hydrogenated graphene, known as graphane, shows insulating properties[30]. Hydrogenation is also reversible and the lattice structure can be reestablished through process of heat treating or annealing. The uses of oxygen with graphene have also been explored. Oxygen-containing functional groups such as the carbonyl, carboxyl, and hydroxyl group[31] allow the control graphene's ability to be more hydrophilic and organophilic. Aryl diazonium salts can be used to regulate the electrical conductivity of graphene through tuning the surface potential of graphene through regiofunctionalization[32-33]. Graphene has a surface rich with delocalized $\pi$
electrons. When aryl diazonium is introduced, it reacts with the graphene; the electrons on the basal of the graphene transfer to the reactant.

1.42 Non-covalent interactions

Transition metals, ions, molecules, and other atomic clusters can be added onto the basal plane of graphene through complexation reactions or charge-transfer adsorption[34]. These interactions do not convert the hybridization of carbon from sp² to sp³. Functionalized by these methods retains the highly conductive nature of graphene.

The delocalized π electrons are very responsive to adsorbates, which can change the local carrier concentration by the molecules absorbed by graphene. This may result in the opening of a band gap due to the charge carrier transfer amongst the adsorbate and graphene[35-38]. This may be beneficial the creation of graphene based sensors that used the change in graphene’s conductivity to detect to the adsorption of molecules.

The adsorption of transition-metals on the basal plane of graphene has been shown to have the potential to be used in future applications in sensors and catalysis due to its high electrical conductivity and large surface area[39-40]. Conventional transition-metal catalyst and transition-metal carbides were beaten out by nano composites created with transition metals and graphene[41-42].

Fluorination of graphene has emerged as an attractive approach toward manipulating the physical, chemical, and electronic properties. Fluorinating graphene may authorize the control of its electronic state. With the addition of a potential difference, one may further enable the control of the graphene’s chemical, physical, and electronic state.
Fluorinated graphene (FEG) is epitaxial graphene that has been exposed to fluorine via the relatively safe sulfur hexafluoride (SF₆) plasma. In this work, incorporation of fluorine moieties on graphene after SF₆ plasma-treatment was confirmed by x-ray photoelectron spectroscopy (XPS). Modifications in the valence band states of graphene after plasma treatment were further characterized by ultraviolet photoelectron spectroscopy. Raman spectroscopy revealed that the majority of carbon atoms in graphene retain their sp²-hybridization after the plasma-treatment. Fluorination increases the work function of plasma-treated graphene and demonstrates the ability of plasma-assisted fluorination to modify the electron emission characteristics of graphene.

Fluorination has an effect on the graphene's electronic structure. Theory has suggested that there may be ferromagnetic properties when fluorine is introduced. Combined with an electric bias; the electronic properties can be further influenced. Biasing is a method which allows the electronic properties of a sample to be tuned. An important aspect in functionalizing Graphene is creating an environment where its structure can be controlled. With the addition of an outside voltage penetrating the sample, the band structure of the graphene begins to stress; using UPS, it is determined that band gap of graphene opens.
CHAPTER 2

EXPERIMENT

2.1 Growth of Graphene

One can prepare graphene in various ways. Geim and Novoselov used the method of exfoliation by way of adhesive tape[6], where they repeatedly removed layers of graphene from graphite. They managed to obtain flakes that were only a few atoms thick. This method is extremely arduous and time consuming but yields graphene flakes with high structural and electronic qualities. This process is sufficient for fundamental research on the structure of graphene but does not produce enough material for the high volume production required for electronic devices. Whereas, chemical vapor deposition (CVD) is an alternative method that produces graphene in large quantities[43-44]. The film develops directly on the surface by a surface catalyzed process yielding a film that is predominantly graphene. The graphene produced by this method is expected to have impurities due to several materials used to perform CVD[43]. This CVD graphene can also be grown on metal substrates via thermal decomposition of hydrocarbons or solid-state carbon sources. This is an attractive approach to graphene growth due to its simple and cost-efficient processes of the metals. A uniform single layer of graphene can be grown over a large area of copper foil but an additional step is needed to remove the graphene from one substrate to another for the graphene to be available for fabrication.
A reliable method for transferring graphene from a metal substrate will assist in the process of industrial use.

