Electronic Transport Investigation Of Chemically Derived Reduced Graphene Oxide Sheets

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ELECTRONIC TRANSPORT INVESTIGATION OF CHEMICALLY DERIVED REDUCED GRAPHENE OXIDE SHEETS

by

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B.S. Soonchunhyang University, 2004
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ABSTRACT

Reduced graphene oxide (RGO) sheet, a chemically functionalized atomically thin carbon sheet, provides a convenient pathway for producing large quantities of graphene via solution processing. The easy processibility of RGO sheet and its composites offer interesting electronic, chemical and mechanical properties that are currently being explored for advanced electronics and energy based materials. However, a clear understanding of electron transport properties of RGO sheet is lacking which is of great significance for determining its potential application.

In this dissertation, I demonstrate fabrication of high-yield solution based graphene field effects transistor (FET) using AC dielectrophoresis (DEP) and investigate the detailed electronic transport properties of the fabricated devices. The majority of the devices show ambipolar FET properties at room temperature. However, the mobility values are found to be lower than pristine graphene due to a large amount of residual defects in RGO sheets. I calculate the density of these defects by analyzing the low temperature (295 to 77K) charge transport data using space charge limited conduction (SCLC) with exponential trap distribution. At very low temperature (down to 4.2 K), I observe Coulomb blockade (CB) and Efros-Shklovskii variable range hopping (ES VRH) conduction in RGO implying that RGO can be considered as a graphene quantum dots (GQD) array, where graphene domains act like QDs while oxidized domains behave like tunnel barriers between QDs. This was further confirmed by studying RGO sheets of varying carbon $sp^2$ fraction from 55 – 80 % and found that both the localization length and CB can be tuned. From the localization length and using confinement effect, we estimate tunable band gap of RGO sheets with varying carbon $sp^2$ fraction. I then studied one dimensional RGO nanoribbon
(RGONR) and found ES VRH and CB models are also applicable to the RGONR. However, in contrast to linear behavior of decrease in threshold voltage ($V_t$) with increasing temperature ($T$) in the RGO, sub linear dependence of $V_t$ on $T$ was observed in RGONR due to reduced transport pathways. Finally, I demonstrate synthesis and transport studies of RGO/nanoparticles (CdS and CeO$_2$) composite and show that the properties of RGO can be further tuned by attaching the nanoparticles.
To my wife and parents
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<td>Coulomb Blockade</td>
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<td>CdS</td>
<td>Cadmium Sulfide</td>
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LB   Langmir–Blodgett
LOR  Lift-off-Resist
MIBK Methyl-isobutyl-ketone
MW   Middleton Wingreen
NR   Nanoribbon
NPGS Nano-Patterned- Generation-System
NPs  Nanoparticles
PMMA Polymethyl-methacrylate
QD   Quantum Dot
RGO  Reduced Graphene Oxide
RGONR Reduced Graphene Oxide Nanoribbon
SAED Selected Area Electron Diffraction
SB   Schottky Barrier
SEM  Scanning Electron Microscopy
SLSC Space Charge Limited Conduction
SLG  Single Layer Graphene
STEM Scanning Transmission Electron Microscopy
STM  Scanning Tunneling Microscopy
TEM  Transmission Electron Microscopy
TR-SCLC Trap Free Space Charge Limited Conduction
VRH  Variable Range Hopping
XPS X-ray Photoelectron Spectroscopy
1 INTRODUCTION

1.1 Motivation

Today, semiconductor industry has put a considerable effort on miniaturizing active feature sizes of devices with faster, lighter and more robust performance. Much has focused on reducing heat and conserving power, all at a lesser cost. However, the current technology on silicon (Si) based electronics will be a roadblock for further shrinkage of the feature size due to their physical limits such as heating, short channel effects, leakage current, and quantum effects.¹ Thus, to overcome these limitations, graphene has risen as a new material to supplant or be incorporated into Si-based electronics.

Graphene, which is a two dimensional single layer of carbon atoms arranged in a hexagonal and honeycomb structure, has attracted a great deal of attention because of its unique electronic properties, making them model systems for the observation of novel quantum phenomenon and building blocks for future nanoelectronic devices.²⁻⁶ The rapid progress in studies of graphene resulted in the discovery of its extraordinary mechanical,⁷ thermal,⁸ chemical,⁹⁻¹⁰ electrical and optical properties¹¹. One of its most remarkable properties is that its charge carrier behaves as massless Dirac fermions. Hence, it shows low electron scattering and ballistic transport at room temperature, even in a few hundred nm device channel length. Graphene exhibits strong ambipolar field effect with carrier mobility of ~ up to 200000 cm²/Vs at electron densities of ~ 2×10¹¹ cm⁻², as compared to maximum electron mobility of silicon (~ 1400 cm²/Vs).¹² This high carrier mobility of graphene has the potential for increasing the cutoff frequencies of over 100GHz.¹³⁻¹⁴ Graphene also sustains high current densities (~10⁸ A/cm²).¹⁵
compared to copper ($\sim 10^6$ A/cm$^2$) as well as high thermal conductivity of $\sim 5000$ Wm/K.\textsuperscript{8} In addition, the highly transparent properties of graphene (transparency of $\sim 90\%$) under visible light are comparable with indium tin oxide (ITO, $\sim 88\%$).\textsuperscript{16-17} Mechanical strength of graphene, with spring constant of $\sim 5$ N/m and Young modulus of 1 TPa,\textsuperscript{7} makes it one of the strongest materials ever seen. It also exhibits highly specific surface area of $\sim 2500$ m$^2$/g.\textsuperscript{18-19} Therefore, a remarkable amount of graphene based research has been performed.

Up until now, a number of approaches have been developed to synthesize and fabricate graphene. The majority of the existing graphene electronic devices involve a mechanical exfoliation technique by peeling layers from highly oriented pyrolitic graphite (HOPG) using scotch tape.\textsuperscript{2,4} Graphene can also be achieved by precipitation on a silicon carbide (SiC) surface, which is a result of the evaporation of Si atom from the SiC surface and the resulting segregation of carbon atom (C) on the surface.\textsuperscript{3} Although precipitation on a mechanical exfoliation technique and a SiC surface offer high quality devices for studying novel physics, they suffer from extremely low throughput and lack the methods for large scale integration into devices. High yield and large scale production of graphene can be achieved through chemical vapor deposition (CVD) techniques. CVD has been used to grow graphene sheets on Ni and Cu substrates and large area graphene can be subsequently transferred onto other substrates, i.e. SiO$_2$.

Graphene can be processed in a form of solution through chemical exfoliation called reduced graphene oxide (RGO) sheets.\textsuperscript{20-23} The easy processibility and compatibility with various substrates including plastics makes RGO an attractive candidate for high yield manufacturing of graphene based circuits.\textsuperscript{24} Another interesting aspect of RGO is its potential in obtaining a band gap in graphene since zero band gap is one of the hurdles for graphene to be a
useful electronic material. Such presence of band gap will able tuning of graphene’s electrical properties from semimetal to insulator. More recently, attractive properties of RGO and its derivatives have made ideal templates for decoration of different nanoparticles (NPs), which attracted tremendous scientific and technological interests; it allows one to obtain a new class of multifunctional materials since defect and oxygen functional groups in RGO can act as nucleation sites for growth of NP structure and create strong chemical bonding.$^{21}$

To summarize, RGO has received great attention due to its (i) high throughput manufacturing; (ii) tunable electrical, optical properties and band gap via controlling the ratio of $sp^2$ C-C and $sp^3$ hybridized carbon (i.e., oxygen functional groups); and (iii) ability to anchor different types of nanoparticles and organic molecules, all of which pave the way for potential applications.

In addition, while the electrical conductivity and field effect mobility values for RGO sheets can be tuned by several orders of magnitudes by controlling the reduction, the values are much inferior to that of pristine graphene due to a large amount of residual disorders in the RGO sheets which localizes charge carriers. Many studies of RGO have been performed based on observations of degree of reduction and investigation of atomic scale features by characterizing with microscope and spectroscopy. However, such studies do not provide detailed information about the origin of lower electronic transport properties and the fundamental understanding of the basic transport properties in this 2D disorder material. Understanding the role of these disorders in charge transport mechanism is of great significance for evaluating and improving the potential applications of RGO and its composites. Moreover, a detailed knowledge of charge conduction and quantitative information about disorder are important for further optimization of
reduction techniques and synthetic strategies to increase conductivity and mobility of RGO towards pristine graphene.

1.2 Chapter Outline

I will begin with a discussion on the background on history, structure, production methods of graphene, and theoretical background of charge transport in disorder system. This information will provide the current progress in this field and set a framework for future discussions.

After discussing the background, I will provide details of the fabrication procedures performed in Chapter 3. This chapter will include a description on the fabrication of electrode patterns using optical and electron beam lithography, and experimental details for the assembly of reduced graphene oxide (RGO) sheets using AC dielectrophoresis (DEP) and measurement setups. I will also describe the characterization of RGO sheets.

In Chapter 4, I will show 100% high yield RGO field effect transistor (FET) assembled by DEP and its FET properties. To elucidate the origin of low mobility, I will show that the conduction is dominated by space charge limited conduction (SCLC) with an exponential distribution of traps in energy at intermediate temperature.

Chapter 5 will present detailed low temperature transport measurements on RGO sheets at a very low temperature. To apply Coulomb blockade (CB) and Efros-Shklovskii variable range hopping (ES VRH), I will show that RGO can be considered as a graphene quantum dot (GQD) array. Further studies on varying carbon sp² fractions of RGO sheets will show tunable localization, energy gap and CB effects.
Subsequently, in Chapter 6, I will focus on electron transport of lithographically fabricated RGO nanoribbon (RGONR) with different channel width and length. This chapter will provide new insight in 1D graphene based materials.

In Chapter 7, I will show synthesis techniques of RGO nanoparticle composites with two different methods, i.e., solvothermal and chemical reduction routes. I will also show how the nanoparticles tune the transport of RGO sheets.

Concluding this dissertation in Chapter 8, I will discuss future directions related to this work and suggest possible future experiments.
References


2 BACKGROUND

2.1 Graphene as a New 2D Material

2.1.1 Historical Overview of Graphene

In 2010, Nobel Prize in physics was awarded to Andre Geim and Konstantin Nivoselov for their 2004 report in Science. In the article, they explained that exfoliation of graphite using sticky tape produces isolated layers of graphite called graphene. This observation has proved that the strictly 2D graphene exhibits superior high crystal and electronic quality, which provides a new class of physics and potential applications. The article has been cited a total of 7,884 times according to Web of Knowledge (accessed 21 September 2012) and created a “Graphene boom in 21 century.” Figure 2.1 shows a graphical representation of increasing interest in graphene after the 2004 report.

Figure 2.1 Number of publications containing the term “graphene” by year (determined by searching for “graphene” in Web of Knowledge database).
What is responsible for this ‘groundbreaking experiments’ of graphene in the physics community? In 1935 and 1937, Peierls\(^2\) and Landau\(^3-4\) argued that strictly 2D crystals could not exist due to thermodynamical instability, and thus, they could not exist in nature without a 3D base. Subsequently, in 1968, Mermin took this theory further and reported experimental observations to support the hypothesis.\(^5\) Therefore, without such a 3D base, 2D materials were believed not to exist until the experimental discovery of graphene in 2004.

However, this historical overview on graphene cannot be completed without a brief mention of graphene oxide (GO).\(^6\) Graphite oxide reduction can be possibly considered the first method of graphene fabrication in history. In 1962, P. Boehm showed “monolayer flakes of reduced graphene oxide”.\(^7\) Boehm’s work has recently been recognized by Andre Geim in graphene research.\(^8\) Boehm also invented the term, ‘graphene’ in 1986.\(^9\)

2.1.2 Structure of Graphene

Graphene is a \(sp^2\) bonded network of hexagonally arranged carbon atoms with two atoms per unit cell, as shown in Figure 2.2. The unit cells labeled A and B are invariant under 120 ° rotation with respect to any other lattice site.\(^10\) The lattice vector can be expressed as:

\[
a_1 = \frac{a}{2} \left(3, \sqrt{3}\right), \quad a_2 = \frac{a}{2} \left(3, -\sqrt{3}\right)
\]  \(2.1\)

where \(a\sim 1.42\ \text{Å}\) is the carbon-carbon distance.\(^11\) This equation gives a reciprocal lattice that is also hexagonal, rotated 90° from the Bravais lattice. The reciprocal lattice vector can be written as:

\[
b_1 = \frac{2\pi}{3a} \left(1, \sqrt{3}\right), \quad b_2 = \frac{2\pi}{3a} \left(1, -\sqrt{3}\right)
\]  \(2.2\)
The K and K’ are the inequivalent corners of the Brillouin zone called, Dirac points, which can be given by:

\[
K = \left(\frac{2\pi}{3a},\frac{2\pi}{3\sqrt{3}a}\right), \quad K' = \left(\frac{2\pi}{3a},-\frac{2\pi}{3\sqrt{3}a}\right)
\]  
(2.3)

These Dirac points are critical to electronic transport of graphene. The Brillouin zone of graphene is hexagonal in shape with high-symmetry point \(\Gamma\), K and M. For B-sublattice atom, the three nearest-neighbor vectors in real space are given by:

\[
\delta_1 = \frac{a}{2}(1,\sqrt{3}), \quad \delta_2 = \frac{a}{2}(1,-\sqrt{3}), \quad \delta_3 = -a(1,0)
\]  
(2.4)

Each carbon atom has four valence electrons: three electrons in the \(sp^2\) orbital and one electron in the \(p_z\) orbital. The electrons in the \(sp^2\) orbital (2s, 2p\(_x\), and 2p\(_y\)) form in \(\sigma\) bonds, while the electrons in 2p\(_z\) orbitals form \(\pi\) bonds with neighboring carbon atoms in the same plane with angles of 120 °. The three in-plane \(\sigma\) bonds bind with a carbon atom to its three nearest neighbors.
while the fourth bond $\pi$ is perpendicular to the plane formed due to the sideward overlap of the $2p_z (\pi)$ orbitals, as shown in Figure 2.3 (a).

Figure 2.3 (a) Schematic of the honeycomb lattice structure of graphene showing in-plane $\sigma$-bonds and $\pi$-bonds perpendicular to the plane of the sheets. $^{12}$ (Reprinted from [12] with permission from the IOP Publishing, Ltd.) (b) Electronic dispersion in the honeycomb lattice over the entire Brillouin zone. Dirac cones are located at six corners of the Brillouin Zone. Right : zoom-in image shows the energy bands close to one of the Dirac points indicating linear dispersion (Dirac cones) to the vicinity of $E=E_F$. $^{10}$ (Reprinted from [10] with permission from the American Physical Society.)

The in-plane $\sigma$ bonds are origins of the hexagonal lattice structure of graphene and not the main contributor for electrical properties of graphene; rather, these are responsible for the large binding energy and the elastic (or mechanical) properties of the graphene sheets.

Thus, the fourth electron in the $2p_z$ orbital is responsible for the band structure of graphene. Since there are two carbon atoms per cell unit, there will be two $\pi$ bonding termed, bonding $\pi$ (valence) and anti-bonding $\pi^*$ (conduction) bonds. The bonds $\pi$ and $\pi^*$ are located near the Fermi energy ($E_F$) and related to the electrical and optical properties of the graphene. $^{10}$

Using a tight-binding approximation, the energy dispersion of $\pi$ electrons in graphene can be obtained:
\[ E(k_x,k_y) = \pm \gamma_0 \left[ 1 + 4 \cos\left( \frac{\sqrt{3}k_xa}{2} \right) \cos\left( \frac{k_ya}{2} \right) + 4 \cos^2\left( \frac{k_ya}{2} \right) \right]^{1/2} \] (2.5)

where \( \gamma_0 \) is the nearest neighbor hopping energy. The plus sign applies to \( \pi^* \) band (conduction band), while the minus sign is the \( \pi \) band (valence band). These two bands touch at two non-equivalent \( K \) points, called \( K \) and \( K' \), found at the corners of the Brillouin zone. At the Fermi energy, these cones touch at six points called Dirac points which reduce the Fermi surface to the six points at the corners of the 2D hexagonal Brillouin zone and turns graphene into a zero band gap semi-metal.\(^{10}\) This is shown in Figure 2.3 (b). Thus, the carrier dynamics in graphene can be expressed in the surrounding areas of the Fermi energy by a linear dispersion relation

\[ E \approx \hbar v_F |\vec{k}'| \] (2.6)

where \( \vec{k}' = \vec{k} - \vec{k}' \) and \( |\vec{k}'| \gg |\vec{k}'| \), and \( v_F \) is the Fermi velocity expressed as \( \sqrt{3} \gamma_0 a / 2\hbar \) and is \( \sim 10^6 \) m/s.

\section*{2.2 Graphene Production}

\subsection*{2.2.1 Mechanical Exfoliation}

Mechanical exfoliation is a simple physical cleavage of graphite using scotch tape. A small piece of graphite is placed on sticky side of scotch tape, as shown in Figure 2.4 (a). Then the tape is placed onto a SiO\(_2\)/Si wafer. Then, graphene can be observed by optical microscopes. As shown in Figure 2.4 (b), thin flakes are found to be composed of a single layer and/or a few layers of graphene on the SiO\(_2\)/Si substrate. Although the mechanical exfoliation of graphene
shows high quality and exciting discoveries of graphene electronic and mechanical properties, the method is limited in large scale and quantities production.

Figure 2.4 Mechanical exfoliation of graphene using scotch tape. (a) A piece of scotch tape prepared with graphite. (b) An optical image of a single layer of graphene and few layers of graphene on the SiO$_2$/Si substrate.\textsuperscript{26} (Reprinted from [26] with permission from Elsevier.)

2.2.2 Chemical Vapor Deposition (CVD)

Besides mechanical exfoliation, chemical vapor deposition (CVD) on metal surfaces is a method to grow wafer scale uniform monolayer graphene.\textsuperscript{14} In this method, methane and hydrogen gases are injected to the high temperature vacuum furnace and these go through a dehydrogenation process on the catalytic-containing metal surface such as Cu (\textasciitilde 1000 °C) or Ni (\textasciitilde 1300 °C). Then, the graphene sheets are transferred from the metal substrates to a target surface. The transfer steps are (i) adhesion of polymer, i.e. PMMA and PDMS, supporting the graphene on the metal substrates; (ii) etching of the metal layer; and (iii) release of the graphene layers and transfer onto a target substrate. As a result, the carbon atoms rearrange themselves with very large size.
2.2.3 Chemically Derived Graphene: Graphene Oxide

Large quantities of solution based graphene oxide (GO) can be produced by reacting graphite powder with strongly oxidizing agents followed by purification and chemical exfoliation in a solution, i.e, water (Figure 2.5 (a)). During oxidation, some bonds of graphene sheet break to form bonds with oxide and other carbon functional groups. Three major methods are used to synthesize GO from graphite: Hummer and Offeman, Staudenmaier, and Brodie. Among them, Hummer method is most commonly used to synthesize GO.

A significant amount of oxygen contained carbon structure makes a complete transition in the electronic properties of the material, from a semimetal to an insulator. This can be improved by a subsequent reduction of GO into reduced graphene oxide (RGO). To date, the most common reduction treatments are thermal and chemical reduction. The thermal reduction utilizes heat treatment at ~ 1000 °C to remove the oxygen functional groups from GO, while chemical reduction of GO is treated with reducing chemical agents such as hydrazine and sodium borohydride (NaBH4). The major difference between these two methods is that the chemical reduction method is performed in a solution, while the thermal reduction can be performed after deposition of GO on substrates. Therefore, the thermal reduction method has limitation of substrate materials. Figure 2.5 (b) shows charges in chemical bonding structure of graphite to RGO sheets. Transmission electron microscopy (TEM) images show that RGO consists of ordered graphene $sp^2$ domains surrounded by areas of oxidized domains $sp^3$ as shown in Figure 2.8 (c). It has been estimated that the graphitic domain size varies from 1 to 6 nm.
Figure 2.5 Synthesis, structural model and microstructures of GO sheets. (a) GO is typically synthesized by reacting graphite powder with strongly oxidizing agents such as KMnO4 in concentrated H2SO4, followed by purification and exfoliation in water to yield a colloidal dispersion of single layers. (b) Structural model of graphene, GO and its reduction product RGO. GO is insulating due to broken conjugation in the basal plane. After reduction, RGO becomes conductive but is still a very defective structure compared to graphene. (c) Color coded high resolution TEM images showing the atomic structures of graphene, GO and RGO. The green, purple and blue areas depict ordered, graphitic \( sp^2 \) domains, disordered highly oxidized \( sp^3 \) domains, and holes on the sheet, respectively.\(^{15} \) (Reprinted from [15] with permission from Elsevier.)

2.3 Charge Transport in Disordered System

Since RGO contains a lot of disorder consisting of localized graphene domains along with oxygen functional group, the low temperature transport exhibits hopping transport
phenomenon. In this section, I will present theoretical concepts relevant to charge hopping transport in disordered system.

2.3.1 Hopping Transport

A disorder system with localized states shows a non-vanishing value of conductivity for finite temperature due to electron hopping between localized states, and its conductivity tends to zero as temperature is reduced. The temperature dependent resistance $R(T)$ can be expressed by:

$$R(T) = R_0 \exp\left(\frac{T_0}{T}\right)^\rho$$  \hspace{1cm} (2.7)

where $R_0$ is a prefactor, $T_0$ is a characteristic temperature and $\rho$ is a characteristic exponent, the value of which distinguishes different hopping conduction mechanism.