In 2004, Walter de Heer and co-workers at Georgia Tech grew ultrathin graphite films composed of three layers on the Si face of 6H-SiC. The group heated the Silicon face of the 6H-SiC to 1250°C - 1450°C in an ultra-high vacuum (UHV) chamber for 1-20 minutes[45]. This method of forming graphene layers on SiC substrates is referred to as vacuum sublimation. Due to the high sublimation rates at relatively low temperatures, the quality of the epitaxial graphene is inadequate. The deformities in the epitaxial graphene grown by this method can be contributed to the low growth temperatures and high graphitization rates. High growth temperatures also lead to very high sublimation rates due to the temperature annealing of vacancies. To control the sublimation rate of Si, the Si can be supplied through a vapor phase compound or flowing an inert gas over a silicon carbide surface that has been heated.

The growth rate of the epitaxial graphene depends on the termination of the silicon carbide crystal face. Graphene grows slower on the Si-face than the C-face of SiC[34,45]. Controllable multi-layer epitaxial graphene growth is possible on the carbon face of silicon carbide. Unlike graphite, which grows as AB stacked layers, graphene layers are composed of a high density of rotational stacking faults. These faults cause the adjacent layers to decouple electronically.
2.2 Graphene Properties

A beneficial property of graphene is that it is a zero band gap semi-conductor. Both electrons and holes are charge carriers and it is very conductive. Its honey comb lattice carbon network yields amazing electronic properties. The $2s$, $2p_x$, and $2p_y$ orbitals hybridize such that carbon atoms are bonded to its three neighboring carbon atoms by strong $sp^2$ or $\sigma$ bonds[46]. This leaves one electron free and available in the third dimension for electronic conduction. The $\pi$ bonded electrons are located above and below the graphene sheet and they are highly mobile and overlapping. The overlapping $\pi$ orbital aids in the carbon to carbon bonds. The $\pi$ orbitals are of significant importance to the electronic properties of graphene since they rely on the bonding and anti-bonding states of these orbitals.

The electrons and holes in graphene have zero effective mass are known as Dirac Fermions. According to the literature, the electronic mobility of graphene is very high and the electrons act like photons due to their lack of mass. These are charge carriers mimic relativistic particles that with an effective ‘speed of light’ at $10^6 \text{ m}^{-1}$. The quality of the graphene and the substrate is ultimately the deciding factor for mobility.

2.3 Fluorinated Graphene

The ability to tune the band gap in graphene makes it an exciting material to use in further applications. An important method in controlling the band gap is chemical functionalization. Production of fluorinated graphene has been reported of having a band gap as large as 3.8 eV after graphene being treated with xenon difluoride ($\text{XeF}_2$)[14]. Graphene is inert in nature and to deposit ultra-thin uniform films atomic layer deposition
is used to deposit a reactive species on the surface to begin the growth process. In this process, graphene must be pretreated with a metal, electron-beam physical vapor deposit oxide layer, or a low-k polymer seed layer. Fluorine is highly electronegative and this indicates that it would be a suitable reactive species to increase the surface reactivity of graphene so that atomic layer deposition can be utilized.

More recently, the method used to fluorinate graphene is to expose the graphene to fluorine gas at high temperatures and exposing the graphene to XeF$_2$ at room temperature. Despite being a manageable way to dope graphene, fluorine gas is toxic and XeF$_2$ hydrolyzes to form HF when exposed to air. Comparatively, plasma-assisted fluorination uses sulfur hexafluoride (SF$_6$), which is a benign source of fluorine. This provides a safer alternative to fluorine gas and XeF$_2$.