Miller and Abrahams introduced “random resistor network” model to describe electron hopping between localized states, as shown in Figure 2.6.\(^{16}\) In this model, hopping is performed between two localized states $i$ and $j$, which can be associated with a resistance $R_{ij}$. In the absence of electric field, the same amount of electrons will hop from $i$ and $j$, and an equal number of electrons are reversely transit from $j$ and $i$. While in the presence of an electric field between $i$ and $j$, the two numbers of electrons will be different, hence, a current can flow between the center of $i$ and $j$. This effective current with potential difference between $i$ and $j$ affords to obtain resistance $R_{ij}$, which, in turn, allows to calculate hopping probability between centers $i$ and $j$ with absorption and emission of a phonon. Then, the $R_{ij}$ can be described by:

$$R_{ij} = R_o \exp\left(\frac{2r_y + E_y}{a} \frac{E_y}{k_B T}\right)$$  \hspace{1cm} (2.8)
where \( a \) is the Bohr radius of the electronic state, \( r_{ij} \) is distance and \( E_{ij} \) is energy difference between site \( i \) and \( j \).

Figure 2.6 Miller and Abrahams random resistor network model.

2.3.1.1 Nearest Neighbor Hopping (NNH)

Considering two electron localized states where an energy separation is \( E_0 \) and the nearest neighbor (NN) localized states, an electron can hop from site to site with the assistance of phonons, as shown in Figure 2.7 (a). The hopping mechanism follows, \( p=1 \) from Equation 2.7:

\[
R(T) = R_0 \exp \left( \frac{E_0}{k_B T} \right)
\]  

(2.9)
Figure 2.7 Schematic illustration of (a) nearest neighbor hopping (NNH) and (b) Mott variable range hopping (VRH) behavior at low temperature regime.

2.3.1.2 Mott Variable Range Hopping (Mott VRH)

At even a very low temperature, Mott described that, when there is not enough thermal energy for the charge to go from valance band to conduction band, the charge conduction occurs via hopping among the localized states, as shown in Figure 2.7 (b), which may be at a larger distance. Thus, the energy difference in $E_{ij}$ will be small in hopping conduction. The states will lie around the Fermi level ($E_F$), $E_F-E_0 < E < E_F+E_0$, and width of the energy band is $2E_0$.

For low enough temperature, Mott considered a constant density of state, $n(E)=n(E_F)$. Then, the number of states $N$ becomes:

$$N(E_0)=2n(E_F)E_0$$  \hfill (2.10)

Now, considering the above equation, $R_{ij}$, $r_{ij}$ can be replaced by $[N(E_0)]^{-1/d}$, where $d$ is the dimensionality of the system. In addition, $E_{ij}$ is replaced to $E_0$. Then, the $R_{ij}$ can be given

$$R_{ij} = R_0 \exp\left(\frac{2}{[N(E_0)]^{1/d} a} + \frac{E_0}{k_B T}\right)$$  \hfill (2.11)

$$= R_0 \exp\left(\frac{2}{2n(E_F)E_0}^{1/d} a + \frac{E_0}{k_B T}\right)$$

The energy width $E_0$ that can provide the maximum of hopping probability can be found from the condition $dR/dE_0$. The results are then given to
\[ E_0 = \exp \left( \frac{2k_bT}{[2n(E_F)]^{1/d} da} \right)^{d/d+1} \tag{2.12} \]

After substitution of Equation 2.12 into Equation 2.11, one can obtain Mott VRH by the following:

\[ R(T) = R_0 \exp \left( \frac{T_0}{T} \right)^{d/d+1} \tag{2.13} \]

where \( T_0 \) is characteristic temperature and can be expressed as

\[ T_0 = T_M = \left( \frac{\beta(d)}{k_b n(E_F)a^d} \right) \tag{2.14} \]

where the numerical constant \( \beta \) depends on dimension of the system. The \( a \) is regarded as localization length.

2.3.1.3 Efros-Shklovskii (ES) VRH

Efros and Shklovskii later pointed out that, at low enough temperature, Coulomb interaction should lead to a dip in the density of states (DOS) at the Fermi energy in VRH. \(^{18-20}\) Thus, the DOS near the \( E_F \) is not constant. This is because, when an electron hops from one site to another, it leaves a hole and the system must have enough energy to overcome this electron-hole Coulomb interaction [See Figure 2.8].
Figure 2.8 Schematic illustration of Efros-Shklovskii variable range hopping (ES VRH) behavior at low temperature regime.

An electron transferred from an occupied state \( E_i > E_F \) to an unoccupied state \( E_j > E_F \) gives

\[
\Delta E = E_j - E_i = \frac{e^2}{\varepsilon r_{ij}} 
\]

(2.15)

where \( \varepsilon \) is the dielectric constant. The \( \Delta E \) is equal to the energy difference between state \( i \) and \( j \), and the Coulomb interaction energy (or electrostatic energy) of the electron-hole pair. Thus, this interaction makes the existence of Coulomb blockade of charges between the localized states, which are the most significant difference between ES-VRH and Mott VRH. With vanishing of density of states, density of states satisfies

\[
n(E_j - E_i) = n(E) \leq d \left( \frac{\varepsilon}{\varepsilon'} \right)^d |E|^{d-1}
\]

(2.16)

This is called the “Coulomb gap, \( E_{CG} \)”. Therefore, at low temperature, the density of states near the Fermi level has a parabolic shape in 3D and a linear shape in 2D, and it vanished at the Fermi
level.\textsuperscript{18-20} This results in the temperature dependence of resistance, which can still be described with Equation 2.7, but with $p = 1/2$ in all dimension. The characteristic temperature in 2D then becomes:

$$T_0 \equiv T_{ES} = \left( \frac{2.8e^2}{4\pi\varepsilon_0 k_B\xi} \right)$$

(2.17)

where $\varepsilon_0$ and $\varepsilon$ are the values for permittivity of vacuum and the dielectric constant of the material. For some samples, the disorder may be very high so that $E_{CG}$ is dominant at all measurable temperatures giving only ES VRH. On the other hand, in other relatively low disordered samples, the energy scale is such that the carriers may have enough energy to overcome $E_{CG}$ at all measurable temperatures, which means the density of states is practically constant. In that case, only Mott VRH will be dominant.\textsuperscript{18} At intermediate disorders, it may be possible to see a crossover from ES to Mott VRH with increasing temperature in the same sample.

Additional evidence of ES VRH can also be obtained from electric field dependent transport study at a fixed temperature. Since the energy necessary for hopping can also be obtained from the electric field ($E$) rather than temperature, at high enough electric field, (high bias regime) the temperature dependence is strongly reduced and one enters the regime of field driven hopping transport, where the conduction is given by:\textsuperscript{21-25}

$$R(E) \sim \exp \left( \frac{E_0}{E} \right)^{1/2},$$

(2.18)

with $E_0 = \frac{2k_B T_{ES}}{\varepsilon_0 e\xi}$.\textsuperscript{21-25}

(2.19)

where $T_{ES}$ and $\xi$ represent the same parameters as in Ohmic ES VRH of Equation 2.17.
References


3 DEVICE FABRICATION AND EXPERIMENTAL METHODS

3.1 Introduction

In this chapter, fabrication of reduced graphene oxide (RGO) device and characterization of RGO sheets discussed throughout this dissertation will be reviewed. The entire process strategies are shown in Figure 3.1. First, I will expound on the fabrication of electrode pattern of photo lithography and electron beam lithography (EBL). Next, I will discuss the synthesis of RGO sheets. I will, then, present an overview on how to optimize dielectrophoresis (DEP) assembly of RGO device. Subsequently, I will discuss the electronic transport measurement set-up in both room and low temperatures. Finally, I will discuss the characterization of RGO sheets.
Figure 3.1  Schematic diagram of experimental procedures. Larger features such as contact pads are first defined by photolithography using double layer resist, developed, followed by electron-beam and thermal evaporation of Cr and Au, and standard lift-off. The small size of electrode was defined by means of electron beam lithography (EBL), developed, followed by e-beam and thermal evaporation of Cr and Au, and standard lift-off. The devices were, then, exposed to O$_2$ plasma for 10 minutes to clean residual resists. Next, a small amount (few µl) of RGO solution was assembled via dielectrophoretic (DEP) between the prefabricated source and drain electrodes. Subsequently, the device was measured in both room and low temperature. For characterization of the RGO sheets and device in this study, microscopes were used.

3.2 Fabrication of Metal Electrodes

I have fabricated metal electrodes with combination of photolithography and EBL. I have been using 3 inch heavily doped silicon (Si, 1.5 µm thick) substrates capped with a thermally grown 250 nm thick SiO$_2$ layer, which was purchased from Silicon Quest International. This substrate is used because it is capable of supporting a field effect transistor (FET) structure with backgating. A photolithography is used for large size electrode pattern (or contact pad) and
alignment markers for EBL. Each chip has a total size of $3 \times 3$ mm$^2$ and contains 18 pairs of contact pads. An EBL is used with small size (less than 1 µm) of electrodes.

3.2.1 Photolithography

3.2.1.1 Bi-layer photo resist

Figure 3.2 shows a schematic diagram of the photolithography process. I have used positive bi-layer photo resists for photolithography due to its ease with lift-off of metal electrodes. There is an undercut formed in the Lift-off-Resist (LOR) 3A layer. This undercut makes the lift-off process easier by avoiding a continuous metal deposition through resist and developed area. The LOR, purchased from MicroChem, is spin coated at 3000 rpm for 30 seconds on top of 3 inch Si/SiO$_2$ wafer. Then, the spin coated wafer is baked at 150 °C for 6 minutes. The second layer Shipley S1318, purchased from MicroChem, is spin coated at 5000 rpm for 30 seconds and baked at 100 °C for 3 minutes. The thicknesses of both resists are ~ 500 nm and 1000 nm, respectively, which are confirmed from MicroChem data sheets. It is noted that
if the resists are not uniformly coated on the substrate, it could create discontinuity and inconsistency of electrodes.

Once bi-layer photoresist coating is done, the wafer is then moved to Karl Suess 3 inch UV mask aligner. As shown in Figure 3.2, the process involves three levels: 1) UV source; 2) photomask (NOTE: Top of the mask is glass and bottom of the mask is Cr.); and 3) wafer. I exposed the wafer for 6 seconds. Then, the wafer is developed in CD-26 for 8 seconds and rinsed with deionized (DI) water. This process is done in a clean room in Advanced Microfabrication Facilities at The University of Central Florida.

3.2.1.2 Metallization

Contact metals are deposited on the sample using a combination of electron beam (e-beam) and thermal evaporations under vacuum condition of less than $5 \times 10^{-6}$ Torr. For the sticky layer, I used Cr (3nm thick) by means of e-beam evaporator. The evaporation rate was ~ 0.2 A/s with 10 kV and 0.2 mA of e beam. On top of the Cr layer, I deposited 47 nm of Au using thermal evaporator. The evaporation rate was ~ 0.5 A/s with current rages of ~ 60 to 70 mA. I have been keeping the metal electrode thickness of 50 nm since this thickness is needed for wire bonding.

3.2.1.3 Lift-off

The PG remover obtained from MicroChem was used for lift-off processing. First, the PG remover was warmed at 60 °C on a hot plate and left for 5 minutes. Then, the metalized wafer was immersed into warm PG remover for 10 minutes. To check the process, I used a plastic pipette to squirt the wafer ensuring no metal is left. The process should not take more than 20
minutes since bi-layer photo resists are used. Extra sonication of ~ 20 seconds can help lift-off. After lift-off of the metal, the wafer is rinsed vigorously with Acetone, IPA and DI water, then blow dried with nitrogen gas. Figures 3.3 (a) and (b) show an example of a photo image of photolithography pattern after lift-off and an expanded view of a chip.

3.2.2 Electron Beam Lithography

The key steps in electron beam lithography (EBL) are: i) proper focusing of the beam; ii) correction of electron-beam parameters for each step; iii) alignment of EBL process with reference to the markers from photolithography; and iv) proper lift-off. These parameters were determined from tests that I have performed with the EBL tool in Material Characterization Facilities at The University of Central Florida.

In EBL process, I used a single layer polymethyl-methacrylate (PMMA) for positive e-beam resist. I used a MicroChem 950 PMMA A4 with molecular weight of ~ 950 k. The PMMA was spun onto substrate at 4000 rpm for 60 seconds and baked at 180 °C for 15 minutes. The
thickness of PMMA is \( \sim 150 \) nm. The thickness of metal in the device is 30 nm, so there was no lift-off problem. (NOTE: The maximum thickness of metal is 1/3 of electron beam resist.)

I used nano-patterned-generation-system (NPGS) with Zeiss 5500 scanning electron microscopy (SEM) system. The advantages of NPGS system are interconnection of CAD program and automatic calculation of writing field and writing time. I used an area dose of \( \sim 300 \) \( \mu \)C/cm\(^2\) at 28 kV. The beam aperture size and current are \( \sim 100 \) \( \mu \)m and 30 pA. The writing field of the electrodes was about 500 \( \mu \)m and SEM magnification of \( \sim 450 \). As I mentioned in the previous section, I also defined the alignment maker during the photolithography step which allows for drawing accurately aligned electrode patterns by EBL.

After e-beam exposure, the developing process is performed by using a solution of Isopropyl-alcohol:Methyl-isobutyl-ketone (IPA:MIBK = 3:1 ratio) for 60 seconds and IPA (stepper) for 10 seconds. 3 nm and 27 nm of Cr and Au were deposited. Then, the samples were immersed into warmed Aceton (60 °C) for 1 hour and sonicated for 20 seconds. After the lift-off process, the samples were rinsed with IPA and DI water. Then, the samples were treated in oxygen plasma for 10 minutes to remove any residual organics.

3.3 Synthesis of Reduced Graphene Oxide (RGO)

I have used two types of graphene oxide (GO) sheets for the study. Solution based graphene oxide (GO) was from the collaboration team (Dr. Lei Zhai Group, University of Central Florida Department of Chemistry), and powder based GO was obtained from Cheaptubes Inc.\(^3\) However, the reduction was performed with same recipe. First, I will present the recipe to produce GO by Hummers methods from collaboration work with Dr. Lei Zhai’s group. Then, I
will discuss the production of solution based GO from powder based GO, which is a commercial product. Finally, I will discuss the reduction of GO.

3.3.1 Synthesis of Graphene Oxide Sheets

*Producing Graphene Oxide from Graphite: Modified Hummers Method*

GO was synthesized by a modified Hummers method.\(^4\) Oxidized graphite in water was ultrasonicated to achieve GO sheets followed by centrifugation for 30 minutes at 3000 rpm to remove any unexfoliated oxidized graphite.

*Producing Graphene Oxide from Powder Form*

Commercial product GO was also prepared by modified Hummers method.\(^3\) 15 mg of GO powder was added to a flask containing 15 mL of deionized (DI) water. Then, the GO solution was stirred with a Teflon-coated magnetic stirring bar in a water bath for 24 hours to obtain a good dispersion.

3.3.2 Reduction of GO to Graphene: RGO

Since GO contains a large amount of oxygen functional group, GO is highly insulating material. Therefore, reduction of the functional group is essential to recover electrical conducting material. In this dissertation, I have used chemical hydrazine method.

For chemical conversion from GO to RGO, the pH of the GO dispersion in water (0.1 mg/ml) was adjusted to 11 using a 5 % ammonia aqueous solution. 15 μl of hydrazine solution (35% in DMF) was then added to the mixture. The mixture was heated at 95-100 °C for 1 h and
cooled to room temperature. The change of color in the resultant solution from light-brown to black was the primary indication of GO reduction.

3.4 Dielectrophoresis of RGO

After RGO sheets were synthesized in solution, I have fabricated RGO field effect transistor via Dielectrophoreis (DEP). The advantage of using DEP is for its ability to position RGO sheets at pre-defined positions of the circuit. This technique offers precise positioning without the need of post etching, is quick, and can be done at room temperature. The DEP assembly of RGO sheets was carried out in a probe station under ambient condition. Figure 3.4 (a) shows a cartoon of the DEP set up. I first drop casted a small drop of RGO solution onto the chip. At the same time, an AC voltage was applied to the electrode pair and gave rise to a time averaged DEP force given by:

\[ F_{DEP} = (p \cdot \nabla)E \]  

(3.1)

where \( p \) is the induced dipole moment of the polarizable object and \( E \) is the non-uniform electric field. The strong electric field gradient caused the RGO sheets to align along the field direction and assemble between the prefabricated source and drain electrodes. Figure 3.4 (b) shows a simulation of the magnitude of the electric field and electric field vector, respectively, using a commercial PDE solver called “Flex PDE”. It can be seen here that the strongest uniform electric field gradient is between the electrodes. Figure 3.4 (c) shows photo images of the DEP set-up.
3.5 Measurements

Electrical transport measurements of DEP assembled RGO sheets are performed with typical 3-probe configuration: source, drain and gate, as shown in Figure 3.5. A DC power supply, electrometer (BNC 2090 from National Instrument) and a current preamplifier (DL 1211) capable of measuring sub-pA signal were used. The BNC 2090 has the maximum voltages of 10V. A Keithley 2400 is operated in order to apply gate voltage, allowing a maximum applied voltage of 100V. Additional 1 MΩ resistor was also connected between device and the Keithley 2400 to avoid accidental application of large voltage to the devices. Applying a gate voltage may induce a leakage current through 250 nm SiO₂ layer. Usually, the leakage current is less than 1 nA for up to ± 40 V of gate voltage. Thus, the maximum gate voltage I chose to use is ± 40 V.
The measurement software used is LabVIEW (National Instrument Co.). During the measurements, careful grounding is required to prevent ground-loops that cause parasitic current that could destroy the device.

For room temperature measurement, I have used a probe station. For low temperature measurement, the contact pads of the devices were bonded to a chip carrier with silver wires. The backgate is connected to the metal surface at the bottom of chip carrier then wired to the chip carrier. The chip carrier is, then, loaded into a variable temperature cryostat (He3, cryogenic) for temperature-dependent electronic transport measurements. Figures 3.6 (a) and (b) show the bonded chip carrier and the holder which is located at the end of the cryogenic sample stick.

The cryostat is loaded into a 30 liter He dewar (NacroFAB), as shown in Figure 3.6 (c), where temperature dependent electrical transport measurements are conducted. Measurement temperature varies from 295 K to 4.2 K. For temperature dependent study, lowering of the cryostat needs to be conducted with extra caution at a rate of 0.04 K/s to produce data (e.g. Resistance versus temperature).
3.6 Characterization of RGO sheets

Key points of characterization of GO or RGO sheets are measurement of thickness and carbon to oxygen ratio. Thickness of pristine graphene is about ~ 0.3 nm, while the thickness of GO or RGO is ~ 1 nm since the oxygen functional groups are attached perpendicularly to carbon atom. Atomic forced microscopy (AFM) is commonly used to measure thickness of materials. Since GO or RGO contains a large amount of oxygen functional group, X-ray Photoelectron Spectroscopy (XPS) and Raman are normally used for finding the amount of carbon to oxygen functional group. In this section, I will first discuss the height analysis of the RGO sheets by
using AFM, and then describe the characterization of RGO sheets using XPS and Raman spectroscopy.

3.6.1 Atomic Force Microscopy

AFM can determine the layer thickness at the nanometer scale. I have used Vecco 3000 system. The RGO suspension was spin coated on a mica substrate and examined using AFM. Figure 3.7 displays a tapping-mode AFM image of the RGO sheets along with their height analysis. The lateral dimension of the RGO sheets varies from 0.2 to 1 μm. The line graph represents the thickness of the RGO sheets which varies from 1 to 5 nm. Approximately 70 % of the sheets displayed a height of 1.0 ± 0.2 nm. This height is similar to the height reported in previous studies of single layer RGO sheets. 7-9

Figure 3.7 Tapping-mode AFM images of RGO sheets with a height profile indicating majority of the sheets are single layer.
3.6.2 Raman Spectra

The degree of orderliness in the materials can be identified by Raman spectroscopy, where the G band ($sp^2$) corresponds to the ordered structure and the D band to the disordered structure ($sp^3$) of the material. \textsuperscript{10-11} Here, Raman spectroscopy was performed using a Jobin-Yvon Lab-Ram HR800 (Micro Raman system) composed of a laser (HeNe laser 632.81 nm), a single spectrograph fitted with holographic notch filters, a confocal microscope (Olympus 50x) and 100 μm pinhole rigidly mounted and optically coupled to the spectrograph. The spectrometer was calibrated with a Si standard using a Si band position at 520.49 cm\(^{-1}\).

The spectra of both the GO and RGO show two peaks at 1604 cm\(^{-1}\) (in plane vibration G band), 1345 cm\(^{-1}\) (disordered vibration D band) and 2600-3000 cm\(^{-1}\) (in 2D band), as shown in Figure 3.8. The broader D band with higher relative intensity compared to that of G-band indicates higher disorderliness in the GO and RGO sheets. In addition, the ratio of 2D:G is correlated with the hole mobility of the RGO devices.\textsuperscript{6} This shows that when the ratio increases, the mobility also increases. The average domain size of graphene ($sp^2$) was estimated by the intensity of D and G bands of the RGO sheets using empirical Tunistra-Koening relation. The details of the domain size calculation are discussed in Chapter 5.
3.6.3 X-ray Photoelectron Spectroscopy

X-ray Photoelectron Spectroscopy (XPS) is used to determine the reduction efficiency of GO sheets. Here, XPS experiments were conducted using a Physical Electronics (PHI 5400 ESCA) spectrometer with a Mg Kα X-ray source operated at 300 W and 15 kV. The XPS analysis was done at a base pressure typically below $5 \times 10^8$ Torr. The X-ray exposure time to the sample was minimized (1 cycle and 10 sweeps) to avoid the radiation-induced change in oxidation state of the sample.