The graphene samples were fluorinated at the Georgia Institute of Technology by Sonam D. Sherpa. Plasmas used to dope graphene are usually low-temperature non-equilibrium plasmas generated at low or atmospheric pressure igniting a gas discharge. Plasmas are generated by supplying energy to electrons that produce ions and new electrons via inelastic collisions. An electric field is produced by a power supply which supplies the energy that is applied to the low pressure gas. The electrons are accelerated by the electric field in the plasma that release energy. The plasma is partially ionized which contain ions, electrons, and photons. Fluorination by plasma generation is an excellent way to fluorinate mono-layer graphene films. SF$_6$ plasma has been used successfully on graphene films grown on Cu and then transferred to Si substrates. The fluorinated graphene was characterized using X-ray photoelectron spectroscopy, ultra-
violet photoemission spectroscopy (UPS), low energy electron diffraction (LEED), and Raman spectroscopy. The Raman spectroscopy and the LEED showed that the integrity of the sp² configuration remained intact and was not disrupted by the plasma treatment. X-ray photoemission spectroscopy (XPS) confirmed that the fluorine atoms in the SF₆ plasma-treated samples. The fluorination was limited to the first one or two layers and the concentration can be changed by exposing the graphene for a longer period of time to the plasma. Ultra-violet photoemission spectroscopy shows the altering effect of fluorine on graphene in the valence electronic states and work function.

2.4 Work function modification

Experimental studies have shown that the work function of graphene was approximated at 4.40 ± 0.05 eV and can be estimated by subtracting the width of the photoelectron spectrum from the photon energy. With the addition of fluorination, the work function changed. The decrease in width of the photoelectron spectrum shows that the work function has increased. Exposing the graphene to SF₆ plasma for 30s, 60s, and 90s increased the work function by 0.64 ± 0.05 eV, 0.71 ± 0.06 eV and 0.48 ± 0.05 eV respectively [34].

The work function is the energy difference between the Fermi level and the vacuum level and there were no shifts in the Fermi level detected. Introducing highly electronegative fluorine containing moieties may result in the creation of surface dipole, which an increase in work function may be due to. A dipole field is produced by the creation of an electrical double layer with a negatively charged outer surface. Electrons are unable to escape from the surface consequently increasing the work function [34].
2.5 Material

The epitaxial graphene samples used were grown at the Georgia Institute of Technology in De Heer’s lab on the C-face of a semi-insulating 4H-SiC by high temperature annealing (~1600°C) in an RF induction furnace. This method is called confinement-controlled sublimation (CCS). To grow high quality epitaxial graphene, the ability to control the sublimation rate of Si is critical to control the epitaxial graphene growth rate. Using CCS technique, SiC sample is enclosed within graphite with a calibrated leak into a vacuum environment. This technique allows the Si atoms to remain confined which reduces the rate at which the atoms escape. In turn, the partial pressure of the Si is maintained which is not possible in an UHV system.

The EG samples were exposed to SF$_6$ plasma generated in a reactive-ion etching system. The RIE system uses chemically reactive plasma to remove materials deposited on wafers.

Figure 8. Schematic of RIE system$^{34}$
The high energy ions from the plasma attack the wafers surface and react with it. A biased power is used to generate the plasma as well as the ion acceleration to the cathode. These processes are not independent of each other. The reactive-ion etching system used in this study at the Georgia Institute of Technology operates on a radio-frequency of 13.56 MHz, an electrode diameter of 11 inches, an RF power of 50 W, for 30 s and a SF₆ partial pressure of 100 mTorr. These experiments were carried out at room temperature.

2.6 Characterization

The epitaxial graphene samples were characterized by XPS/UPS at the Georgia Institute of Technology by Sonam D. Sherpa. XPS/UPS were used to determine the elemental composition, estimate the thickness of the film, determine the work function, and confirm that there were fluorine-carbon bonds. The fluorinated epitaxial graphene samples were depth profiled in a XPS system using argon ion-bombardment (3 keV). The UPS spectra used HeI radiation (21.2 eV), for valence band spectra. To determine the thickness of the epitaxial graphene grown on C-face, an ellipsometer was used. To determine if there was notable change is the graphitic structure of the epitaxial graphene after it was exposed to the SF6 plasma, Raman spectroscopy was used. To investigate the effects of the SF₆ on the surface of the epitaxial graphene, low-energy electron diffraction (LEED) was used. The XPS/UPS system used in this study were by the Axis UltraDLD and Kratos Analytical. The ion-bombardment via argon used the Thermo Scientific K-alpha. All the XPS spectra used monochromatized ALKα radiation. Raman spectroscopy was obtained using the confocal Raman microscope by JY Horiba LabRam HR800 using
532 nm laser excitation. The low-energy electron diffraction patterns were obtained with a LK Technologies Model RVL2000 Reverse View LEED system[34].

2.7 Fluorinated Epitaxial Graphene with electronic bias

Understanding the electronic properties of graphene in addition to the interlayer interactions in multilayer graphene is important in furthering graphene into nanoelectronic devices. The planar structure of graphene makes it an acceptable model for uses of traditional surface science techniques. In tandem with fluorination, the addition of an electric bias may be a valuable technique in controlling the band structure of graphene. The evolution of electronic properties of FEG as a function of the applied bias is studied using experimental ultra-violet photoemission spectroscopy.

2.8 Ultraviolet Photoemission spectroscopy

The angle integrated kinetic energy distribution of the photoemitted electrons was measured with a PHI 15-255 GAR double pass cylindrical mirror analyzer operated in the retarded mode with an instrumental resolution of ±0.105 eV. The kinetic energy distribution of the electrons provides a surface sensitive (4-5 Å) measurement of the joint density of states of the filled electronic states in the valence band of the material. The sample was annealed under UHV conditions using radiative heating from a resistive filament mounted behind the wafer block.

The FEG sample was mounted with Indium (In) (99.9999% purity) at 160°C onto a molybdenum (Mo) wafer block in a nitrogen filled glove box at atmospheric pressure. The In surrounds the outer edge of the FEG samples to the top surface to attenuate charging effects. The wafer block was then placed into a sealed container and removed
from the glove box for transport into the UPS load lock system. The block was removed from the container, placed into the nitrogen purged load lock in less than one minute, sealed, and then pumped down to $5.5 \times 10^{-9}$ Torr. UPS analysis was performed on the sample in the ultrahigh vacuum analysis chamber with a base pressure of $4 \times 10^{-10}$ Torr.

The optical source for UPS was the He I (21.2 eV) line from a VSW UV-10 discharge lamp. He I is used for the valence band spectra and He II (40.8 eV) is used for shallow core levels. During the UPS measurements, the analysis pressure was $6.9 \times 10^{-7}$ Torr. A PHI 15-255 GAR double pass cylindrical mirror analyzer (CMA) measured the angle integrated kinetic energy distribution of the photoemitted electrons. The CMA operated in the retarded mode with an instrumental resolution of $\pm 0.105$ eV. The sample was outgassed at 160°C using radiative heating from a resistive filament. The UPS spectrum was acquired at a ground potential and negative bias potential difference conditions.
CHAPTER 3

RESULTS

The linear bands at the band edge of the density of states for single layer graphene correspond to transport by massless Dirac Fermions. Experimental studies of multilayer epitaxial graphene (MEG) by Williams, et al [47] indicate that the electronic states of the layers are decoupled as a result of rotational fault stacking. An array of experimental and theoretical studies display the rotational stacking order in MEG leads to decoupling of the layers and a linear dispersion band structure consistent with single layer graphene. Consequently, MEG grown by thermal decomposition on SiC substrates and patterned through standard lithographic procedures has been considered as a platform for carbon-based nano-electronics and molecular electronics. Therefore, the characteristics of the electrons of MEG are expected to vary sensitively with interlayer coupling. A comprehensive understanding of the interlayer coupling of MEG is of central importance to tune the electronic properties of FEG.

To trace the effect of interlayer coupling experimentally UPS spectra of FEG samples were collected under and electric field and compared with the MEG spectra published by Williams, et al [47]. The spectra of the FEG have been shifted in energy so that the photoemission thresholds coincide with that of the grounded spectrum. The MEG, similarly, has been shifted to correspond to the -1.0 V biased spectrum. The thresholds of the photoemission are determined by linearly extrapolating the low kinetic
energy edge of each electron distribution curve (EDC) from the full width at half maximum of the lower energy spectral peak to the spectral baseline. The shifts are non-rigid. This indicates that the band structure has been altered of both the FEG and MEG with an applied bias.