Figure 3.9 (a) shows deconvolution of the $C1's$ peak in the XPS spectrum of the GO and RGO sheets. Here, we can see the four components of carbon based atom in different functional groups of GO: (i) the non-oxygenated C-C bond (284.5 eV, red curve); (ii) C-O bond (286.6 eV, green curve); (iii) the C=O bond (287.6 eV, blue curve); and (iv) C(O)O (289.1 eV, cyan curve). Figure 3.9 (b) shows $C1's$ spectrum after reduction of GO sheets (RGO sheets). It can be seen that the peaks for oxygen functional groups were significantly reduced (green and blue
curves), and C(O)O bond (cyan curve) that was present in Figure 3.9 (a) has disappeared in RGO film. In addition, there was another peak at 285.9 eV, which indicated that C bound to nitrogen (N) corresponding to the reduction with hydrazine hydrate. The intensity ratios of the C-C and C-O bonds changed from 1.4 to 7.6 verifying effective reduction of GO and is consistent with previous observations.\textsuperscript{12,15-16}

Figure 3.9 XPS data of a GO and RGO thin film on Si/SiO\(_2\) substrate. The four deconvoluted peaks indicate the non-oxygenated ring carbon C (284.5 eV), C in C-O bond (286.6 eV), carbonyl C (287.6 eV) and carboxylate carbon (O-C=O, 289.1 eV).
References


4 PARALLEL FABRICATION OF RGO FIELD EFFECT TRANSISTOR AND THEIR ELECTRICAL PROPERTIES

4.1 Introduction

As I discussed in Chapter 2, one of most promising advantages in using reduced graphene oxide (RGO) sheets is the possibility of large scale production of graphene through solution route. In this regard, several fabrication methods have been demonstrated such as drop cast, spin coating, inkjet printing, Langmuir-Blodgett, layer by layer assembly, vacuum filtration and Dielectrophoreis (DEP). Amongst these, the DEP technique is most noteworthy; it provides the assembly of graphene devices at selected positions of the circuit with high yield RGO fabrication. There are a few reports discussing the DEP assembly of graphene nanostructures from solution. Burg et al. demonstrated DEP assembly of a few layers (3–10 layers) of insulating GO, which became metallic upon thermal reduction at 450 °C. Kang et al. carried out DEP assembly of 4–13 layers of GO sheets and reduced the GO devices, either chemically using hydrazine or thermally at up to 1000 °C, to restore electrical conductivity. Vijayaraghavan et al. also demonstrated DEP assembly of few layer graphene flakes.

Apart from the high-yield manufacture of RGO device, the electrical conductivity and field effect mobility values for RGO sheets are much inferior to that of pristine graphene. These traits have been attributed to a large amount of disorder present in the RGO sheets. Therefore, a detailed knowledge of charge conduction and quantitative information about the disorder (or defects) in RGO sheets is important for further optimization of reduction techniques and

synthetic strategies to increase conductivity and mobility of RGO towards pristine graphene. Similar strategies have been successfully used for passivating defects in silicon (Si) to fabricate high quality complementary metal oxide semiconductor circuits.

In this chapter, I report on the high yield complementary metals oxide semiconductor (CMOS) compatible FET fabrication using RGO sheets from solution via AC DEP and elucidate the origin of low electrical properties by using space charge limited conduction (SCLC) model. I will first discuss the optimization of the DEP technique for the 100 % high yield assembly of RGO FET. With the application of a backgate voltage, all the devices showed FET behavior with the majority of them demonstrating ambipolar behaviors. The maximum hole and electron mobilities of the devices reached 4.0 and 1.5 cm²/ Vs, respectively. Although the mobility values are comparable with other RGO FET values, these values were much lower than that of pristine graphene. To elucidate the origin of the low mobility, I will show temperature dependent current density (J) -voltage (V) characteristics to explain the nature and density of charge traps in the RGO sheets. I show that the J-V characteristic of the RGO devices measured at different temperatures (295 to 77 K) follows power law behavior, $J \propto V^m$. At low bias, the conduction is Ohmic with $m=1$, while at higher bias voltages $m$ increases from 2 to 3 with reducing temperature signifying space charge limited conduction (SCLC) with a transition from trap free (TF-SCLC) regime at room temperature to exponentially distributed trap (EDT-SCLC) regime at low temperatures. I estimate an average trap density of $1.75 \times 10^{16}$ cm⁻³ for the samples in this study.
4.2 Fabrication of RGO Device Using Dielectrophoresis

4.2.1 Optimization of DEP Parameter

The RGO sheets were assembled between the prefabricated source and drain electrodes using AC dielectrophoresis (DEP). To get a high quality and reproducible device, I first tried different electrode geometries, trapping times, voltages and frequencies of applied AC voltage. A 2 µl of RGO solution was placed onto source and drain electrodes. Different shapes of electrodes geometries were tried first. The shape and size of the electrode geometry was changed by electron beam lithography (EBL) process. For all the different geometries of electrodes, I fixed the AC voltage to 5 V<sub>pp</sub> and used a frequency of 1 MHz on function generator. The length of AC application was 1 minute. For taper shapes of electrodes, I fabricated 300 and 500 nm channel length as shown in Figures 4.1 (a) and (b). They show very high yield fabrication. However, thickness of RGO sheets vary from few nm to 30 nm and thus, difficult to estimate channel length when conductivity is calculated. Next, I applied DEP on round shape electrode as shown in Figure 4.1 (c). This shape gives high yield fabrication and lower thickness of RGO sheets which was less than 5 nm. From the fabrication with different shapes of electrodes, this shape seems to be the best shape to obtain a single layer RGO device. However, it is also difficult to estimate channel width because of 2D properties of RGO sheets. Then, I moved onto the square shape electrodes. As shown in Figures 4.1 (d)-(f), I increased the channel width from 100 nm to 2 µm. The fabrication yield is high for both 100 and 500 nm. For 100 nm channel length of the device, the thickness of the RGO sheets is too high, normally higher than 20 nm, and it may be due to the presence of strong electric field between source and drain. On the other hand, yield of 2 µm channel width is less than 30 % since the average lateral dimension of RGO sheets is less
than 1 μm, hence, the RGO sheets need to be bridged in the channel. Similar behavior was also observed in taper shape as shown in Figure 4.1 (g). Thus, these shapes often result in non-uniform thickness of RGO sheets in the channel. Finally, I fabricated large size channel length and width as shown in Figures 4.1 (h) and (i). The problem with this geometry is non-uniform distribution of RGO sheets in the channel; they tend to scatter all around the channel. It could be solved with increase in concentration of RGO sheets, trapping time and application of AC voltage with decreasing AC frequency. However, I mainly focused on a few reproducible and high yield layers of RGO device. Analysis showed that a box shape electrode with 500 × 500 nm channel width and length is most suitable for RGO sheets.

Figure 4.1 Different shapes of electrode geometries of RGO DEP assembly. (a) Taper shape electrode with 300 nm channel length. (b) Taper shape electrode with 500 nm channel length. (c) Round shape electrode with 600 nm channel length. (d) Box shape electrode with 100 nm × 1 μm of channel width and length. (e) Box shape electrode with 500 × 500 nm of channel width and length. (f) Box shape electrode with 500 nm × 2 μm of channel width and length. (g) Taper shape electrode with 2 μm channel length. (h) Box shape electrode with 20 × 5 μm of channel width and length. (i) Box shape electrode with 20 × 10 μm of channel width and length.
Subsequently, I experimented with different parameters of applied AC voltages and frequency with fixed channel lengths and widths of 500 × 500 nm. I also fixed trapping time of 30 seconds. I started with an AC voltage of approximately 5 V_p,p and changed the frequency of applied AC voltage from 100 kHz, 500 kHz, 1 MHz to 3 MHz, as shown in Figures 4.2 (a)-(d). When the frequency is lower, RGO sheets tend to gravitate toward the outer areas of the electrodes and were more spread out, while RGO sheets tend to assemble only in the center. This result indicates that the trapping time of 30 seconds is a little too long for low frequency of applied AC. However, although 3 MHz produced a cleaner concentration of RGO sheets in the center of the electrode, their device yield was only about 80%.

Figures 4.2 (e)-(h) show application of 3 V_p,p with the frequency range of applied AC voltage, from 100 kHz, 500 kHz, 1 MHz to 3 MHz. As shown in Figures 4.2 (e)-(f), with 100 kHz and 500 kHz, RGO sheets were also spread out similar to 5 V_p,p. However, the amount of RGO sheets on the electrode was less than the amount in application of 5 V_p,p which means that the DEP force is less when lower voltage is applied. Similarly, with 3 MHz, the amount of RGO sheets in the channel was less in 3 V_p,p than in 5 V_p,p as shown in Figure 4.2 (h) and gave lower yield of assembly. Based on this approach, I found the best parameters to be 3 V_p,p and 1 MHz (Figure 4.2 (g)), which gave reproducible few layer RGO devices.
Figure 4.2 (a) Scanning electron microscope (SEM) images of DEP optimization process are shown from (a) to (h). Frequencies of 100 KHz, 500 KHz, 1 MHz and 3 MHz with $5 V_{pp}$ were applied from (a) to (d), respectively while 100 KHz, 500 KHz, 1 MHz and 3 MHz with $3 V_{pp}$ were applied from (e) to (h), respectively.

4.2.2 100 % Yield Fabrication of RGO Device

Upon this optimization process, a 2 μL of RGO solution was drop casted onto the electrode pattern and an AC voltage of $3 V_{pp}$ with a frequency of 1 MHz was applied between the source and drain electrodes for 30 seconds for all of the devices. After the DEP assembly, atomic force microscope (AFM) was used to characterize the RGO devices. Figures 4.3 (a) and (b) show tapping-mode AFM images of two representative devices along with their height analysis. It can be seen that the thickness varies from 2 nm to 10 nm in the channel indicating that up to 10
layers of RGO sheets have been assembled in the channel. The thickness of RGO sheets in the channel varied between 5 and 15 nm. This is typical for all of the devices in this study. The thickness is lower at the edges, demonstrating one or two layers of graphene sheet near the edge, while the thickness is higher in the middle of the channel due to overlap of several individual sheets or folding of sheets. Among the 100 pairs of electrodes that I have used for the DEP assembly, I found that all of the electrodes were bridged by a few layers of RGO sheets giving a 100% device yield. Figure 4.3 (c) shows scanning electron microscope (SEM) image of RGO sheets assembled from one of the devices. Each of the chips contains 18 electrode pairs (E1-E18). The maximum thickness of RGO sheets in the channel varied between 5 nm to 15 nm from device to device. It is not clear why few layers of RGO sheets have been assembled in all the devices despite the presence of a large number of single layers RGO in the solution. However, it is clearly seen that the DEP assembly of RGO at each electrode pair is successful, demonstrating 100 % yield of my assembly method.
Figure 4.3 (a)-(b) Tapping-mode AFM of two RGO devices assembled via DEP along with height profile. The thickness varies from 2 nm to 10 nm indicating that up to 10 layers of RGO sheets have been assembled. (c) Demonstration of high yield assembly: Top: SEM of an active area of a chip containing after DEP assembly. The chip contained 18 pairs of electrodes numbered E1 to E18.
4.3 Room Temperature Transport Properties

4.3.1 Room Temperature RGO FET

Figure 4.4 (b) shows a representative plot of drain current ($I$) versus source–drain voltage ($V$) for one of the RGO devices. The dotted curve represents the as-assembled device, while the solid curve represents the device after mild thermal annealing. The thermal annealing was done in Ar/H$_2$ gas at 200 °C for one hour to improve device performance. The effects of the annealing on the RGO device area explained in the next section. From the linear $I$-$V$ curves, a resistance of 10 MΩ and 980 kΩ was calculated before and after mild annealing, respectively, with an improvement by a factor of ten. All of the devices show similar improvement upon annealing. The measured conductivities of the RGO devices were about 200 S/cm.
Figure 4.4 (a) Cartoon of electronic transport measurement set-up. (b) Current–voltage characteristics of a representative DEP assembled sample before and after thermal annealing at 200°C in Ar/H₂ gas. The two terminal resistance improved by almost an order of magnitude from 10 MΩ to 980 kΩ. (c) I-V₉ characteristic of one of the RGO FET’s before and after thermal annealing. Upon annealing, the mobility improved and Dirac point shifted from V₉ = -20 V to 0 V. (d) I-V₉ characteristic of another device. This device changed from p-type to ambipolar upon thermal annealing.

Figures 4.4 (c) and (d) show transfer characteristics of two representative RGO FETs (device A and device B) where current (I) is plotted as a function of gate voltage (V₉) with fixed source-drain voltage V = 1 V. The field-effect mobility, µ, was estimated from the I – V₉ relation as:

$$\mu = \left( \frac{L}{W C_{OX} V} \right) \left( \frac{\Delta I}{\Delta V_G} \right)$$

(4.1)
where, $L$ is channel length, $W$ is channel width and $C_{ox}$ is capacitance per unit area of the gate insulator.

Figure 4.4 (c) shows the $I-V_g$ characteristics of device A with a maximum thickness of ~5 nm in the middle of the channel. The as assembled device (dashed curve) shows ambipolar behavior with estimated hole and electron mobilities of 0.21 and 0.06 cm$^2$/Vs, respectively. After mild thermal annealing, the mobility value increased to 0.25 and 0.07 cm$^2$/Vs for hole and electron, respectively. In addition, the Dirac point shifted from $V_g = -20$ V to $V_g = 0$ V upon annealing. Figure 4.4 (d) shows transfer characteristics of device B with maximum thickness of ~ 14 nm in the middle of the channel. The as assembled device showed p-type FET behavior with hole mobility of 2 cm$^2$/Vs. Upon mild annealing, it shows ambipolar behavior with Dirac point around zero gate voltage. The estimated hole and electron mobilities are 4 and 1.5 cm$^2$/Vs, respectively.

4.3.2 Annealing Effects on RGO FET

As I mentioned in the previous section, thermal annealing was performed in Ar/H$_2$ gas at 200 °C for an hour to obtain high quality RGO devices. The average conductivity was increased by a factor of 10, as shown in Figure 4.5. In this section, I will discuss the detailed study of annealing effects on the transport properties of RGO sheets.
I observed that the thinner devices show ambipolar behavior, whereas the thicker ones show p-type behavior before thermal annealing. The p-type behavior in thicker devices before annealing is most likely due to the polarization of trapped water and oxygen molecules between the layers which were removed upon mild annealing, transforming the device to ambipolar.\(^5\)

In order to check the effect of moisture on the transport properties, I carried out a controlled experiment on one of the devices. Figure 4.6 shows the I-V\(_g\) curves for the (i) as assembled device (blue curve); (ii) after mild thermal annealed device (black dot curve); and (iii) device exposed in air for 1 month (red curve). Initially, the as assembled device shows p-type behavior, while after annealing, the characteristic was transformed to ambipolar behavior. When exposed to air for a month, the device recovers its original p-type behavior.
Figure 4.6 I-V\textsubscript{g} characteristics of an as assembled device (blue curve), after mild thermal annealing (black dotted curve), and after being exposed to air for a month (red curve). The device recovers its p-type behavior once again after being exposed to air for long periods of time.

However, the resistance did not go back to the same level recorded before annealing which indicated that the resistance and on-current improvement are not correlated to moisture only. So, what other factors cause the resistance improvement and increase in on-current upon mild annealing? Is it due to the improvement of contact resistance by improving mechanical coupling between RGO sheets and electrode, and/or further thermal reduction of already chemically reduced GO sheets?\textsuperscript{6} In order to check whether there was further reduction due to mild annealing, I took X-ray photoelectron spectroscopy (XPS) data on the RGO films before and after annealing. Figure 4.7 (a) shows the XPS of the RGO film before annealing, while Figure 4.7 (b) shows the XPS data after annealing. The only peak that shows a change is the C-O bond (286.6 eV, green curve) where I observed the C-C to C-O ratio change from ~8.0 to 14 before and after annealing, respectively.
Figure 4.7 (a) XPS data for RGO device before annealing. (b) XPS analysis of RGO sheets upon annealing at 200 °C in Ar/H₂ environment for 1 hour. The C-C to C-O ratio is reduced by ~ 40% due to the annealing process.

Such observation indicates that there may be a marginal reduction due to annealing. Additionally, contact resistance improvement cannot be ignored. In multi-layer RGO sheets, there are some interface gaps between sheets, and sheets and electrodes. The interface gap possibly affected the conductivity and mobility of the device. The thermal annealing possibly helped reduce the size of the interface gaps, as shown in Figure 4.8. Also, the inside-vacuum measurements possibly reduced moistures between layers.
Contact resistance improvement upon annealing in similar conditions has been observed in DEP assembled carbon nanotube devices, and it is not surprising that DEP assembled graphene devices can also show similar improvement. Additional experiments are needed to separate the effect of reduction and contact resistance. I also took an AFM image after the annealing and did not notice any morphology or height change.

Overall, 60 % of the DEP assembled RGO transistors showed p-type, while 40 % of the transistors showed ambipolar behavior before thermal annealing. After mild thermal annealing, all ambipolar RGO FET remained ambipolar with increased hole and electron mobility, while 60 % of the p-type RGO devices were transformed to ambipolar. The maximum hole and electron mobility of the RGO FET were 4.0 and 1.5 cm²/Vs, respectively.

4.4 Electrical Breakdown of RGO sheets

Before measuring temperature dependence of I-V characteristics of RGO sheets, I have estimated the limitation of applied voltage by using electrical breakdown voltage of RGO sheets.
Figure 4.9 (a) shows the $I$-$V$ characteristics of RGO sheets during an electrical breakdown. With increasing voltage, the current increased in a non-linear fashion. At $V=8.2$ V, the current suddenly drops to pA range, signaling that an electrical breakdown of RGO has occurred. The breakdown current is about 70 $\mu$A which corresponds to the current density of $2.8 \times 10^4$ A/cm$^2$. In order to avoid electrical breakdown during the measurements, I limited the measurement bias voltage from -5V to 5V. Figure 4.9 (b) shows SEM image of electrical breakdown of RGO sheet.

4.5 Temperature Dependent Transport Properties

In this chapter, I focused on temperature dependent transport properties of RGO sheets. In the previous chapter, I reported that the maximum hole and electron mobility of the RGO FET were 4.0 and 1.5 cm$^2$/Vs, respectively. While the average mobility values of RGO sheets are
about 0.7 and 0.6 cm²/Vs for hole and electron. In this chapter, I am dealing with the average mobility RGO FET devices with hole mobility ranges of 0.4 to 1 cm²/Vs. A total of nine devices were investigated.

4.5.1 Temperature Dependent I-Vg Characteristics

In order to study charge transport properties of the DEP assembled RGO FETs in more detail, I carried out temperature dependent electronic transport measurements from 295 K to 77 K. Figure 4.10 (a) shows transfer characteristics (I-Vg) of one of the samples measured at different temperatures with fixed source-drain voltage 0.5 V. For the unified view of all I-Vg curves, the recorded current for 200 K, 150 K, 100 K, and 77 K were multiplied by 3.3, 6.3, 15.4, and 26.5, respectively. The plot indicates that the ‘V’ shape of the ambipolar transfer characteristics is more pronounced and shows clear Dirac point (Vg=0) with decreasing temperature which is similar to what is observed in pristine graphene indicating that pristine graphene domains are preserved within the processed RGO. The temperature dependence of hole mobilities were 0.71, 0.31, 0.23, 0.11, and 0.07 cm²/Vs, and electron mobilities were 0.65, 0.3, 0.2, 0.1 and 0.6 cm²/Vs for temperature of 300, 200, 150, 100 and 77 K, respectively.
Figure 4.10 I-V$_g$ curve of a representative RGO FET measured at different temperatures. The currents for 200, 150, 100, and 77K were multiplied by 3.3, 6.3, 15.4, and 26.5, respectively.

4.5.2 Temperature Dependent I-V Characteristics

Figures 4.11 (a) and (b) show the $I$-$V$ characteristics of one of devices at various temperatures measured from -5 V to 5 V with $V_g=0$. The $I$-$V$ curves are highly symmetric at all temperatures. In addition, the $I$-$V$ curve became increasingly nonlinear with decreasing temperature. The nonlinearity in $I$-$V$ curves in disordered semiconductor systems has been explained using (i) Fowler-Nordheim (FN) tunneling, (ii) Schottky barrier (SB) between metal electrode and semiconductor, and (iii) space charge limited conduction (SCLC).
Fowler-Nordheim tunneling can be ruled out as in FN model, the \( I-V \) curves are independent of temperature, while the \( I-V \) curves here are highly sensitive to temperature. In addition, the model does not allow having current in low voltages regime. Therefore, I only focused on SB and SCLC model.

Figure 4.11 (a) Current – Voltage \((I-V)\) characteristics at different temperatures for a typical device. (b) \( I-V \) curves at different temperatures plotted in semi log scale to clearly show highly symmetric nature of the curves. (c) Current density \((J)\) versus voltage \((V)\) plotted in a log-log scale for different temperatures. (d) Expanded view of the SCLC regime. For clarity, \( J \) at 77K was divided by 1.2.

4.5.3 Schottky Barrier Model

In general, the \( I-V \) curve of a metal-semiconductor-metal junction should be highly asymmetric if the Schottky barrier (SB) dominates. Previous studies of individual GO devices and GO thin films showed asymmetric non-linear \( I-V \) curve and was explained using SB model. However, the \( I-V \) curves here are highly symmetric [See Figure 4.11 (b)] giving evidence that charge transport is not dominated by SB. In SB model, the value of current \( I \) is given by:
where $A$ is constant, $\Phi$ is Schottky barrier height and $k$ is Boltzmann constant. In order to see whether SB model dominates in RGO sheet, I plot in Figure 4.12 $I/T^2$ versus $1000/T$ in a semi-log scale. The bias voltage was kept fixed at 0.5 V for all temperatures. For a good fit, a straight line is expected. It can be clearly seen that the data does not fit well to SB model. Therefore, charge transport of the RGO sheets is mainly governed by the intrinsic sheets properties, rather than the contact between RGO and Au electrodes.

Figure 4.12 Fitting of current ($I$) with SB model for a typical device. Solid squares represent the data points, while the dashed line is a fit to SB model. The fitting is not good. Bias voltage was 0.5 V.

4.5.4 Transition from Trap Free SCLC and Exponential Trap Distribution of SCLC

Now, I will discuss space charge limited conduction (SCLC) mechanism. SCLC occurs in low mobility semiconductors when injected charge density exceeds the intrinsic free carrier
density of the material. Analysis of the current density–voltage ($J$-$V$) characteristics using the SCLC model is one of the experimental methods for the detection of charge trap states in disordered semiconductors. Here, two types of SCLC are introduced: (i) trap free SCLC behavior and (ii) trapped-SCLC behavior. In the absence of any trap states or when trap states do not dominate the transport, the $J$-$V$ characteristics are described using the following:

$$J = 9\varepsilon_0 \varepsilon_r \mu V^2 / 8d^3$$

(4.3)

where $\varepsilon_0$ is the permittivity of free space, $\varepsilon_r$ the dielectric constant of the RGO, $\mu$ is the charge carrier mobility, and $d$ is the spacing between electrodes.$^9$

However, in presence of trap states that is exponentially distributed in energy, the $J$-$V$ relationship is given by:

$$J = \frac{\mu N_v}{q^{l+1}} \left( \frac{2l+1}{l+1} \right)^{l+1} \left( l \frac{e\varepsilon_0}{l+1 N_t} \right)^l \frac{V^{l+1}}{d^{2l+1}}$$

(4.4)

where $l$ is an exponent and should be greater than 1, $q$ is the electronic charge, $N_v$ is effective density of states, and $N_t$ is the trap density.$^{10}$ By plotting $J$ and $V$ in log-log scale, one can determine the value of exponent $m$. For trap free (TF-SCLC) regime, $m=2$, while for exponentially distributed trap (EDT-SCLC) regime $m=l+1>2$. 

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In order to examine whether the data can be explained using SCLC model, I have plotted, in Figure 4.13 (a), $J$ versus $V$ curves at different temperature in a log-log scale. The dotted symbols are the experimental data points and the solid lines are a fit to $J \propto V^m$. At low voltages, $m$ equals 1 at all temperatures signifying Ohmic conduction. However, at higher voltages, $m$ deviates from 1. $V_{th}$, the onset voltage where log $J$ – log $V$ curves begin to inflect to higher slope region, shifts to lower voltage with decreasing temperature. For $V > V_{th}$, $m=2$ at room temperature implying TF-SCLC regime. However, as the temperature is reduced, the value of $m$ for $V > V_{th}$ is increased to 2.3 at 200 K, 2.6 at 150 K, 2.8 at 100 K and 3 at 77 K for sample A. The $J-V$ curves for higher values of $V$ are more clearly shown in Figure 4.13 (b). For these temperatures, the conduction is governed by traps that are exponentially distributed in energy (EDT-SCLC).

A transition from TF-SCLC regime at room temperature to EDT-SCLC regime at low temperature can occur for the following reason: At room temperature, the free career density is
higher than the trap density. However, as the temperature is reduced, free carrier density is also reduced and the trap states start to dominate by localizing charge carriers and enter EDT-SCLC regime with \( m > 2 \).

### 4.5.5 Calculation of Trap Density Using SCLC Model

More quantitative information about traps can be obtained from characteristic voltage \( V_c \). If charge traps are distributed in energy, they will be gradually filled with increasing electric field at all temperatures, and at a certain critical voltage, all traps will be filled. According to Kumar et al.\(^{11}\) this critical voltage is independent of temperature and is given by:

\[
V_c = qN_t d^2 / 2\epsilon_r \epsilon_0
\]

By extrapolating the \( J-V \) curves, I can obtain values for \( V_c \) and calculate trap density \( N_t \). In Figure 4.14, I extrapolate the log \( J \) and log \( V \) characteristic at higher bias voltages for all temperatures except room temperature. \( V_c = 10 \) V was found.

![Figure 4.14 Extrapolation of the \( J-V \) curves at low temperatures plotted in log-log scale for device A. From this plot, I determine the temperature independent crossover voltage \( V_c = 10 \) V.](image)
In order to calculate the trap density from $V_c$, I need to know the dielectric constant, $\varepsilon_r$, of RGO. The value of $\varepsilon_r$ can be calculated by using:

$$\varepsilon_r = n^2 - k^2$$  \hspace{1cm} (4.6)

where $n$ and $k$ are refractive index and extinction coefficient of RGO film, respectively. The $n$ and $k$ are given by Cauchy dispersion formula:

$$n(\lambda) \approx A_n + \frac{B_n}{\lambda^2}, \text{ and } k(\lambda) \approx A_k + \frac{B_k}{\lambda^2}$$  \hspace{1cm} (4.7)

where $\lambda$ is the wave length, and $A_n, B_n, A_k,$ and $B_k$ are Cauchy coefficient. Jung et al.\textsuperscript{12} reported Cauchy coefficient of few layer thermally reduced GO sheets as $A_n \sim 1.99, B_n \sim 3000 \text{ nm}^2, A_k \sim 0.69$, and $B_k \sim 1500 \text{ nm}^2$, and $\lambda$ as 517nm. By using these values, I obtained $n = 1.991$ and $k = 0.696$ and calculated $\varepsilon_r \sim 3.5$. Using this value, I obtained trap density $N_t = 1.54 \times 10^{16} \text{ cm}^{-3}$.

Similar EDT-SCLC regime at low temperatures was observed in all nine samples that I have measured. In Table 4.1, I summarized all measured RGO devices where I tabulate room temperature hole mobility, and $V_c$ and $N_t$ values. All measured devices show similar trap density. The average trap density was about $1.75 \times 10^{16} \text{ cm}^{-3}$. The value of trap density is similar to what has been reported for CdSe nanocrystal and amorphous polymer semiconductors.\textsuperscript{13}

An exponential distribution of trap in energies is expected for the traps originating from surface defects and structural disorders.\textsuperscript{14} When GO is produced via oxidation, some C–C bonds can break creating vacancies.\textsuperscript{15} During the reduction process, carbon can also get eliminated from the GO backbone.\textsuperscript{16} Although this has been theoretically shown for thermal reduction cases, such study for chemical reduction cases is yet to be done. In addition, line defects such as wrinkles and folding of RGO sheet also create defects.\textsuperscript{17} Because of the presence of a large
number of trap states, charge in the gate would induce charge in the traps rather than free charge carrier in the semiconducting RGO sheets causing a low mobility in these sheets. This study suggests that a large number of trap states exists in RGO and calls for more theoretical and experimental investigations to understand how the trap states are created and can be minimized.

Table 4.1 The values for room temperature hole mobility, cross over voltage ($V_c$), and trap densities ($N_t$) for all nine samples that I measured.

<table>
<thead>
<tr>
<th>sample</th>
<th>Hole mobility (cm²/Ns)</th>
<th>$V_c$ (V)</th>
<th>$N_t$ ($10^{16}$cm⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.72</td>
<td>10.0</td>
<td>1.54</td>
</tr>
<tr>
<td>B</td>
<td>0.67</td>
<td>10.0</td>
<td>1.54</td>
</tr>
<tr>
<td>C</td>
<td>0.72</td>
<td>12.5</td>
<td>1.90</td>
</tr>
<tr>
<td>D</td>
<td>0.48</td>
<td>10.0</td>
<td>1.54</td>
</tr>
<tr>
<td>E</td>
<td>0.38</td>
<td>11.5</td>
<td>1.80</td>
</tr>
<tr>
<td>F</td>
<td>0.96</td>
<td>12.0</td>
<td>1.85</td>
</tr>
<tr>
<td>G</td>
<td>0.71</td>
<td>11.5</td>
<td>1.80</td>
</tr>
<tr>
<td>H</td>
<td>1.05</td>
<td>12.5</td>
<td>1.93</td>
</tr>
<tr>
<td>I</td>
<td>0.68</td>
<td>11.0</td>
<td>1.70</td>
</tr>
</tbody>
</table>

4.6 Conclusion

I demonstrated the first ever high yield fabrication of field effect transistors (FET) using chemically derived RGO sheets. The RGO sheets, suspended in water, were assembled between prefabricated gold source and drain electrodes using AC dielectrophoresis (DEP). The two terminal resistances of the devices were improved by an order of magnitude upon mild annealing at 200 °C in an Ar/H₂ environment for 1 hour. All of the devices showed FET behavior with the application of a gate bias, with the majority of them demonstrating ambipolar behavior. The
maximum hole and electron mobility of the RGO FET were 4.0 and 1.5 cm$^2$/Vs, respectively. These values were much lower than pristine graphene due to the presence of residual disorders including oxygen functional group and topological defects in the sheets. To elucidate the nature and density of defects in RGO sheets, I measured and analyzed temperature dependent current-voltage characteristics at intermediate temperature (down to 77 K). I showed that at low bias voltage the conduction is Ohmic, while at high bias voltage the conduction becomes space charge limited conduction (SCLC). At room temperature, the conduction is governed by trap free SCLC while at a lower temperature it is dominated by traps that are exponentially distributed in energy. I estimated an average trap density of $1.75 \times 10^{16}$ cm$^{-3}$. I believe that the high yield fabrication of FETs using graphene nanostructures is a significant step forward in realizing scaled up fabrication of graphene based nanoelectronic devices. In addition, quantitative studies of charge traps using SCLC presented in this work will facilitate further development of strategies for the chemical modification of RGO surfaces to passivate traps. In turn, these strategies will help improve the carrier transport by providing quantifying evidences of the developed strategies of passivating defects in order to fabricate high quality solution processed graphene devices.
References


5 EFROS-SHKLOVSKII VARIABLE RANGE HOPPING TRANSPORT IN RGO SHEETS*

5.1 Introduction

In chemical structure, graphene oxide (GO) has a wide range of oxygen functionalities, such as hydroxyl and epoxy groups on basal plane, and a host of functional groups at the edges.\textsuperscript{1-14} These functional groups produce isolated and localized states of graphene domain which contributes to the absence of percolating pathways among $sp^2$ graphitic domains leading to electrical insulating properties. By chemical and thermal reduction treatments, significant amounts of these oxygen functional groups are removed, and conductivity is restored producing reduced graphene oxide (RGO).\textsuperscript{6,15-18} Interestingly, the electronic conductivity properties of the RGO sheets are strongly influenced by the amount of residual oxygen functional groups which can be tuned by varying amount of carbon to oxygen functional groups.

Functionalization of graphene creates disorders and the low temperature electronic transport properties of these structures are akin to that of disordered semiconductors where electron localization and hopping conduction play a significant role. Thus, understanding the electron transport properties of RGO is of great significance to realize the overarching goals of functionalized graphene.

In this chapter, I will present significant new understanding of the electron transport properties of RGO using low temperature electron transport measurements. At very low temperature (down to 4.2 K), we observe Coulomb blockade (CB) and Efros-Shklovskii variable

range hopping (ES VRH) conduction in RGO implying that RGO can be considered as a graphene quantum dots (GQD) array, where graphene domains act like QDs while oxidized domains behave like tunnel barriers between QDs. This was further confirmed by studying RGO sheets of varying carbon $sp^2$ fraction from 55 – 80 % and found that both the localization length and CB can be tuned. From the localization length, we estimate tunable band gap of RGO sheets with varying carbon $sp^2$ fraction.

5.2 Graphene Quantum Dot Arrays in RGO sheet

RGO should behave as a two dimensional array of graphene quantum dots (GQD) which should be verified from low temperature electron transport measurements. Previous electrical transport studies of RGO in limited temperature range show 2D Mott variable range hopping (VRH), which is not expected from a QD array model.\textsuperscript{19-21} Additionally, Mott VRH neglects the Coulomb interaction between localized graphitic domains which may be significant at low temperatures as recent study of individual 10 nm sized graphene quantum dots show room temperature Coulomb blockade (CB).\textsuperscript{22-23} It is, therefore, quite puzzling why CB effect was not observed in low temperature transport of RGO sheets. A clear understanding of electron transport properties of RGO sheet is still lacking which is of great significance for the development of RGO as an important electronic and optoelectronic material. Since the GQD size is tunable during the oxidation and reduction process, this study suggests that RGO will find many novel electronic and optoelectronic applications through tuning of GQD sizes.
5.2.1 Coulomb Blockade: Middleton Wingreen Model

Figure 5.1 (a) shows current-voltage (I-V) characteristics of a representative device at 30, 25, 20, 15, 10 and 4.2 K. The backgate voltage $V_g$ was kept fixed at 0 V. With decreasing temperatures, the $I$-$V$ curves become increasingly nonlinear. However, all the curves are highly symmetric. As the temperature is lowered to less than 15 K, a complete suppression of current below a threshold voltage ($V_t$) was observed. Similar current suppression was observed in a previous study of individual GO devices with highly-asymmetric $I$-$V$ curve and was explained by a Schottky barrier (SB) between metallic contact and GO.\textsuperscript{24} However, as I discussed in Chapter 4, the $I$-$V$ curves I observed are highly symmetric giving evidence that the current suppression and symmetric nonlinear behavior is not due to SB. Rather, such current suppression is due to CB of charges, as at low temperatures there is not enough energy for the charges to overcome Coulomb charging energies of the QD array formed by graphitic domains. In this scenario, the RGO sheet behaves as a GQD array where graphitic domains are quantum dots, and oxidized domains are tunnel barriers.
Figure 5.1 (a) Current($I$–voltage($V$) characteristics of a representative RGO device at temperatures 30, 25, 20, 15, 10 and 4.2 K. Below 15 K, the current is zero for $V<V_t$ due to Coulomb blockade of charges. Inset: AFM image of the device. Scale bar = 500 nm. (b) $I$ vs. $(V-V_t)/V_t$ curves plotted in a log-log scale. Slope of the curves gives the value of exponent $\alpha = 3.1$, 3.3, and 3.4 at 4.2 K, 10 K, and 15 K, respectively.

Theoretical studies of QD arrays by Middleton and Wingreen (MW) predict that the $I$-$V$ curves should follow the relation below:

$$I \propto \left( \frac{V-V_t}{V_t} \right)^\alpha, \text{ for } V>V_t$$

(5.1)

where $\alpha$ is the scaling exponent that depends on the dimensionality of the arrays.\textsuperscript{25-26} Although this theory was developed for nanocrystal arrays of uniform sizes (monodisperse array), experimentally, it was found to be true for polydispersed array as well.\textsuperscript{26-27} Figure 5.1(b) shows $I$ plotted versus $(V-V_t)/V_t$ in a log-log scale using $V_t = 0.18, 0.24, 0.28$ V at $T = 15, 10, \text{ and } 4.2$ K, respectively. The symbols are the experimental data points, while the solid lines are fits to the above equation. From the fits, I obtained $\alpha = 3.1$, 3.3 and 3.4 at 4.2 K, 10 K, and 15 K, respectively. For a two-dimensional array of nanoparticles, the theoretical value of $\alpha$ was predicted as 1.6, while numerical simulations yielded 2.0.\textsuperscript{25} However, in previous experimental
studies of two dimensional metal nanocrystal arrays, the exponent $\alpha$ was reported to vary from 2 to 2.5 which depends on size distribution, while for quasi 2D system with multilayered nanoparticles the value was 2.6 to 3.0.\textsuperscript{26-30} Although system in this study is a quasi-2D system, the $\alpha$ values are slightly higher than what has been reported. Recent experimental and computer simulations involving gold nanoparticles array with strong topological inhomogeneity show large scaling exponents $\alpha \approx 4.0$ as shown in Figures 5.2 (a) and (b).\textsuperscript{31-32}

Figure 5.2 (a) A simulated Au nanoparticle network structure of the type used in transport calculations. (b) $I$-$V$ characteristic (log-log plot) of a cellular nanoparticle network measured at 4.5 K across an electrode gap width of 500 nm. The inset is an AFM image ($3 \times 3 \, \mu\text{m}^2$) of the network. The $I$-$V$ curve is associated with an average exponent, $\alpha$ of 3.7. (Reprinted from [31] with permission from American Chemical Society)

Since RGO has a lot of topological defects which comes from oxidation and reduction process, the high value of $\alpha$ is in agreement with charge transport in an inhomogenous quasi 2D QD array network. In Figure 5.3, I show a schematic of RGO as a GQD array with strong topological inhomogeneity. The light gray areas represent GQDs, and the white regions represent
oxidized carbon groups and topological defects. This figure shows that the GQDs are isolated (or localized) by oxidized carbon atom and topological defect, and there is a strong size distribution of GQDs. The lines between GQDs indicate tunnel barriers. More details on the effects of these topological defects on RGO sheet will be discussed in Section 5.4 below.

Figure 5.3 Schematic of RGO as GQD array. The light gray areas represent GQDs, the white regions represent oxidized carbon groups and topological defects. The lines between GQDs represent tunnel barriers.

Figure 5.4 shows $V_t$ plotted versus $T$ from which I see that $V_t$ increases linearly with decreasing $T$. Extrapolation of the $V_t$ plot to 0 K provides the global threshold voltage $V_t(0) = 0.32$ V. Similar $I-V$ curves were observed for all 8 samples with $\alpha$ varying from 2.52 to 2.80 and $V_t(0)$ varying from 0.32 to 0.42. For an array of nanoparticles of uniform size, $V_t(0)$ can be expressed as:

$$V_t(0) \approx E_C(\beta N)$$  \hspace{1cm} (5.2)
where $E_c$ is charging energy of a QD, $\beta$ is a prefactor whose value depends on the dimensionality and arrays geometry (for a 2D array $\beta = 0.3$), and $N$ is the number of QDs in the conduction path. From here, I can estimate the number of GQDs in the array contributing in the charge transport, but $E_c$ needs be estimated first.

Figure 5.4 $V_t$ as a function of $T$. From the plot, $V_t(0)$ was estimated as 0.32 V.

5.2.2 Charging Energy: Classical Orthodox Model (Estimation of GQD size)

In order to calculate the $E_c$ of the GQDs, I measured $I$ as a function of gate voltage ($V_g$) at temperatures $T = 4.2$ to 120 K as shown in Figure 5.5. For clarity, the data in Figure 5.5 (a) is plotted in a semi-log scale with $I$ at 50, 60 and 70 K were divided by a factor of 1.5, 2, and 3.5 respectively. The reproducible peaks in $V_g$ correspond to single electron tunneling (Coulomb oscillations) through GQD arrays. The bias voltage was kept fixed at $V = 0.3$ V. The peaks in $V_g$ are not periodic, in agreement with the sequential tunneling of charges through multiple QDs. Such Coulomb oscillations have never been observed in previous studies of 2D metallic or
magnetic QD array systems. This result may be due to the fact that the density of states (DOS) in those systems is higher and gate voltage has negligible effect in DOS. While in RGO, the DOS is low, allowing the gate to tune the DOS giving rise to Coulomb oscillations. As the temperature is increased from 4.2 K to 120 K, two important features can be noticed. The peaks around $V_g = 0$ wash out around 70 K corresponding to a thermal energy of 6.2 meV. This observation is more clearly shown in Figure 5.5 (b), where I plot $-10 < V_g < 10$ V regime up to $T = 70$ K of Figure 5.5 (a). For clear presentation, curves from bottom to top were multiplied by a factor of 49, 41, 31, 23, 17, 12.5, 9, 6.7, 3.5, and 2.2, respectively. The other peaks survive up to 120 K, as shown in Figure 5.5 (c), which corresponds to a thermal energy of 10 meV.
Figure 5.5 (a) Current ($I$) as a function of gate voltage ($V_g$) for $T = 4.2, 10, 15, 20, 25, 30, 35, 40, 50, 60$ and $70$ K. The reproducible peaks correspond to Coulomb oscillations. For the unified view, $I$ at 50, 60 and 70 K were divided by 1.5, 2, and 3.5. At 70 K, peaks around $V_g=0$ were washed out. This is more clearly shown in (b). For clarity, curves from bottom to top in (b) were multiplied by a factor of 49, 41, 31, 23, 17, 12.5, 9, 6.7, 3.5, and 2.2, respectively. (c) $I$-$V_g$ curves for $T = 80 - 120$ K with a step of 10 K. At 120K, all the oscillations were washed out. Bias voltage was 0.3 V.