Figure 9. UPS of multilayer epitaxial graphene with 0 to -10 electric bias.\textsuperscript{47}
Figure 10. UPS of fluorinated epitaxial graphene with 0 to -10 electric bias

With the addition of a perpendicularly applied electric field, the corresponding UPS signals bear varying changes that are unique from simple shifts. Particularly, for MEG and FEG, there is an increase of the DOS starting at the Fermi energy.

There seems to be significant changes between 0 – 1 eV below the Fermi level. With a further increase in bias, it appears that the slope of the FEG increases between -1 eV and -2 eV. UPS investigation of MEG states that the applied electric bias affects the
interlayer coupling. The electronic structure of FEG can perhaps be attributed to the contribution of its stacking orders under the bias, provided that it mixed phase like MEG. This suggests that the transport behavior of electronic devices can be changed with an easy application of an electric field.

Experimentally, we identified the change in work function of FEG by obtaining the change in width from the UPS spectra. The change in width was acquired by subtracting the photoemission threshold from the valence band maximum, obtained from the UPS data. The electric field was applied with an increase in even voltage from 0 to -10 eV, and then reversed from -9 to -1 eV.

![Sample mounted on SiC with voltage](image)

Figure 11. Sample mounted on SiC with voltage.

This latter sequence was done to identify if there was a hysteresis loop. Hysteresis occurs in ferromagnetic materials and ferroelectric materials, as well in the deformation of materials in response to varying force. The results are shown in Figure 12.
The valence band width hits a maximum at a bias of -3 eV before decreasing. A possible explanation for this could be a saturation of spin. The addition of an electric field floods the valence band with electrons, the spin of those electrons are aligned with the direction of the electric field. Maximum saturation is all of the electrons aligning with the electric field. Another possible reason would be change in dipole strength. When dipole strength is maximized, the work function begins to decrease.

![Figure 12. Change in valence band width of FEG as a function of increased bias](image-url)
Instead of rigid shifts in the kinetic energy with an increase in the electric field, the shifts in spectra are off by substantially. This is of interest because it could reference properties in fluorinated graphene that are apparent with the addition of an electric bias. The change in shift decreases linearly until it reaches a bias of -4 eV and -5 eV, and then increase linearly with an increase in bias as shown in figure 13.

Figure 13. Applied bias vs. change in shift
CHAPTER 4

CONCLUSION

Graphene is an incredibly versatile and awesome material with properties that can be used for a variety of applications including but not limited to; transparent devices, circuits, supercapacitors, flexible devices, and sensors. The ability to tune the band structure and control the properties of graphene is an integral part into fulfilling its use for application purposes. Methods to alter the electronic and mechanical properties of graphene have been demonstrated. Functionalization of graphene as a result of chemically doping has risen as an appealing method in controlling graphene’s physical, electronic and chemical properties. Surface chemical functionalization is attractive because graphene consists of only surface atoms. Studies have shown that chemical functionalization can be used as a means to controlling graphene’s properties. Conventional chemical functionalization using oxygen, hydrogen, and fluorine has been used for band gap opening [45].

Fluorinated graphene has emerged as a stand out star as a possible wide band gap semiconductor as well as a high quality insulator[27,48]. The addition of fluorine allows the ability to engineer the electronic properties of graphene. Fluorination improves graphene’s surface reactivity of its relatively inert sp² bonded graphene. This will open up a wide range of modifications. Additionally, fluorine improves the atomic layer deposition of ultra-thin films of high-k dielectrics [49]. Reactive ion etching (RIE)
was used to investigate the results of fluorination and UPS was used to determine the change in work function with the addition of an electric field. It has been found that plasma technology is an easy way to fluorinate the graphene without disrupting its lattice and surface topography.

Studies have shown that the work function of graphene can be changed with the addition of fluorine, but this depends on the polarity of the carbon-fluorine bonds. In contrast, other theoretical results have shown that the band structure of graphene remains intact with the addition of fluorine, but ferromagnetic properties appear.