From the semi classical orthodox theory of CB, the charging energy $E_c$ required to add an electron to a QD is given by:

$$E_c = \frac{e^2}{2C_z}$$  \hspace{1cm} (5.3)

where $C_z$ is the total capacitance which depends on the size of each QD and their inter-dot separation. In order to observe the Coulomb oscillations, $E_c$ should be larger than thermal energy $k_BT$. Therefore, temperature dependent data in this study give an estimate of $E_c$ to vary from $6.2$ – $10$ meV. I suggest that this variation in charging energy is indicative of a large size distribution of GQDs in the transport pathway (polydispersed GQD array).
Using the $E_c$ values, the total capacitance is estimated to vary from $C_\Sigma = 8$-13 aF. Neglecting the size variation for the time being, $C_\Sigma$ can also be estimated from the geometrical consideration and can be written as:

$$C_\Sigma = C_g + 9C$$  \hspace{1cm} (5.4)  \\
where $C_g \approx 4\pi\varepsilon\varepsilon_0 r$  \hspace{1cm} (5.5)  \\
$$C \approx 2\pi\varepsilon_0\varepsilon_0 r\ln\left(\frac{r+d}{d}\right)$$  \hspace{1cm} (5.6)

are self-capacitance and mutual capacitance of QDs respectively.\textsuperscript{27} Here, $r$ is the radius of GQD, $2d$ is spacing between QDs, $\varepsilon$ is the dielectric constant of RGO which is calculated in the previous chapter, $\varepsilon_0$ is value for permittivity of vacuum and the factor 9 is the average number of nearest neighbors of each QD in a quasi 2D system.\textsuperscript{27,34} The factor 9 was estimated as follows: For 2D and 3D hexagonal arrays, each nanocrystal has between 6 and 12 nearest neighbors. It was estimated in ref 27 and 34 that for a quasi 2D array, each GQD has ~ 9 nearest neighbors on average. By comparing experimental value and theoretical equation of $C_\Sigma$, I can calculate the value of $r = 2.5$ to 4 nm (domain size 5 - 8 nm) using $d = 0.75$ nm. These values obtained from electron transport spectroscopy are in excellent agreement with microscopic studies using TEM which highlighted that the size of graphitic regime varies from 3 to 10 nm.\textsuperscript{35-36} I used $d = 0.75$ nm as the recent TEM study showed that the typical size of oxidized or defective region varies from 1-2 nm\textsuperscript{35}, giving an average value of $2d = 1.5$ nm. The calculated domain size of GQD is also in good agreement with the domain size obtained from Raman study. An estimate of graphene domain size can also be obtained by comparing the intensity of D and G peaks of the Raman spectrum of the RGO sheets using the empirical Tunistra-Koening relation.\textsuperscript{37}

$$I(D)/I(G) = C(\lambda)/L_a$$  \hspace{1cm} (5.7)
where \( C(\lambda) \) is wavelength of light nm and \( L_a \) is graphene domain size. I obtained a mean domain size of \( \sim 4 \) nm.

I can now estimate the number of GQDs in the conduction pathway \((N)\) of the array using the global threshold voltage formula, Equation 5.2, \( V_t(0) \approx E_c (\beta N) \). Using an average value of \( E_c \) to be 8.1 meV, I estimated \( N = 131 \). This estimate is a slightly overestimation since considering the average size of each dot as 6.5 nm and average inter-dot separation of 1.5 nm, I would expect about 65 QDs in 500 nm channel. The discrepancies may be due to the fact that I am using MW formula which neglects size disorder that can have a great influence in \( V_t \). For example, if I consider that the smallest dot size has the most influence in the determination of \( V_t \) as pointed out by Muller et al. \(^{38}\), then I obtain a more reasonable value of \( N \sim 90 \).

### 5.2.3 Signature of Efros-Shklovskii (ES) VRH

In order to further understand the electronic transport mechanism of the GQD array, I observed the temperature dependence of the resistance of the devices in this study. Temperature-dependence of resistance can provide evidence about size distribution and the degree of disorder of the GQD array. Figure 5.6 (a) shows the resistance \((R)\) versus temperature \((T)\) plot in the temperature range of 250-30 K for one of the devices. It can be seen that \( R \) changes by over three orders of magnitude over this temperature range. \( R \) was calculated by measuring the current at a constant \( V = 100 \) mV as the temperature was lowered (see solid line in Figure 5.6 (a)). I have also measured \( I-V \) curves at a few selected temperatures and obtained the \( R \) values from the Ohmic part of the \( I-V \) curves (open circle in Figure 5.6 (a)). The \( R \) values of the two
measurements were in agreement. Below 30 K, the $I$-$V$ curves were non-Ohmic under 100 mV and those data were discarded from this plot.

According to the QD array model, the temperature dependent resistance $R(T)$ is given by

$$R(T) = R_0 \exp\left(\frac{T_0}{T}\right)^p$$  \hspace{1cm} (5.8)

where $R_0$ is a prefactor, $T_0$ is a characteristic temperature and $p$ is a characteristic exponent the value of which distinguishes different hopping conduction mechanism.

If QDs are monodispersed, the temperature dependence of resistance should follow thermally activated behavior, $p=1$, whereas, if the nanocrystals have significant size variation (polydispersed), it should follow Efros- Shklovskii (ES VRH), $p=1/2$. Fitting resistance data with different behavior can be tricky, and the same data can often fit several behaviors (such as $p=1$, $1/2$, and $p=1/3$). A better way of determining the exponent value is to consider a generalized formula, and then calculate the value of $p$ from reduced activation energy ($W$):

$$W = -\frac{\partial \ln R}{\ln T} = p\left(\frac{T_0}{T}\right)^p$$  \hspace{1cm} (5.9)

where $W$ is the reduced activation energy and $A$ is a constant. This leads to the form of

$$\ln W = A - p \ln T.$$

Figure 5.6 (b) shows $\ln W$ plotted versus $\ln T$. From the slope (indicated by the red line) of this curve, I obtained $p = 0.48 \pm 0.05$, which is consistent with ES VRH over the whole temperature range. For comparison, I have also plotted two lines for $p =1/3$ and $p =1$ which unequivocally show that the transport is only described by $p =1/2$ model. In previously reported data on single layer RGO devices, 2D Mott VRH ($p =1/3$) was reported.\textsuperscript{19-21}
Figure 5.6 (a) Resistance ($R$) versus temperature ($T$) in a semi-log scale showing four orders of change in $R$ for $T = 30$-$250$ K. The solid line represents $R$ measured at a fixed $V=100$ mV as $T$ was decreased. The open symbols show $R$ measured from the Ohmic part of the $I-V$ curves measured at a few selected $T$. (b) Reduced activation energy $W = -\frac{\partial \ln R(T)}{\partial \ln T} = p(T_0/T)^p$ plotted vs $T$ on a log-log scale. From the slope of this plot, I obtained $p = 0.48 \pm 0.05$ corresponding to the ES VRH. For a comparison I also show lines with $p = 1$ (activated hopping) and $p = 1/3$ (Mott VRH). The data does not fit with those models. (c) $R$ in log scale as a function of $T^{-1/2}$. From the slope I obtained $T_0 = 4200$ K.

This observation is in clear contrast than the previous report of Mott VRH in RGO sheets of varying degrees of reduction treatments. The reason could be the limited temperature range used in their study. In addition, the same data might also fit with $T^{-1/2}$. Indeed, I have analyzed some of those results by extracting the points from the graph and found the data to also fit very well with $T^{-1/2}$ as shown in Figure 5.7, where (a) is their results fitting $T^{-1/3}$ behaviors and (b) is what I plotted based on Figure 5.7 (a). This result suggests that extreme caution should be taken in analyzing temperature dependence data.
Figure 5.7 (a) Temperature and electric field dependence of the RGO device properties. Minimum conductivity $\sigma_{\text{min}}$ of RGO as a function of $T^{-1/3}$. The linear fits show agreement with the VRH transport. For samples 16 h, HG-A and HG-B, deviation to thermally activated transport is observed at temperatures indicated by the arrows. (b) A plot of $\sigma_{\text{min}}$ as a function of $T^{-1/2}$. The data point obtained from Figure (a). (Reprinted from [20] with permission from American Chemical Society.)

The self-consistent analysis of the resistance data that span over three orders of magnitude clearly indicates that there is no conduction mechanism other than the $T^{-1/2}$ (ES VRH) for the whole temperature ranges. The characteristics of ES VRH model is in strong agreement with what is expected for a polydispersed GQD array.

The ES VRH indicates strong localization of wave functions in GQDs. Further analysis of ES VRH data allows to calculate the localization length $\xi$ by plotting $R$ against $T^{-1/2}$ in a semi-log scale. This is shown in Figure 5.6 (c) which shows a straight line, as expected. From the slope of this curve, I obtained $T_0 = 4200$ K. $T_0$ is related to $\xi$ through
where $\varepsilon_0$ and $\varepsilon$ are the value for permittivity of vacuum and the dielectric constant of the material. $\varepsilon$ of RGO is 3.5, which discussed in Chapter 4. The calculated value of $\xi$ is about 3.5 nm which is comparable to the calculated GQD sizes, indicating strong localization of the wave function inside each graphitic domain. Similar ES VRH was observed for all 8 samples with $\xi$ varying from 2.3-3.8 nm.

5.3 ES VRH in RGO sheets by Varying sp$^2$ fraction

Another potential interest in RGO is energy bandgap opening in graphene and thereby the capability to tune the electrical properties from semimetal to insulator. In particular, solution processed route for producing RGO sheets, which has a wide range of oxygen functionalities such as hydroxyl and epoxy groups, received great attention due to its tunable electrical properties via controlling the ratio of sp$^2$ C-C and sp$^3$ hybridized carbon (i.e., oxygen functional groups). In this section, I show tunable properties (i.e, localization length and bandgap) of RGO sheets by varying carbon sp$^2$ fraction of RGO sheets.

5.3.1 Varying sp$^2$ fraction of RGO sheets

The carbon sp$^2$ fraction was tuned from 55 to 80 % by varying reduction time in hydrazine hydrate reduction method. The individual GO sheets in powder form were obtained from Cheaptubes InC. 15 mg of GO powder was added to a flask containing 15 mL of deionized (DI) water. Then, the GO solution was stirred with a Teflon-coated magnetic stirring bar in a water bath for 24 hours to obtain a good dispersion. The average lateral dimension of the
GO sheets was about ~ 0.8 μm and the average thickness was ~ 1 nm, indicating single layer GO sheet as shown in Chapter 3, Figure 3.7. 100 μL of 5 % ammonia aqueous solution and 15 μL of hydrazine hydrate (Sigma-Aldrich St. Louis, MO, 35 % DMF) were added to the GO solution. The mixture was then heated at 90 °C for either 10, 20, 30, 45 or 60 minutes under stirring to produce RGO sheets of different reduction efficiency. Another mixture was left in hydrazine for 24 hours without any heating.

The reduction efficiency was determined from carbon \( sp^2 \) fraction using X-ray Photoelectron Spectroscopy (XPS). Figures 5.8 (a)-(f) show XPS spectrum (symbols) of RGO sheets of different reduction efficiency along with deconvolution of the \( C1' \)’s peak (solid lines). Figure 5.8 (a) (sample A) represents the resulting RGO sheet that was not heated, while Figures 5.8 (b), (c), (d), (e) and (f) represent the resulting RGO sheets (defined as B, C, D, E and F) obtained from different heating (reduction) time for either 10, 20, 30, 45 or 60 min, respectively. The four deconvoluted peaks indicate the deoxygenated graphene C-C at 284.6 ± 0.1 eV, oxygen-containing functional groups for hydroxyl (C-OH) at 286.0 ± 0.1 eV, carbonyl (C=O) at 287.0 ± 0.2 eV, and carboxyl acid (O=C-OH) at 288.6 ± 0.1 eV.\(^{52-54}\) The C-C peak refers to the amount of \( sp^2 \) carbon components, while the oxygen-containing functional groups located on the basal plane of the sheets and the edges of the sheets refer to the amount of \( sp^3 \)-hybridized carbon.\(^{18, 21, 55-56}\) Since the presence of \( sp^3 \) defect sites distorts the intrinsic \( \pi \) state of the \( sp^2 \) sites,\(^ {1, 3, 56-58}\) residual carbon \( sp^2 \) fraction is an important clue for RGO sheets and regarded as a reduction efficiency. The carbon \( sp^2 \) fraction was calculated by taking the ratio of the integrated peak areas corresponding to the C-C peak to the total area under the \( C1' \)’s spectrum. The percentage of the carbon \( sp^2 \) fraction can be determined by the following expression:
where $A$ denotes the area under the corresponding peaks as marked in Figures 5.8 (a)-(f). The carbon $sp^2$ fractions are 55, 61, 63, 66, 70 and 80% for A, B, C, D, E, and F, respectively. This result indicates that the carbon $sp^2$ fraction (or reduction efficiency) of RGO sheets increases with increasing reduction time.

Figure 5.8 Deconvolution of the C1’s peaks of XPS spectra for different reduction efficiency of RGO sheets. The reduction time was (a) 0, (b) 10, (c) 20, (d) 30, (e) 45 and (f) 60 min. The peaks containing different groups C-C, C-OH, C=O and O=C-OH are labeled for clarity.

5.3.2 Room Temperature Electronic Properties of RGO sheets by Varying $sp^2$ fraction

Figure 5.9 (a) shows the representative room temperature current-voltage ($I-V$) characteristics of RGO devices A, B, C, D, E and F containing different carbon $sp^2$ fraction.
Within the voltage range of -100 to 100 mV, the I-V curves are Ohmic, allowing to calculate the resistance of the samples. For each sp\textsuperscript{2} fraction, I measured resistance values of 20 samples. The average room temperature resistance (R) of the devices is presented in Figure 5.9 (b) with their corresponding carbon sp\textsuperscript{2} fraction. The decrease in carbon sp\textsuperscript{2} fraction resulted in increase of R (or decrease conductivity). The average R for device A is \( \sim 1.06 \times 10^9 \) \( \Omega \) while for device F it is \( \sim 0.6 \times 10^6 \) \( \Omega \), demonstrating that the value of R can be tuned by more than 3 orders of magnitude but by tuning the carbon sp\textsuperscript{2} fraction from 55 to 80%. The decrease of resistance with increasing sp\textsuperscript{2} fraction demonstrates that restoration of \( \pi-\pi \) bond improves charge percolation pathways in the RGO sheet. However, I note that initially the decrease of resistance with increasing sp\textsuperscript{2} fraction (55 to 70%) is more dramatic and then it starts to level off above 70 %. This behavior is due to the fact that even though the \( \pi-\pi \) bonds are restored, transmission electron microscopy (TEM) images from Erickson et al. and Gómez-Navarro et al. show that such improvement occurs at the expense of increasing topological defects.\textsuperscript{35-36} Thus, I believe, at about 70 % sp\textsuperscript{2} fraction, topological defects started to play a major role in resistance than the remaining sp\textsuperscript{3} fraction. In other words, even if I am able to reduce the sample such that sp\textsuperscript{2} fraction is close to 100 %, the R of RGO will not come close to graphene due to the residual topological defects. In Figure 5.9 (c), I present representative room temperature current – backgate voltage (I - V\textsubscript{gs}) curves for samples A to F measured from -40 to + 40 V at a fixed bias voltage of 1 V. For clarity, the current was normalized to its minimum current \( I_{\text{min}} \). Typical ambipolar characteristics are observed for all devices with highest current on-off occurring for lowest sp\textsuperscript{2} fraction, as expected.\textsuperscript{20}
Figure 5.9 (a) Room temperature current – voltage ($I$-$V$) characteristics of RGO devices with different carbon $sp^2$ fraction. Inset shows zoomed in $I$-$V$ for device A. (b) Room temperature resistance ($R$) of RGO sheets with different carbon $sp^2$ fraction. (c) current-gate voltage ($I$-$V_g$) characteristics of all RGO devices with fixed bias voltage of 1V. For clarity, the current was normalized to its minimum current $I_{min}$.

5.3.3 Ohmic ES-VRH

5.3.3.1 Temperature Dependent Resistance

In order to determine the hopping conduction mechanisms, I measured temperature dependence of resistance ($R$). Figure 5.10 (a) shows semi-log scale plot of $R$ versus (vs) $T$ for samples A, B, C, D, E and F containing different carbon $sp^2$ fraction. The values of $R$ for each sample was measured at a fixed low bias voltage of ~ 100 mV when the temperature was lowered from 295 to 4.2 K at a rate of 0.04 K/s. I observed non-Ohmic behavior below 200 K for device A and below 40 K for device F within the voltage range of 100 to + 100 mV. This behavior is more clearly seen in Figures 5.10 (b) and (c) where I show the $I$-$V$ characteristic at a few selected temperatures measured from -100 to + 100 mV for device A and device F, respectively. Since $R$ is defined from the Ohmic part of the $I$-$V$ curve, in Figure 5.10 (a), I discarded data below those temperatures that did not have linear $I$-$V$ curves at 100 mV. In addition, the resistance measured from the $I$-$V$ curve at a few selected temperatures agrees well with the resistance values plotted in Figure 5.10 (a), indicating the accuracy of the data. I also
note that except for device A, the resistance for all of the samples varied from 2 to more than 3 orders of magnitude with temperature. Such a large variation is important for accurate analysis of hopping conduction.

Figure 5.10 (a) Semi-log scale plot of resistance ($R$) versus (vs) temperature ($T$) for samples A, B, C, D, E and F in the temperature range of 295-40 K. (b) $I$-$V$ characteristics of device A in the temperature range of 295-150 K at bias voltage range from -100 to +100 mV. Inset shows $I$-$V$ at 150 K. (c) $I$-$V$ characteristics of device F in the temperature range of 295-30 K. Inset shows zoomed in $I$-$V$ at 30 K.

The usual practice of determining 2D hopping conduction mechanism is by plotting $\ln R$ vs either $T^{1/3}$ (Mott-VRH) or $T^{1/2}$ (ES-VRH). As I discussed in Section 5.2.3, most work on RGO only showed a plot of $\ln R$ vs $T^{1/3}$ claiming Mott-VRH without making any comments.
whether the data could also be fitted with $T^{-1/2}$.\textsuperscript{19-21, 59} Figures 5.11 (a), (b), (c) and (d) show $\ln W$ vs $\ln T$ plot for samples C, D, E and F, respectively. The symbols are the experimental data points and the solid red lines are a plot of $p = 1/2$, while the dashed lines are a plot of $p = 1/3$ shown for a guide to the eye. It can be clearly seen that for all the samples, the data follow $p = 1/2$ line. In order to determine the accurate values of $p$, I did a least square fit of the data and obtained $p = 0.464 \pm 0.004$, $0.465 \pm 0.058$, $0.475 \pm 0.001$ and $0.483 \pm 0.004$ for C, D, E, and F, respectively. These values are close to 0.5, as expected from ES VRH. I could not do a similar analysis for samples A and B due to a limited number of data points within a small temperature range. However, since samples A and B are more disordered than C, D, E and F, I can only expect the ES VRH to dominate there as well. Figure 5.11 (e) shows a semi-log scale plot of $R$ vs $T^{-1/2}$ for all the samples. The symbols are the experimental points and the solid lines are a fit to $T^{-1/2}$ behavior. As expected, the data for all the samples fit very well with $T^{-1/2}$ behavior. By extrapolating solid lines in Figure 5.11 (e), I obtained the pre-factor $R_0$ values for all RGO sheets. It can be seen that all the traces collapse to almost a single $R_0$ value with a small variation (within experimental error) from 14.8 to 12.6 kΩ. The self-consistent analysis of finding the value of $p = 1/2$, the excellent fit of $\ln R$ with $T^{-1/2}$ and a nearly universal value of $R_0$ for all RGO samples clearly indicate that there is no conduction mechanism other than the ES VRH for the entire temperature ranges for all the samples of varying $sp^2$ fraction in this study.
Figure 5.11 (a)-(d) Reduced activation energy ($W$) plotted vs temperature ($T$) in a log-log scale for devices C, D, E, and F, respectively. From the slopes of the plots, I obtained $p = 0.464 \pm 0.004, 0.465 \pm 0.058, 0.475 \pm 0.001$ and $0.483 \pm 0.004$ for C, D, E, and F corresponding to the ES VRH for all samples. For a comparison, I also show lines with $p = 1/2$ (ES VRH) and $p = 1/3$ (2D Mott VRH) for a guide to the eye. (e) Semi-log scale plot of $R$ vs $T^{-1/2}$ for all RGO devices. The symbols are the experimental points and the solid lines are a fit to $T^{-1/2}$ behavior. From the slopes, I obtained $T_{ES} = 3.1, 2.5, 1.3, 0.87, 0.59$ and $0.42 \times 10^4$ K for devices A, B, C, D, E, and F, respectively. By extrapolating the solid lines, I determined $R_0$ values of 14.8, 13.6, 14.1, 13.8, 13.1 and 12.6 kΩ for device A, B, C, D, E, and F, respectively.

5.3.3.2 Localization length

From the slopes of Figure 5.11 (e), I obtained the characteristic temperature $T_{ES}$ for all of the samples. The values of $T_{ES}$ are $3.1 \times 10^4$ K (device A), $2.5 \times 10^4$ K (B), $1.3 \times 10^4$ K (C), $0.87 \times 10^4$ K (D), $0.59 \times 10^4$ K (E) and $0.42 \times 10^4$ K (F) [See solid symbols in Figure 5.12 (a)]. From these values of $T_{ES}$ and using Equation 5.10, I determined the localization length ($\xi$) to be 0.46,
0.54, 1.03, 1.54, 2.27 and 3.21 nm for samples A, B, C, D, E and F, respectively. In determining $\xi$, I used an effective dielectric constant of $\varepsilon = 3.5$ for RGO sheet. Figure 5.12 (b) shows a plot of $\xi$ vs its corresponding carbon $sp^2$ fraction of the sheets which demonstrates that with increasing $sp^2$ fraction, the localization length increases. This result is what is expected. It is well known that RGO consists of ordered graphene domains surrounded by areas of oxidized domains and point defects. It has been estimated from XPS, Raman and TEM studies that the graphitic domain size in RGO can vary from 1 to 6 nm with reduction efficiency. These values are surprisingly close to the value of $2\xi$ in this study demonstrating that the wave-function is localized inside each graphitic domain. The agreement between localization lengths with the domain size is rather extraordinary given the complexity of the measurements and analysis.

Figure 5.12 (a) shows that, even for the highest reduction sample, $T_{ES}$ is much higher than the room temperature, making it impossible to see Mott VRH. I extrapolated the data using a second order polynomial fit to see what the $T_{ES}$ will be at 100 % reduction efficiency. I found a value of $T_{ES} = 1800$ K. Similarly, I also found a value of $\xi = 7.44$ nm as shown in Figure 5.12 (b). These findings suggest that even at 100 % carbon $sp^2$ fraction, Mott VRH may not be observed possibly because of residual topological defects and structural disorders.
5.3.3.3 Energy gap

The $\xi$ values obtained in ES VRH allow us to estimate the bandgap ($E_g$) of RGO for different $sp^2$ fraction. From the linear dispersion relation of graphene $E(k) = \hbar v_F k$, we can replace $k \sim 1/\xi$ to obtain $E_g \sim \hbar v_F / \xi$, where $v_F$ is the graphene Fermi velocity. This is due to the confinement of the wave function inside each graphitic domain of size $L \sim \xi$, the $k$ values are quantized and in the ground state $k \sim 1/\xi$. Interestingly, this equation is similar to 1D graphene nanoribbon except that $\xi$ is replaced by the width of the nanoribbon. Using the value of $\xi$ from Figure 5.13, I calculated the values of $E_g$ as 1.43, 1.22, 0.64, 0.43, 0.29 and 0.21 eV for samples A, B, C, D, E and F, respectively. These $E_g$ values are plotted against their corresponding carbon $sp^2$ fraction in Figure 5.13 (square symbols). I have also compared the $E_g$ values with that of theoretical $E_g$ (circular symbol) predicted by the DOS calculation. The agreement between the
experimental results and theoretical prediction are quite remarkable providing further evidence of the applicability of ES VRH for all of the RGO sheets in this study.

![Graph](image)

Figure 5.13 Bandgap ($E_g$) of RGO samples plotted vs their corresponding carbon $sp^2$ fraction. Square symbols demonstrate $E_g$ calculated from $\xi$, while circular symbols are from theoretical predictions.

5.3.4 Non-Ohmic ES VRH

Additional evidence of ES VRH can be obtained from the high bias nonlinear $I-V$ curve. At high enough electric field (high bias regime) and low temperature, the temperature dependence is strongly reduced and one enters the regime of field driven hopping transport, $^{65-69}$

\[
R(E) \sim \exp \left( \frac{E_0}{E} \right)^{1/2},
\]

with $E_0 = \frac{2k_B^2T_E}{e^2\xi}$.  \hspace{1cm} (5.12)

(5.13)
where $T_{ES}$ and $\xi$ represent the same parameters as in Ohmic ES VRH of Equation (5.10). Figures 5.14 (a) and (b) show $ln R$ vs $E^{-1/2}$ characteristics of two representative devices A and F at a few selected temperatures down to 4.2 K. The value of $R$ is calculated by dividing the current with voltage. At higher temperatures, the curves are still temperature dependent within the measured bias voltage range (up to 5 V). However, as the temperature gets close to 4.2 K, the curves become weakly temperature dependent. It is possible to see temperature independent regime at higher bias voltage. However, I did not apply more than 5 V as the devices undergo electrical breakdown slightly above this voltage. I fitted the 4.2 K data with $E^{-1/2}$ (solid line) in high bias regime and the data fit very well, indicating that the $R$ follows field driven (or non-Ohmic) ES VRH. Similar fits were also obtained for samples B, C, D and E (not shown here). It has been noted that the field dependent hopping equation is only valid when the electric field is higher than a critical field $E_C = 2k_B T / e \xi$. $^{65-66, 68-70}$ Here, this condition is satisfied as the values for $E_C$ at 4.2 K for device A and F are $16.7 \times 10^5$ V/m ($E_C^{-1/2} = 7.74 \ (10^8 V/m)^{-1/2}$) and $2.28 \times 10^5$ V/m ($E_C^{-1/2} = 20.9 \ (10^8 V/m)^{-1/2}$) and the fit was for $E^{-1/2} < E_C^{-1/2}$. 
Figure 5.14 (a) $\ln R$ vs $E^{-1/2}$ for device A at temperature ranges from 4.2 to 60 K. (b) $\ln R$ vs $E^{-1/2}$ for device F at temperature ranges from 4.2 to 30 K. Dashed lines show a linear fit $E^{-1/2}$. (c) Comparison of hopping parameter $E_0$ determined from Ohmic and non-Ohmic ES VRH with different carbon $sp^2$ fraction of RGO sheets. Solid symbols are calculated from Ohmic (low electric field regime) ES VRH. Open symbols are found from experimental non-Ohmic (high electric field regime) ES VRH.

From the slope of the fitted line in Figures 5.14 (a) and (b), I obtained the value of $E_0$ as $16.1 \times 10^8$ and $1.38 \times 10^8$ V/m for device A and F, respectively. The value of $E_0$ can also be calculated from Equation 5.13, using the values of $T_0$ and $\xi$ obtained from the Ohmic ES VRH. The corresponding values for $E_0$ were $123 \times 10^8$ V/m and $2.29 \times 10^8$ V/m for device A and F, respectively. Similar analysis was done for all other samples (B, C, D, and E) and the corresponding values of $E_0$ from Ohmic ES VRH (marked as solid symbols) and experimentally measured values obtained from the slope in the high electric field regime (marked as open symbols) are plotted against their corresponding carbon $sp^2$ fractions in Figure 5.14 (c). The results from two different regimes are in fairly good qualitative agreement. The small variation, also seen for ES VRH in other materials, may indicate that the constants in Equations 5.10 and
5.13 may not be very accurate. A summary of all the results obtained from the measurements is presented in Table 5.1.

Table 5.1 Summary of ES VRH fitting results with varying carbon \(sp^2\) fraction in RGO sheets.

<table>
<thead>
<tr>
<th>Devices (carbon (sp^2) fraction (%))</th>
<th>(R_{Room}) (M(\Omega))</th>
<th>(R_0) (k(\Omega))</th>
<th>(T_{ES}) (10(^4) K)</th>
<th>(\xi) (nm)</th>
<th>(E_g) (eV)</th>
<th>Calculated (E_0) (10(^8) V/m)</th>
<th>Measured (E_0) (10(^8) V/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A (55)</td>
<td>1060</td>
<td>20</td>
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<td>0.46</td>
<td>1.43</td>
<td>123</td>
<td>16.1</td>
</tr>
<tr>
<td>B (61)</td>
<td>83.5</td>
<td>14</td>
<td>2.5</td>
<td>0.54</td>
<td>1.22</td>
<td>80.1</td>
<td>9.05</td>
</tr>
<tr>
<td>C (63)</td>
<td>13.8</td>
<td>17</td>
<td>1.3</td>
<td>1.03</td>
<td>0.64</td>
<td>22.7</td>
<td>6.91</td>
</tr>
<tr>
<td>D (66)</td>
<td>3.4</td>
<td>15.4</td>
<td>0.87</td>
<td>1.54</td>
<td>0.43</td>
<td>9.73</td>
<td>4.60</td>
</tr>
<tr>
<td>E (70)</td>
<td>1.2</td>
<td>14.4</td>
<td>0.59</td>
<td>2.27</td>
<td>0.29</td>
<td>4.47</td>
<td>2.19</td>
</tr>
<tr>
<td>F (80)</td>
<td>0.6</td>
<td>11.2</td>
<td>0.42</td>
<td>3.21</td>
<td>0.21</td>
<td>2.29</td>
<td>1.38</td>
</tr>
</tbody>
</table>

5.4 Tuning Coulomb Blockade by Varying Carbon \(sp^2\) fractions

Tunable properties in RGO sheets encourage manipulation of Coulomb blockade (CB) effects. CB is strongly influenced by the structural disorder of the systems: global structural disorder, local structural disorder and local charge disorder. Therefore, to advance nanoscale system, manipulation of CB has been explored with a metallic island (or nanoparticle) \(^{71-74}\), quantum dot (QD) array\(^ {28,75-78}\), molecular array \(^ {79}\) and carbon nanotube (CNT)\(^ {80}\). For example, studies have included tuning size of a metallic island, tuning structure configuration and dimension in QD array, tuning of the length of the organic barrier in molecular array and local gate in CNT. Structurally, in GO, the \(sp^2\) graphene domain is isolated by \(sp^3\) domain and hence, the electric and optical properties of GO are strongly influenced by the degree of disorder which can be tuned by varying the amount of the \(sp^2\) carbon. \(^1,5,20,81-82\) These observations led to the
possibilities of tunable CB effects due to cumbolic charging interaction between graphene
domains in RGO sheets by varying $sp^2$ carbon fractions.

5.4.1 Coulomb Blockade Regimes

Figure 5.15 (a) shows the current-voltage ($I$-$V$) characteristics of RGO devices A, B, C, D, E and F containing different carbon $sp^2$ fraction, measured at 4.2 K with channel length and width of 500 nm. Within the voltage ranges of -3.5 to 3.5 V, the $I$-$V$ curves of all RGO sheets are non-linear and highly symmetric. The non-linear $I$-$V$ behaviors increased with decrease in carbon $sp^2$ fraction. Interestingly, all $I$-$V$ curves exhibit a complete suppression of currents below a $V_t$. The $V_t$ were found to be 3.34, 2.1, 1.19, 0.8, 0.5 and 0.25 V for device A, B, C, D, E and F, respectively, demonstrating that the values of $V_t$ decreased by more than 1 order of magnitude by increasing the carbon $sp^2$ fraction from 55 to 80 % in this temperature (4.2 K). These behaviors, current suppression below $V_t$ at very low temperature, are characteristic of CB of charge transport and have been observed in QD array system where there is not enough energies for charges to overcome charging energy of the QDs so that the charging energy is much larger than thermal energy. This observation indicates that RGO behaves as a GQD array where the $sp^2$ graphene domains are QD and $sp^3$ oxidized domain are tunnel barriers. Within this picture, with lower carbon $sp^2$ fraction RGO sheets, they require higher $V_t$ to overcome the CB regimes because they have larger amount of $sp^3$ fraction and hence, contain high tunnel barriers in the conduction path.

Similarly, at 30 K as shown in Figure 5.15 (b), $V_t$ values of 2.9, 1.55, 0.62 and 0.25 V were observed for samples A, B, C and D, respectively. However, I could not observe $V_t$ for
samples E and F which contain higher carbon $sp^2$ fraction (> 70 %). This may be due to that the temperature is not low enough to observe CB in devices E and F.

Figure 5.15 (a) Current ($I$) – voltage ($V$) characteristics of device A, B, C, D, E and F at 4.2 K. The current is zero for $V < V_t$ due to Coulomb blockade (CB) of charges. (b) $I$-$V$ characteristics of devices A, B, C, D, E and F at 30 K. In this temperature, $V_t$ was observed in device A, B, C and D, while for device E and F, $V_t$ was not observed. The channel length of all devices is 500 nm.

5.4.2 Scaling Factor for $V > V_t$: Middleton Wingreen Model

Theory in QD array predicted that at sufficiently low temperature and $V > V_t$, current ($I$) follows a power law behavior, Equation 5.1, $I \sim (V - V_t)^\alpha$, where scaling factor $\alpha$ reflects the dimensionality of the conduction pathway. The current ($I$) depends on the nature of the branching of the percolation path within the system and $\alpha$ depends on the topology of the percolation path which, in turn, depends on dimensionality and structural topology (or charge trapped sites).$^{25, 33, 74}$ Therefore, this model has been used to understand structural disorder of the system.

Figures 5.16 (a)-(f) show $I$ plotted versus $(V-V_t)/V_t$ in a log-log scale for devices A, B, C, D, E and F, respectively, obtained from Figure 5.15 (a). The solid symbols are the experimental
data points while the red solid lines fit the Equation 5.1. It can be clearly seen that for all the samples, the data follow Equation 5.1.

![Figure 5.16](image)

Figure 5.16 (a)-(f) Current (I) versus \((V - V_t)/V_t\) curves plotted in a log-log scale at 4.2 K. From the slopes of the plots I obtain scaling factor \(\alpha = 2.11, 2.15, 3.24, 3.35, 3.33\) and 3.4 for A, B, C, D, E, and F corresponding to the MW CB model for all samples.

From the slopes, we obtained the scaling factor \(\alpha\) for all of the devices. The values of \(\alpha\) are 2.11 (device A), 2.15 (B), 3.24 (C), 3.35 (D), 3.33 (E) and 3.40 (F) [see solid symbols in Figure 5.17]. This demonstrates that in lower carbon \(sp^2\) fraction (\(< 61\%\)) of RGO sheets \(\alpha\) is
close to theoretical 2D arrays system (~ 2), while higher $sp^2 (> 63 \%$) RGO sheets show higher $\alpha$ value ~ 3.4. In previous experimental and simulation study on an inhomogenous quasi-2D QDs network, $\alpha$ is sensitive on the topology of the percolation path due to charge trapping. The local trapped charges cause the blockade of percolation path and are influenced by the morphology of the system so that the $\alpha$ can be up to 4 with large amount topological defects. Thus, it is believed that at about 63 % $sp^2$ fraction, topological defects started to play an important role in electron transport in RGO sheets. The results indicate that by chemical hydrazine reduction treatments, significant amounts of oxygen functional groups are removed and hence, carbon $sp^2$ faction increases. However, such process or properties produce increasing topological defects.

It is also important to note that although the reduction method could reduce most of the functional groups on RGO sheets ($sp^2$ fraction of ~ 100 %), the presence of topological defects can make additional trapped charges on the sheets which is a hurdle for high quality graphene based electronics through the RGO sheets. Therefore, there still are significant challenges on reduction treatment ahead before RGO can be used in high quality electronic devices.
Figure 5.17 Scaling factor $\alpha$ versus their corresponding carbon $sp^2$ fraction of the RGO sheets. As the carbon $sp^2$ fraction is higher than 63%, the $\alpha$ increased to ~ 3.4.

5.4.3 Temperature Dependent Threshold: Effective Charging Energy estimation

In QD array system, at zero temperature, the $V_t$ can be expressed as $V_t(0) = \beta N\Delta V$, where $\beta$ is a prefactor whose value depends on the dimensionality and array geometry, $N$ is the number of QDs in the conduction pathway and $\Delta V$ corresponds to the charging energy of QD associated with single electron tunneling between neighboring QD in the array. As the temperature increases, the $V_t$ will decrease since a fraction of the CB effects, $p(T)$, will decrease because the electron has enough thermal energy to overcome the CB. This temperature dependent $V_t$ can used to define charging energy and expressed as

$$V_t(T) = V_t(0) \left[1 - \frac{p(T)}{p_c}\right], \text{ with } p(T) = 4.8k_B T p(0)$$

(5.14)

where $1/p(0)$ is an effective charging energy and same as $e\Delta V$, $p_c$ is the percolation threshold and $N$ is number of QDs in the conduction pathway.

In order to further understand Coulomb blockade (CB) in RGO sheets, I measured temperature dependent $V_t$ for all samples to find $V_t(T=0)$. Figure 5.18 (a) shows $V_t$ versus
temperature \((T)\) for samples A, B, C, D, E and F. The symbols are the experimental data points and the solid lines are extrapolation of the data points to estimate \(V_t(0)\). By extrapolating the temperature dependent \(V_t\) values, we can estimate \(V_t(0)\). The \(V_t(0)\) were 3.50, 2.20, 1.25, 0.90, 0.55 and 0.30 V for samples A, B, C, D, E and F, respectively. This result demonstrates that with increasing \(sp^2\) fraction, the \(V_t(0)\) decreases. From these \(V_t(0)\) values, we can find a number of GQD, \(N\), in conduction. To do this, we first estimate effective charging energy using temperature dependent \(V_t\).

The \(V_t\) increases linearly with decreasing temperature for all of our samples and the slopes are almost constant \((\sim 0.025 \pm 0.003)\). This allows finding effective charging energy, \(1/p(0)\), of all RGO sheets by using Equation 5.14. Using the slope of \(V_t\) versus \(T\), I determined \(1/p(0)\) values for all of the samples. The \(1/p(0)\) values were 160, 110, 60, 45, 30 and 20 meV for samples A, B, C, D, E and F respectively. These results are shown in Figure 5.18 (b). They show that the \(1/p(0)\) of RGO sheets is also varied by one order of magnitude by tuning the carbon \(sp^2\) fraction from 55 to 80 %. This observation is a clear demonstration of the need for higher \(V_t\) in order to overcome higher charging energy in low carbon \(sp^2\) fraction of RGO sheet. In addition, it has been shown that individual GQD using mechanical exfoliation methods show room temperature CB effects, and electron interactions become stronger as the dimensions of graphene sheets are reduced.\(^{22-23}\) Therefore, this observation, increases of charging energy with decreases of \(sp^2\) fraction, indicates that with lower \(sp^2\) carbon in RGO sheets, the transport barrier between the GQDs narrows and allows for small fraction of electron to tunnel along GQDs. In other words, decreasing carbon \(sp^2\) fraction in RGO sheets lead to reduction of GQD domain sizes and increases in tunnel barriers.
Figure 5.18 (a) $V_t$ plotted against the temperatures $T$. Extrapolating of temperature $V_t$ allows to estimate $V_t$ at 0 K ($V_t(0)$). $V_t(0)$ were found to be 3.61, 2.17, 1.33, 0.91, 0.58 and 0.41 V for devices A, B, C, D, E and F, respectively. (b) Effective charging energy $1/p(0)$ versus their corresponding carbon $sp^2$ fraction of RGO sheets.

In addition, the CB or $V_t$ is observed at higher temperature for lower $sp^2$ carbon fraction sample. The $V_t$ starts to disappear at 100 K (device A), 80 K (B), 50K (C), 30 K (D), 25 (E) and 15 K (F). This behavior is expected since the CB is observed when the charging energy of a QD is higher than thermal energy and the charging energy is inversely proportional to the size of QDs. Thus, if carbon $sp^2$ fraction is low (or the size of GQD is small), then the charging energy of GQD is high which, in turn, means that the CB would be observed in higher temperature.

Now I estimate the number of GQD ($N$) in conduction pathway of the array using $V_t(0)$ and $1/p(0)$. The N values were estimated as 74, 65, 73, 66, 69 and 68 for samples A, B, C, D, E and F, respectively. The $N$ values are not $sp^2$ fraction dependent and are similar to each other. Why do the values of $N$ not change even the $sp^2$ fraction is varied? As the $sp^2$ carbon is further increased in RGO sheets, interaction (or tunneling) among graphene domain increases since removal of oxygen groups leads to increases in interconnection between graphene domains by
formation of new small graphene domains. A structural model of this is shown in Figure 5.19. This result is in good agreement with previous structure investigation of RGO sheets.\textsuperscript{57} Thus, the $sp^2$ fraction increases the size of graphene domain and decreases inter distance, and $N$ values are not much varied with different $sp^2$ fractions.

Figure 5.19 Structural model of GO at different stages of reduction.\textsuperscript{57} (Reprinted from [57] with permission from John Wiley and Sons.)

To characterize GQD distributions in the 500 nm channel, we considered the structural formation of RGO sheets. The GQD distribution can be expressed as $500 \text{ nm} = (2r+2d)N$, where the $2r$ is size of average GQD and $2d$ is the average inter distance between GQD. In chapter 5.3.3, I have determined the localization length ($\xi$) to be 0.46, 0.54, 1.03, 1.54, 2.27 and 3.21 nm for samples A, B, C, D, E and F respectively.\textsuperscript{83} The values of $2\xi$ are close to the size of graphene domain ($2r$).\textsuperscript{83} With this estimated graphene domain size, I calculated the average inter distance ($2d$) between graphene domains. The $d$ values are 2.90, 3.31, 2.39, 2.25, 1.35 and 0.47 nm for samples A, B, C, D, E and F, respectively.

A summary of all the results obtained from measurements in this study is presented in Table 5.2.
Table 5.2 Summary of CB fitting results with varying carbon \( sp^2 \) fraction in RGO sheets.