Preliminary studies have shown that SF$_6$ RIE plasma can fluorinate multi-layer and single-layer EG films while the integrity of the sp$^2$-hybridized structure remains intact. Altering the fluorine content can be controlled by exposing the fluorine for a longer or shorter period of time; this process is restricted to one or two surface layers. In the semiconductor industry, there is a universal existence of plasma technology. It has been reported that there are semiconductor properties in fluorinated graphene. With further experimentation of plasma-assisted dopants of graphene, the scientific community can begin using graphene based technology instead of the current semiconductor based technology. Additionally, it has been revealed that plasma-assisted fluorination can modify the work function of graphene and increase the hydrophobicity, thus making it a great contender for future applications in bio electronic devices.

A controllable work function is an important step in integrating graphene into electronic devices. A change in work function is noted with the addition of SF$_6$ plasma-treatment in previous studies and revealed that the change in work function ultimately
comes down to the polarity of C-F bonds and this is dependent on whether the bonds between the C and F atoms are ionic, semi-ionic, or covalent[50]. A practical approach into understanding the polarity of the C-F bonds is to explore the likelihood of the presence of ionic bonds. The bonding will keep the integrity of the sp²-hybridized carbon atoms as well as the work function, surface energy, and electrical conductivity. What regulates the polarity of the carbon-fluorine bonds remains unknown. Additional studies were implemented using Scanning Kelvin Probe Microscopy (SKPM). The SKPM revealed that the increase in work function following the SF₆ plasma-treatment is autonomous of the surface structure and the treatment is not damaging to the surface of the EG.

The electronic properties of FEG were further studied as a function of applied bias using experimental UPS measurements and theoretical work. We demonstrated a noteworthy control of the low-energy electronic states produced by tuning the interlayer interactions in the FEG samples. This condition is similar to the effects of an applied bias on MEG samples. The control of the electronic properties of FEG as a function of electric bias is a necessary application if to be used in future electronic devices which may be under an electric field or strain.

Interlayer coupling may also play a role in different graphene-based systems such as hetero-bilayers. Heterostructures are commonly used in semiconductors since their electronic properties can be tuned with relative ease[32]. The results of this experiment yield some fascinating discoveries. There is an interlayer coupling of the FEG that can be
tuned with an electric bias. Having this understanding creates a brighter future for its applications in graphene-based electronics.

The addition of the electric bias also modified the valence band width of the FEG. It was noted that with an increase in bias from 0 to -10 eV, there was an increase in the valence band width peaking at -3 eV. This could be identified a spin saturation in the valence band at -3 eV. The addition of an electric field floods the valence band with electrons, the spin of those electrons are aligned with the direction of the electric field. Another possible reason would be change in dipole strength. Once you hit a maximum in dipole strength, the work function begins to decrease. Additionally, the shifts on the UPS spectra were not rigid with the increase in bias. It is not yet apparent what makes up for those additional states and non-rigid shifts. Theoretical studies have shown that ferromagnetic properties were created with the addition of fluorine atoms; the additional states in the UPS spectra may corroborate those claims.

In summary, the work in this thesis establishes multiple claims. Plasma technology is a practical and facile method for the functionalization of graphene without destroying the integrity of its lattice and surface structure. Work function changes in fluorinated graphene occur using plasma-fluorination and a work function increase is dependent on the polarity of the C-F bonds. The band structure and work function of FEG changes with an addition of an electric field. Spin saturation and dipole strength are a factor in creating a continuous increase in work function.
CHAPTER 5

FUTURE WORK

The purpose of this work is to describe the effects of graphene when functionalized with a highly electronegative dopant and then stressed with an electric field. A thorough understanding of FEG is needed to further develop experiments to test the limits of this fascinating material. Current issues include controlling the polarity between the C-F bonds. It remains unknown what regulates the polarity. Regulating the polarity of the C-F bonds essentially means controlling the work function of FEG. Furthermore, additional test applying an electric field on various materials will be done.
REFERENCES


27. X. Li, Epitaxial Graphene Films on SiC: Growth, Characterization, and Devices, Georgia Institute of Technology, 2008


43. R. Kou, Y. Shao, D. Wang, M.H. Engelhard, J.H. Kwak, J. Wang, V.V. Viswanathan, C. Wang, Y. Lin, Y. Wang, I.A. Aksay, and J. Liu, Electrochemistry Communications 11, 954

44. B. Pollard, thesis, Pomona College (2011)