<table>
<thead>
<tr>
<th>Devices (Carbon ( sp^2 ) fraction (%))</th>
<th>( \alpha )</th>
<th>( V'_f(0) ) (V)</th>
<th>( 1/p(0) ) (meV)</th>
<th>( N )</th>
<th>( 2r ) (nm)</th>
<th>( d ) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A (55)</td>
<td>2.11</td>
<td>3.50</td>
<td>160</td>
<td>74</td>
<td>0.96</td>
<td>2.90</td>
</tr>
<tr>
<td>B (61)</td>
<td>2.15</td>
<td>2.20</td>
<td>110</td>
<td>65</td>
<td>1.08</td>
<td>3.31</td>
</tr>
<tr>
<td>C (63)</td>
<td>3.24</td>
<td>1.25</td>
<td>60</td>
<td>73</td>
<td>2.06</td>
<td>2.39</td>
</tr>
<tr>
<td>D (66)</td>
<td>3.35</td>
<td>0.90</td>
<td>45</td>
<td>66</td>
<td>3.08</td>
<td>2.25</td>
</tr>
<tr>
<td>E (70)</td>
<td>3.33</td>
<td>0.55</td>
<td>30</td>
<td>69</td>
<td>4.54</td>
<td>1.35</td>
</tr>
<tr>
<td>F (80)</td>
<td>3.40</td>
<td>0.30</td>
<td>20</td>
<td>68</td>
<td>6.42</td>
<td>0.47</td>
</tr>
</tbody>
</table>

5.4.4 Channel Length Dependent Effect on Coulomb Blockade

As mentioned in Chapter 3, I have measured 500 \( \times \) 500 nm channel length and width of RGO device via DEP assembly. For this channel length study, I fabricated source and drain electrode patterns of 0.1, 0.5, 1 and 2 \( \mu \)m channel length (\( L \)) with fixed 0.5 \( \mu \)m channel width (\( W \)) as defined by electron beam lithography (EBL). The DEP parameter was the same for all devices. In brief, a 3 \( \mu \)L of RGO solution was drop casted onto the electrode pattern. An AC voltage of 3 \( V_{p-p} \) with a frequency of 1 MHz was applied between the source and drain electrodes for 1 minute. Figures 5.20 (a)-(d) show scanning electron microscopy (SEM) images of RGO devices with different \( L \) of 0.1, 0.5, 1 and 2 \( \mu \)m, respectively.
In order to see channel length effects on the CB, I measured the fixed $sp^2$ carbon fraction (~63%) of RGO sheets with varying channel length (L) of 0.1, 0.5, 1 and 2 μm with fixed channel width of 0.5 μm. Figure 5.21 (a) shows temperature dependent $V_t$ for different channel length of the device. As the channel length becomes longer, the slope of the $V_t(T)$ is steeper which is different than carbon $sp^2$ fraction dependent $V_t(T)$.

Temperature dependent $V_t$ values are increased with increasing L as shown in Figure 5.21 (b). The $V_t(0)$ were 0.6, 1.3, 2.4 and 3.5 V for $L$ of 0.1, 0.5, 1 and 2 μm devices, respectively. This observation demonstrates that with increasing length $V_t(0)$ increases. This result was predicted on the following: $V_t$ is proportional to the number of tunneling barriers or QDs ($N$) in the conduction path hence, longer $L$ of RGO should have larger $N$. The behavior also supported by Equation 5.14. Similar behaviors also have been shown in NP array system when the size of NPs are the same.\textsuperscript{76}
Figure 5.21 (a) Temperature dependent resistivity with different channeling length of the devices with fixed carbon \( sp^2 \) fraction of 63%. Extrapolated temperature threshold voltage was used to estimate \( V_t \) at 0 K \( (V_t(0)) \). (b) Threshold voltage as a function of temperature for different channel length of the devices.

From Equation 5.14, I can find \( 1/p(0) \) values for all the devices and they are 0.071, 0.067, 0.057 and 0.049 eV with \( L \) of 0.1, 0.5, 1 and 2 μm devices, respectively. If width and length of array system are the same, often termed square lattice structure in QD array, the charging energy of the system needs to be close to each other. However, in this case, the charging energy decreased with decreasing channel length of device with fixed channel width. This result is not what I expected. However, if I assume that the size of quantum confinement (or graphene domain) to be the same, the charging energy of the all system needs to be the same although the channel length is varied. From Equation 5.14, I fixed the \( 1/p(0) \) values as 0.06 eV. Then, I found \( p_c \) values of 0.237, 0.345, 0.34, and 0.5 for \( L \) of 0.1, 0.5, 1 and 2 μm devices. This result demonstrates that the shorter channel length of the RGO sheets shows lower \( p_c \) (≈ 0.237) values due to the existence of multiple pathways, while in longer channel of RGO sheets, less conducting path way (\( p_c \approx 0.5 \)) is needed for tunneling. In other words, by reducing the length of
the RGO device, the $p_c$ parameter is reduced as less Coulomb Blockades are included in the pathways, thus, leading to a reduction in $V_t$. Similar properties have been observed in NP array systems.\textsuperscript{76}

To elucidate the effects of channel length on the topological complexity of the RGO sheets, I find $a$ for all samples. Figure 5.22 shows $a$ value for their corresponding $L$ of the device. The values of $a$ are 3.5, 3.21, 3 and 2.4 for $L$ of 0.1, 0.5, 1 and 2 $\mu$m devices, respectively. In fixed carbon $sp^2$ fraction of RGO sheets, $a$ was shown to increase as the $L$ is lowered. This result indicates that the enhancement in $a$ with decreasing device length was a result of an increase in the tortuosity of the percolation path.\textsuperscript{31-32, 74} In other words, as $L$ is decreased, the tortuosity of the array is increased due to a reduction in available percolation pathways for the electrons to flow through. Similar properties are also shown in topologically complex 2D Au nanoparticle array system.\textsuperscript{31}
Figure 5.22 Scaling factor $\alpha$ versus different channel length ($L$) of RGO devices.

All of these results suggest that the CB is tunable by varying $sp^2$ fraction. Therefore, room temperature RGO CB device, e.g. single-electron switching device, can be achieved by reducing $sp^2$ fraction with increases in channel length of the device.

5.5 Conclusion

I showed that the properties of RGO sheets can be described as a transport through an array of GQD where graphitic domains acts like QDs, while oxidized domains behave like tunnel barriers between QDs. From the temperature-dependence data, I obtained the GQD sizes to vary from 5 to 8 nm, in excellent agreement with previous TEM studies. Observation of ES VRH with a localization length comparable to the size of each GQD shows that Coulomb interaction and size disorder play important roles. I also demonstrated ES VRH in RGO sheets of varying carbon $sp^2$ fractions, both in Ohmic and non-Ohmic regime. In Ohmic regime, the temperature dependence of resistance for all the samples follow $R = R_0 \exp[(T_{ES}/T)^{1/2}]$ and localization length $\xi$ increased from 0.46 to 3.21 nm with increasing carbon $sp^2$ fraction from 55 to 80 %. From the localization length, I calculated a bandgap variation of the RGO from 1.43 to 0.21 eV with
increasing $sp^2$ fraction from 55 to 80 % which agrees remarkably well with theoretical prediction. At low temperature and high electric field (high bias regime), these data can be explained with field dependent ES VRH model $R \sim \exp[(E_0/E)^{1/2}]$ with the values of $E_0$ obtained from the slope in good agreement with that of $E_0$ obtained from the Ohmic regime. By extrapolating the data to 100 % $sp^2$ fraction, I conclude that Mott VRH may not be observed in the chemically reduced RGO sheets. In the last part of this chapter, I reported on tunable CB in RGO sheets of varying carbon $sp^2$. The scaling parameter ($\alpha$) increases from 2.1 to 3.5 with increasing carbon $sp^2$ fractions from 55 to 80 % due to increases in topological defects. From this, it is predicted that even if we are able to reduce the sample such that $sp^2$ fraction is close to 100 %, the electron transport properties of RGO will not come close to pristine graphene due to the residual topological defects. From temperature dependent $V_t$, we calculate effective charging energy variations of our RGO from 160 to 20 meV with increasing $sp^2$ fraction from 55 to 80 % which strongly supports the significance of Coulomb effects as the $sp^2$ fraction is reduced since decreasing carbon $sp^2$ fraction in RGO sheets lead to reduction of graphene domain sizes and increases in tunnel barriers. By increasing channel length of the device, from 100 nm to 2 $\mu$m, with fixed channel width of 500 nm and $sp^2$ carbon fraction of RGO sheets, $V_t$ increases and $\alpha$ decreases due to an increase in the tortuosity of the percolation path. The description of the RGO sheet as a 2D GQD array suggests that RGO will find many novel electronic and optoelectronic applications through tuning of GQD sizes via controlled oxidation and reduction.
References


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6 ELECTRON TRANSPORT IN RGO NANORIBBON

6.1 Introduction

Graphene has ignited an intense research interest for its potential applications in nanoelectronics as well as model systems to investigate novel quantum transport phenomenon in confined geometries.\(^1\text{-}^4\) Recently, much attention has been focused on creating an energy band gap for conventional semiconductor device applications. This energy band gap can be achieved through quantum confinement by patterning graphene into nanoribbon, graphene nanoribbon (GNR),\(^5\text{-}^{10}\) as well as via chemical functionalization by means of oxidation and reduction of graphene sheets\(^11\text{-}^{12}\) which creates nanoscale domains. The transport studies of the former have been explained using Anderson localization or Coulomb blockade (CB) effects and nearest neighbor hopping.\(^6\text{-}^{13}\text{-}^{15}\) The transport properties of the latter, reduced graphene oxide (RGO) sheets, has been understood either 2D Mott variable range hopping\(^16\text{-}^{18}\) or Efros-Shklovskii (ES-) VRH.\(^19\text{-}^{20}\) Up until now, 1 dimensional RGO nanoribbon (RGONR), has been made with un-zipping of carbon nanotubes (CNT).\(^21\text{-}^{25}\) The structural information of the un-zipping obtained through X-ray photoelectron spectroscopy (XPS) and Raman shows that it is very close to its RGO system.

In this chapter, I demonstrate lithographically fabricated RGONR field effect transistor (FET) with various width and lengths, and describe detailed electron transport properties of RGONR. RGONR was lithographically fabricated from AC dielectrophoresis (DEP) assembled 2D RGO sheets. With the application of a backgate voltage, all of the devices showed FET behavior with maximum hole and electron mobilities of 6 and 4 cm\(^2\)/Vs, respectively, at room
temperature. From low temperature measurements, I found that even for such quasi-1D system, ES VRH and CB characteristics similar to those of RGO sheets are observed for all RGONRs. However, in contrast to linear behavior of decreases in threshold voltage \( V_t \) with increasing temperature \( T \) in the RGO, in this quasi-1D RGONR, sub-linear dependence of \( V_t \) on \( T \) at high temperature due to reduced transport pathway was observed. In addition, the scaling factor is in agreement with its theoretical 1D array system. This may be due to additional trap state that is created at the edge of the RGONRs.

6.2 Fabrication of RGONR

Here, I describe the process for fabricating RGONR that is used in experiments throughout this chapter. Figure 6.1 outlines this process. I begin with 2D DEP assembled RGO sheet which was previously explained in Chapter 3. As shown in Figure 6.1 (a), RGO sheets were assembled via DEP on prefabricated source and drained electrode patterns of \( 1 \times 1 \) µm or \( 1 \times 2 \) µm (channel width \( \times \) length). Then, positive e-beam resist, polymethyl-methacrylate (PMMA), is spun coated on the surface of aligned RGO sheets with 400 rpm to coat with 200 nm thickness, as shown in Figure 6.1 (b). Next, it is baked at 180 \(^\circ\)C for 15 minutes. Subsequently, a precise window of un-wanted area is opened by electron beam lithography (EBL), as shown in Figure 6.1 (c). The area dose of 300 µC/cm\(^2\), current of 30 pA and power of 28 keV were used for e-beam parameter. Afterwards, the device is developed in a solution of methyl isobutyl ketone:isopropal alcohol (MIBK:IPA; 1:3) for 50 seconds. Subsequently, the sample is kept in an oxygen plasma etching for 10 second to etch the RGO sheets. The devices, then, were thermally
annealed in argon:hydrogen (1:3) gas at 200 °C for 1 hour. Figure 6.3 (d) shows final fabrication results of RGONR.

Figure 6.1 Process flow for RGONR fabrication. Atomic force microscopy (AFM) image (top row) and cartoon view (bottom row). (a) DEP assembled RGO FET. (b) PMMA coating on RGO device. (c) EBL writing on the designed area. (d) RGONR device after plasma etching. Scale bar in AFM images is 1 µm.

In order to understand the effects of 1D transport in RGO sheet, I have fabricated different channel width (W) and length (L) of the RGONR. The different dimensions of RGO sheets are characterized by atomic force microscopy (AFM). Figures 6.2 (a)-(d) show representative AFM images of RGONRs with W × L of 200 nm × 2 µm (device A), 100 nm × 2 µm (B), 50 nm × 2 µm (C) and 50 nm × 1 µm (D). Figure 6.2 (e) is zoomed-in image of 50 nm width of RGONR. The brighter regime is thicker than other regions. The total thickness of the RGONR is varied from 1 to 4 nm. This is typical for all of the devices in this study.
The devices were, then, bonded to a chip carrier and loaded into a variable temperature cryostat for temperature-dependent electronic transport measurements. The measurements were performed using a Keithley 2400 source meter, and a current preamplifier (DL 1211) capable of measuring pA signal interfaced with the LABVIEW program.

6.3 Room Temperature Transport Properties

For each of the four dimensions of RGONR, I measured performances of three devices. Instead of discussing all three devices, I am going to focus, in detail, on performance of one device for each dimension of RGONR. The four dimensions of RGONR are labeled as the following: Device A: RGONR with length (L) and width (W) of 2 µm× 200 nm; Device B: 2 µm× 100 nm; Device C: 2 µm× 50 nm; and Device D: 1 µm× 50 nm. Figure 6.3 (a) shows room temperature current-voltage (I-V) characteristics of all devices. Within the voltage range of -5 to 5 V, the I-V curves are all symmetric. However, as the device width is reduced from 200 (device
A) to 50 nm (device C) at fixed 2 um, increases in non-linear behaviors of $I-V$ were observed. The non-linear behavior is even higher for device D, which has width of 50 nm and length of 1 um. For clarity, I zoomed in $I-V$ curves of device D, as shown Figure 6.3 insets.

Figure 6.3 Room temperature current-voltage ($I-V$) characteristics of RGONRs. (a) $I-V$ curve with voltage ranges of -5 to 5 V. Device A is almost linear, while devices B, C and D show non-linear behaviors. As the width and length of RGONR are reduced, the non-linearity of $I-V$ curve increased. Inset shows zoomed in $I-V$ for device D. (b) $I-V$ curve with voltage ranges of -0.1 to 0.1 V. All of the devices show linear $I-V$, which allows resistance of the RGONR. Inset shows zoomed in $I-V$ for device D.

However, with low voltage range (-0.1 to 0.1 V), all of the devices show Ohmic behavior allowing to calculate the resistivity of the samples. The resistivities of all RGONRs are 0.006, 0.004, 0.003, and 0.173 $\Omega$m for devices A, B, C and D, respectively. These results indicate that with fixed length of RGONR, smaller width of RGO shows lower resistivity, while with fixed
width of RGONR, shorter length of RGONR shows higher resistivity. It is also noted that the current ranges of device are higher for device B in high voltage compared to device C, as shown in Figure 6.3 (a). The values of I were 7.39 and $6.41 \times 10^{-7}$ A at 5V for devices B and C. However, there is not much difference between devices B and C in low voltages, as shown in Figure 6.3 (b). The values of I were 1.16 and $1.18 \times 10^{-8}$ A at 0.1 V for devices B and C. This observation indicates that there may be geometrical effects in transport of RGONR, specifically in low voltage and high voltage regimes. I will discuss details on the effect in later sections.

6.4 Ohmic Efros-Shklovskii Variable Range Hopping (ES VRH)

In order to understand the hopping transport properties of RGONR, I measured temperature dependent resistance of RGONR. Figure 6.6 (a) shows semi-log scale plot of resistance $R$ versus (vs) temperature $T$ for sample devices A, B, C and D containing different dimensions of RGONRs. $R$ for each sample was measured at a fixed low bias voltage of ~ 100 mV and the temperature was lowered from 295 to 4.2 K at a rate of 0.04 K/s. It is also observed that except for device D, the resistance for all of the RGONRs varied more than two orders of magnitude with temperature. In all of the RGONRs, Ohmic-regime vanished below curtain temperature, Device A: 50 K, B: 60 K, C: 70 K and D: 140 K, due to Coulomb blockade (CB) of charges, which will be explained in later section.

The usual practice of determining 1D or 2D hopping conduction mechanism in temperature dependent resistance ($R$) is expressed by: $^{26-29}$

$$R(T) = R_0 \exp\left(\frac{T_0}{T}\right)^\nu$$  \hspace{1cm} (6.1)
where \( R_0 \) is a prefactor, \( T_0 \) is a characteristic temperature and \( p \) is a characteristic exponent the value of which distinguishes different conduction mechanism. For Mott VRH \( p=1/(d+1) \), where \( d=1, 2, \) or \( 3 \) depends on dimensionality of the hopping conduction.\(^{30}\) Up until now, hopping transport of 1D graphene based NRs has been studied with 2D Mott VRH \( (\ln R \sim T^{-1/3}) \), 1D Mott VRH \( (\ln R \sim T^{-1/2}) \) or ES VRH \( (\ln R \sim T^{-1/2}) \).\(^{25,31-32}\) For 1D RGONR through un-zipping of CNT, which also has high disorder in structure, the hopping is governed by 2D Mott VRH.\(^{25}\) For 1D RGONR fiber, the transport is governed by 1D Mott VRH.\(^{31}\) On the other hand, lithographically fabricated GNR\(^{10}\) and vacuum filtrated GNR films exhibited ES VRH.\(^{22}\)

In RGONRs in this study, the temperature dependent \( R \) strongly followed \( T^{-1/2} \) behaviors which is the same as 2D RGO system, as shown in Figure 6.6 (b). The symbols are the experimental points and the solid lines are a fit to \( T^{-1/2} \) behavior.
From the slopes of Figure 6.6 (b), I obtained the characteristic temperature $T_{ES}$ for all of the samples. The values of $T_{ES}$ are $0.54 \times 10^4$, $0.73 \times 10^4$, $1.00 \times 10^4$ and $2.01 \times 10^4$ K for devices A, B, C and D, respectively.[See solid symbols in Figure 6.6 (b)]. From these values of $T_{ES}$, the localization length ($\xi$) can be found by using the following equation: \(^{28-29}\)

$$T_0 \equiv T_{ES} = \left( \frac{2.8\varepsilon^2}{4\pi\varepsilon\varepsilon_0 k_B \xi} \right)$$

where $\varepsilon_0$ and $\varepsilon$ are the value for permittivity of vacuum and the dielectric constant of RGO ($\sim 3.5$). From this relation, I determined $\xi$ of 2.5, 1.8, 1.3 and 0.7 nm for devices A, B, C and D,
respectively. Figure 6.7 (a) shows a plot of $\zeta$ for all devices. It is observed that the localization length is not varied by changing the geometry of RGONR. As I discussed in 2D RGO transport, the localization length of RGO system is governed by its disorder or $sp^2$ carbon fraction which is related to room temperature resistance of the RGO sheets; this also applies to 1D RGONR.

As I mentioned in the previous section, room temperature resistance of devices B and C is almost the same, but resistivity is different due to their different width, while the $T_{ES}$ or localization length is $\sim 8\%$. There are two possible questions that are needed to be addressed. First, can Equation 6.2 also be applied in 1D structure? The above ES VRH is successfully analyzed for 2D RGO sheets. However, no theoretical 1D or quasi 1D ES VRH has been investigated thus far. Second, can the localization length depend on degrees of disorder in RGONR? From the previous 2D RGO of varying degrees of carbon $sp^2$ fraction study, the localization length depends on the amount of $sp^2$ fraction.

In addition, it is also noted that the RGONR in this study did not show any transition from ES VRH. For lithographically patterned GNR, the charge transport exhibits a transition from thermally activated behavior at higher temperatures to ES VRH at lower temperatures.\textsuperscript{10} This may be due to a larger amount of defects in the RGONRs in this study.
Figure 6.5  Estimated $\xi$ values of all RGONRs. Device A: RGONR with length and width of 2 $\mu$m × 200 nm; Device B: 2 $\mu$m × 100 nm; Device C: 2 $\mu$m × 50 nm; and Device D: 1 $\mu$m × 50 nm.

6.5 Non-Ohmic Efros-Shklovskii Variable Range Hopping (ES VRH)

As I described earlier in Chapter 2, in both 2D Mott VRH and ES VRH, temperature dependent resistance follows $R \sim T^{-1/2}$ behaviors. To support the ES-VRH in RGONR, I also analyzed the non-Ohmic ES-VRH, where the conduction is given by: \( R(E) \sim \exp\left(\frac{E_0}{E}\right)^{1/2}, \) \hspace{1cm} (6.3)

with \( E_0 = \frac{2k_BT_{ES}}{e\xi}. \) \hspace{1cm} (6.4)

where $T_{ES}$ and $\xi$ represent the same parameters as in Ohmic ES VRH.

As the temperature is further reduced (~ 4.2 K), temperature dependent properties of $R$ is strongly reduced and it goes to field driven hopping transport regime. These characteristics were also observed in 2D RGO sheets. Figure 6.8 shows $ln R$ vs $E^{-1/2}$ characteristics of devices A, B, C.
and D at temperatures of 4.2 to 50 K. The value of $R$ is calculated by current ($I$) over voltage ($V$). As the temperature gets close to 4.2 K, the curves become weakly temperature dependent. It is possible to see temperature independent regime at higher bias voltage. I fitted the 4.2 K data with $E^{-1/2}$ (solid line) in high bias regime and the data fit very well, indicating that the $R$ follows non-Ohmic ES VRH. The slopes ($E_0^{-1/2}$) of devices A, B, C and D were found to be 15000, 17350, 21700 and 23450, respectively.

![Figure 6.6](image)

Figure 6.6 (a) $\ln R$ vs $E^{-1/2}$ characteristics of device A at temperatures of 4.2 to 50 K. Solid line shows a linear fit $E^{-1/2}$ (b) $\ln R$ vs $E^{-1/2}$ for device B. (c) $\ln R$ vs $E^{-1/2}$ for device C. (d) $\ln R$ vs $E^{-1/2}$ for device B. From the solid lines, slopes were found to be 15000, 17350, 21700 and 23450 for devices A, B, C and D, respectively.

From the slopes of the fitted lines, I obtained the values of $E_0$ as 2.3, 3.0, 4.7 and $5.5 \times 10^8$ V/m for devices A, B, C and D, respectively. The value of $E_0$ can also be calculated from Equation 2.11, using the values of $T_{ES}$ and $\zeta$ obtained from the Ohmic ES VRH. The corresponding values for $E_0$ were 0.9, 1.8, 3.8 and $6.5 \times 10^8$ V/m for A, B, C and D, respectively. The results from two different regimes are in fairly good qualitative agreement. Therefore,
overall observation of both ohmic and non-ohmic ES VRH behaviors of RGONR provides that the hopping of RGONR is governed by ES VRH.

![Comparison of hopping parameter $E_0$ determined from Ohmic and non-Ohmic ES VRH with different dimension of RGONR. Square symbols are measured form non-Ohmic ES VRH regime, while Dot symbols are from Ohmic ES VRH.](image)

6.6 Coulomb Blockade: Sub Linear Properties of Temperature Dependent $V_t$

I now discuss Coulomb blockade (CB) regimes. Figure 6.9 (a) shows the $I-V$ characteristics of all RGONR devices containing different width and length of RGONR, measured at 4.2 K. Within the voltage ranges of -5 to 5 V, the $I-V$ curves are highly symmetric and show a complete suppression of currents below a certain threshold voltage ($V_t$) for all devices. The decrease in low localization length of the device resulted in increases of non-linear behaviors. The $V_t$ found to be 1.6, 2.2, 2.9 and 2.3 for devices A, B, C and D, respectively.
Figure 6.8  (a) Current ($I$) – voltage ($V$) characteristics of all RGONRs at 4.2 K. The current is zero for $V < V_t$ due to Coulomb blockade (CB) of charges. (b) $V_t$ plotted against the temperatures $T$ for devices A, B and C. (c) $V_t$ plotted against the temperatures $T$ for device D. Extrapolating of temperature $V_t$ allows to estimate $V_t$ at 0 K ($V_t(0)$). The $V_t(T)$ shows sub linear behavior at higher temperature. (d)-(g) Differential conductance ($dI/dV$) as a function of $V$ and $T$ for devices A,B, C and D, respectively. The color scale shows intensity of the conductance. Grey color regions are unmeasured regions.

In order to further understand CB in RGONR, I measured temperature dependent $V_t$ for all samples to find $V_t(T=0)$. Figure 6.8 (b) shows $V_t$ vs. $T$ for devices A, B and C. Figure 6.8 (c) shows $V_t$ vs $T$ for device D. The symbols are the experimental data points and the solid lines are extrapolation of the data points. The significant difference between 2D RGO and RGONR is the slope of the $V_t(T)$. In Figure 6.8 (b), for device A at lower temperature from 4.2 to 30 K, the $V_t(T)$
slope is linear, however, as temperature further increased \((T>25 \text{ K})\), the slope of \(V_t(T)\) is reduced. This behavior is even more clearly shown in 50 nm width device (i.e., devices C and D). For device C, the sub-linear behavior is observed as \(T\) is higher than 30 K, and for device D, the sub-linear behavior is observed at \(T>50\text{K}\). For clarity of this behavior, I present in Figures 6.8 (d)-(g) the differential conductance \((dI/dV)\) measured on all of the RGONR respect to both \(V\) and \(T\). From here, the sub linear behaviors in temperature dependent \(V_t\) also can be identified.

At low temperature, some of the CB will disappear as the thermal energy of the electron increases. Hence, as the temperature increases, the \(V_t\) will linearly decrease. However, as temperature increases, charge transport pathway is reduced and the CB will be more apparent and thus, \(V_t\) will decrease at a slower rate. Such sub linear behavior is also seen in 1D NPs array system\(^{37}\).

Another interesting property is that the linear slope regimes of \(V_t(T)\). At low temperature depends on the dimensionality of RGONR. For same dimensions of RGONR, the slope of \(V_t(T)\) is almost constant although the \(V_t\) values are different. The slopes are varied as dimensions of RGONR are varied. As shown in the above figures, slopes of the devices A, B, C and D are 0.06, 0.067, 0.072 and 0.03, respectively. These results indicate that as the width of RGONR is reduced, from 200 to 50 nm, the slope of \(V_t(T)\) is increased and as the length of RGONR is increased from 1 to 2 µm, the slope \(V_t(T)\) is increased. As I mentioned in the previous chapter, the \(V_t(T)\) follows \(V_t(T)=V_t(0)[1-4.8k_BTp(0)/p_c]\). Thus, the slope of \(V_t(T)\) is related with the \(p(0)/p_c\), where \(1/p(0)\) is related with charging energy of the system and \(p_c\) is the percolation threshold of the network and related with the dimension of the system. Therefore, when the width of RGONR is reduced, the \(p_c\) values are increased. Theoretical prediction indicated that for 1D, the \(p_c\) value
is \( \sim 1 \) and for 2D the \( p_c \) value is \( \sim 0.337 \). \(^{37-38}\) There are fewer charge transport paths in RGONR compared to 2D RGO.

### 6.7 Limitation of Scaling Factor for \( V>V_t \) in RGONR

Now, I discuss \( V>V_t \) regimes. In this regime, theory and simulations predict that the current follows a power law, \( I\sim(V-V_t)^\alpha \), with \( \alpha=1 \) in 1D and 2 in 2D. \(^{39-40}\) As discussed in the previous chapter, \( \alpha \) is varied from 2.2 to 3.5 depending on its carbon \( sp^2 \) fraction and channel length in 2D RGO sheet. The higher \( \alpha \) was due to topological properties of the sheets. \(^{38, 40-45}\) Yet, 1D graphene systems have never been studied with the model, whereas studies have been performed on quasi 1D nanoparticle (or chain) system. However, \( \alpha=1 \) has not yet been achieved since true 1D structure arrays is difficult to achieve and \( \alpha \) is very sensitive to residual disorder in the particle arrangements.\(^{46}\)

Figures 6.9 (a)-(d) show \( I \) plotted versus \( (V-V_t)/V_t \) in a log-log scale at 4.2 K for devices A, B, C and D, respectively. For each device, I determined the \( V_t \) and the \( \alpha \) from best straight line fits. From this, I obtained the scaling factor \( \alpha \) for all of the devices. The values of \( \alpha \) were 3.4, 2.67, 3.46 and 3.23 for devices A, B, C and D, respectively. These values are very close to 2D RGO sheets. These observed \( \alpha \) values demonstrate that transport along the RGONR may not be reached due to the 1D limit or additional topological defects at the edge. To find the origin of the 1D limitation in scaling factor, I found the charge trap density (\( \sim 30 \times 10^{16} \) cm\(^{-3} \)). The values were much higher than 2D RGO sheets (\( 2 \times 10^{16} \) cm\(^{-3} \)). This result indicates that the edge side contains a large amount of topological defects, which can affect the scaling factor \( \alpha \).
Figure 6.9 (a)-(d) Current ($I$) versus $\frac{(V-V_t)}{V_t}$ curves plotted in a log-log scale at 4.2 K. From the slopes of the plots, I obtained scaling factor $\alpha = 3.4, 2.67, 3.46, \text{ and } 3.23$ for devices A, B, C and D corresponding to the Middleton Wingreen CB model for all samples. The solid symbols are the experimental data points, while the solid lines fit the best linear line.

6.8 Conclusion

In this chapter, I reported on the electron transport properties of RGONR made by lithographical fabrication of RGO sheets. With the application of a backgate voltage, all of the devices showed FET behavior with maximum hole and electron mobilities of 6 and 4 cm$^2$/Vs, respectively. Temperature dependent resistance of all RGONR shows Ohmic ES type VRH and is independent of size or dimension of RGONR. At low temperature and high electric field (high bias regime), data in this study can be explained with field dependent (or non-Ohmic) ES VRH, providing further evidence of ES-VRH in RGONRs. I showed that the current is totally suppressed below a certain threshold voltage $V_t$ at certain a temperature depending on charging energy of RGONRs. From temperature dependent $V_t$, I observed sub linear behavior where at lower temperature $V_{t}(T)$ slope is linear, however as temperature further increased, the slope of $V_{t}(T)$ is reduced. This sub linear behavior is a signature of 1D array system. For $V > V_t$, the
current follows a scaling behavior $I \propto [(V-V_0)/V_d]^{\alpha}$, however the scaling factor $\alpha (> 2.6)$ is not in agreement with theoretical 1D array system. This may be due to additional trap state, which is created at the edge of the RGONRs.
References


7 RGO/NANOPARTICLE COMPOSITES

7.1 Introduction

In practical point of view, disorder structure of reduced graphene oxide (RGO) sheets, i.e. surface defects and oxygen functional group, makes it an ideal template for synthesis of nanoparticles (NPs) since no molecular linkers are needed to bridge the NPs and the RGO sheets. Recently, various metals and metal oxide NPs and semiconducting quantum dots (QD) have been incorporated to RGO structures aiming to realize exceptional properties in composite form, as extraordinary properties of RGO opened new frontiers for their composite with NPs to achieve the synergistic effects of individual components.1-14 For example, Au, Ag, Pd, CdSe, CdS, ZnO and TiO$_2$ NPs decorated on RGO have been reported for novel catalytic activities, tuning electric, magnetic and catalytic properties of RGO.1-14 Therefore, such integration of 2D with large surface areas can be an exciting material for use in future nanotechnology.

However, most of these studies only focused on the synthetic strategies and characterization of RGO composite application. There are no reports on how the metal NPs and semiconducting QDs affect transport properties of RGO sheets. In the first part of this chapter, I will discuss how the semiconducting QDs, i.e. cadmium sulfide (CdS), affect low temperature transport of RGO sheets. The RGO/CdS is synthesized through solvothermal, often called one-pot strategy, reduction method. In the second part, I will discuss tunable field effect properties of RGO by anchoring metal oxide NPs, i.e. cerium oxide (CeO$_2$). RGO/CeO$_2$ is synthesized through hydrazine reduction methods.

7.2 Low Temperature Transport Properties of RGO/Semiconducting QDs Composites

One area of significant interest is the photocurrent generation in RGO sheets. Recently, novel strategies have been proposed to tune the photo-response of RGO by incorporating semiconducting QDs onto RGO sheets to create new hybrid architectures. However, all of these studies only focused on the synthetic strategies and characterization of RGO composite application. There are no reports on how the QDs affect transport properties of RGO sheets. Here, I present measurements and analysis of temperature dependent current density (J) - voltage (V) characteristics to elucidate the nature and density of charge traps in the RGO/ cadmium sulfide (CdS) composites. The CdS decorated RGO sheets were synthesized directly from GO in a one-step solvothermal reaction where the reduction of GO, the synthesis of CdS QDs and the decoration of CdS onto RGO were done simultaneously. The composites were assembled via AC dielectrophoresis (DEP). The mobility of the composite is much lower than its RGO only sheets. The J -V characteristic of the RGO/CdS composite measured at different temperatures (295 to 77 K) follows space charge limited conduction (SCLC) which is the same as RGO only sheets. However, the estimated trap density of the composites \(8 \times 10^{16} \text{ cm}^{-3}\) is \(~4\) times higher than RGO only sheets.

7.2.1 Synthesis of RGO/CdS: One Pot Solvothermal Reduction

There are two main types of methods: solvothermal and chemical reduction. Here, I have used both types of methods. With solvothermal methods, I have synthesized RGO/CdS composite, and with chemical reduction methods, I have synthesized RGO/CeO\(_2\).

15 mg of GO was dispersed in 36 ml of dimethyl sulfoxide (DMSO) by vigorous sonication for about 1 hour. 0.3 g of CH\(_3\)COOH powder and 0.032 g of Sulfur with 3H\(_2\)O were
mixed with GO and DMSO solution by vigorous stirring. The solution was then transferred onto a Teflon lined stainless steel autoclave of volume 60 ml. Next, the autoclave was sealed and maintained at a constant temperature (180 °C) for 12 hours. Briefly, in the second method, 15 mg of GO was dispersed in 15 ml of deionized (DI) water by vigorous sonication of about 1 hour. 0.3 g of CH₃COOH powder and 0.032 g of Sulfur with 3H₂O were mixed with the GO solution by vigorous stirring. Hydrazine hydrate was added and the solution was heated for 1 hour at 90 °C.

7.2.2 Characterization of RGO/CdS

Figure 7.1 (a) shows a cartoon of CdS-NP decorated over RGO sheets. Transmission electron microscopy (TEM) clearly indicates that the CdS nanoparticles are decorated on RGO sheets, as shown in Figure 7.1 (b). The CdS decorated RGO sheets were studied by X-ray photoelectron spectroscopy (XPS) to verify the reduction of GO as well as the evaluation of existence of CdS. The survey of the sample over a wide range of binding energy from 0 to 660 eV is shown in Figure 7.1 (c). The Cd, S, C and O peaks are observed in the survey. Deconvolution of the C1s’ peak (shown in Figure 7.1 (d)) indicates about 70 % of non-oxygenated ring C which confirms effective reduction of GO which is calculated from Chapter 5. The results show that both RGO and CdS kept their own properties even after the reduction process.
7.2.3 Temperature Dependent Transport Properties of RGO/CdS

The solution based RGO/CdS composites were, then, assembled via DEP between the prefabricated gold source and the drain electrodes. The channel width and length were 500 nm and 500 nm, respectively. The assembled device is shown in Figure 7.2 (a) inset. Figure 7.2 (a) shows the room temperature transport properties of a representative DEP assembled RGO/CdS device, where current \( I \) is plotted as a function of gate voltage \( V_g \) in a vacuum. The gate voltage was applied from -40 to 40 V with fixed source–drain voltage, \( V = 1 \) V. The device shows ambipolar field effect transistor (FET) behavior which is the same property seen in RGO only sheets as shown in Chapter 3. The room temperature hole and electron mobilities are calculated as 0.02 and 0.008 cm\(^2\)/Vs which are about two orders of magnitudes lower than RGO.
only sheets. To find the origin of low mobility of the composites, I measured and analyzed temperature dependent transport properties.

Figure 7.2 (b) shows the $I-V$ characteristics at various temperatures measured from -5 V to 5 V with $V_g = 0$. The $I-V$ curves are highly symmetric at all temperatures and the $I-V$ curve became increasingly nonlinear with decreasing temperature with different temperature ranges. This behavior indicates that the $I-V$ curve shows similar properties with RGO devices.

However, when the temperature decreased below 150 K, there were no measurable current below certain threshold voltages. The threshold voltages are 2, 2.3, 2.5 and 2.7 for 150, 125, 100 and 77 K, respectively. This result seems like Coulomb blockade (CB) of RGO sheets as discussed in Chapter 5.

First, I considered XPS results. The $sp^2$ fraction of the composite is ~ 70%. For 70% of carbon $sp^2$ fraction of RGO only sheets, the CB is observed around ~ 40 K. What makes this huge change in transport of the composite? It may be due to the presence of trapped charges at the interface between CdS and RGO sheets.
Figure 7.2 (a) $I-V_g$ plot at room temperature. Inset shows DEP assembled RGO/CdS. (b) Current – Voltage characteristics at different temperatures. (c-d) $I-V$ curves at different temperatures plotted in semi log scale from 295K to 175 K and from 150K to 77K, respectively.

In order to examine the trapped charges in the composite, I applied space charge limited conduction (SCLC) model. Figure 7.3 (a) shows current density versus voltage ($J-V$) curves at different temperature in a log-log scale. Similar to RGO sheets discussed in Chapter 4, the $J-V$ characteristic of the composite devices measured at different temperatures (295 to 77 K) follows power law behavior, $J \propto V^m$. At low bias, the conduction is Ohmic with $m=1$, while at higher bias voltages $m$ increases from 1.8 to 5.7 with reducing temperature signifying SCLC with a transition from trap free (TF-SCLC) regime at room temperature to exponentially distributed trap (EDT-SCLC) regime at low temperatures.
By extrapolating the $J-V$ curves, I can obtain values for $V_c$ and calculate trap density $N_t$. In Figure 7.3 (b), I extrapolated the log $J$ and log $V$ characteristic at higher bias voltages for all temperatures except room temperature. $V_c = 38$ V was found. Using this value, I obtained trap density, $N_t = 8 \times 10^{16}$ cm$^{-3}$. This value is 4 times higher than RGO only sheets. Since an exponential distribution of trap in energies is expected for the traps originating from surface defects and structural disorders, I believe, the interface can also create charge trap states.

![Graph](image.png)

Figure 7.3 (a) Current density ($J$) versus $V$ plotted in a log-log scale for different temperatures. The symbols are the experimental points, while the solid lines are fits to $J \propto V^m$. Two regions are separated by $V_{th}$. For $V < V_{th}$, $m=1$ and the conduction is Ohmic. $V > V_{th}$ the conduction is due to SCLC with exponentially distributed trap states. (b) Extrapolation of the $J-V$ curves at low temperatures plotted in log-log scale for device A. From this plot, I determined the temperature independent crossover voltage $V_c=38$ V.

### 7.3 Tuning Electrical Properties of RGO by Anchoring CeO$_2$

Recently, rare earth materials (REM) received significant attention due to their versatility specificities and potential applications in energy efficiency, coating, catalytic converter, permanent magnet, computer devices, rechargeable batteries, laser, superconductors, and
chemical and bio sensors.\textsuperscript{17-22} It is, therefore, desirable to fabricate composite systems consisting of RGO and REM for a broad range of applications in the field of materials’ engineering. Hybridization or interaction of RGO with REM has so far rarely been reported. In addition, the bonding characteristic of REM is different from that of the simple and transition metals,\textsuperscript{23} and it is of great fundamental scientific interest to understand how the characteristics will alter the properties of RGO. Nanocrystalline ceria (CeO\textsubscript{2}), a rare earth metal oxide, could be considered as one of the promising materials for RGO/REM hybrids since CeO\textsubscript{2} is one of the most abundant and least expensive REM materials and has many applications in chemical, materials and biological area.\textsuperscript{24-28} Specifically, ultra small ceria nanoparticles (CNPs, < 5 nm) with excellent redox properties contain higher density of surface oxygen vacancies which is a function of the population of mixed valence states.\textsuperscript{29-32} The creation of oxygen vacancies generate localized electrons on CNP surface which may interact with the functional group in the RGO sheets and thus, able to tune the properties of RGO.

In this section, I will report on uniform decoration of CNPs onto RGO sheets suspended in water and discuss the effect of oxygen vacancies on the resulting CNP/RGO hybrids. Two types of CNPs with varying +3/+4 ratios were incorporated onto the RGO sheets. Structural characterizations through XPS and Raman spectroscopy reveal a strong electrostatic interaction between the CNPs and the RGO with non-disruption of the graphitic $sp^2$ lattice structure. Electrical characterization shows both n-type and ambipolar behaviors in the CNP/RGO hybrids depending on +3/+4 states on the CNP surface. The CNPs interaction with RGO provides an important possibility which might be further exploited to develop applications in electronic and electrochemical energy devices, fuel cells, batteries, and sensors.
7.3.1 Synthesis of RGO/CeO2: Chemical Hydrazine Reduction

CNP1 were prepared by wet chemical process. All chemicals were procured from Sigma-Aldrich. The stoichiometric amount of cerium nitrate (Ce(NO$_3$)$_3$·6H$_2$O, 99.99%) was dissolved in DI water, and 30 wt% hydrogen peroxide solution was added rapidly at vigorous stirring (500 rpm). The solution was then heated at 110 °C with continuous stirring to obtain a stable suspension of 5 mM CNP1. On the other hand, the CNP2 were prepared using stoichiometric amount of cerium nitrate dissolved in DI water. Then, 1.0 N ammonium hydroxide solution was added and stirred for 4 hours for precipitation. The particles were washed with DI water and centrifuged to remove any adsorbed nitrate ions. Finally, nanoparticles were dried in the vacuum oven at 80 °C and re-dispersed in DI water to get 5mM concentration of solution.

15 mg of GO (Cheap Tubes Inc.)$^{33}$ was dispersed in 30 ml of DI water by vigorous sonication. 2 ml of GO solution was mixed with 2 ml of CNP1 (or CNP2) aqueous solution in a round bottom flask with a magnetic stir bar and a water-cooled condenser. Hydrazine hydrate (Sigma-Aldrich St. Louis, MO, 35 % DMF) was added, and the solution was heated at 90 °C under constant stirring. The change of color in the resultant solution from light brown to black was the primary indication of GO reduction. Then, the RGO/CNP1 (or CNP2) nano-composites were separated from solvent either by using centrifuge to obtain powder or by filtration to obtain free-standing films followed by a wash with DI water. The obtained powder was then re-suspended into DI water.
7.3.2 Characterization of RGO/CeO$_2$

7.3.2.1 Transmission Electron Microscopy (TEM)

The GO was synthesized by modified Hummers’ method and dispersed in DI water. Figure 7.4 (a) displays a tapping-mode atomic force microscopy (AFM) image of the GO sheets along with their height analysis. The lateral dimension of the GO sheets varied from 0.2 - 2 µm. Approximately 70% of the sheets displayed a height of 1.0 ± 0.2 nm. Two types of CNPs were synthesized consisting of predominantly Ce$^{3+}$ valence states (CNP1: contains high oxygen vacancies) or predominantly Ce$^{4+}$ valence states (CNP2) suspended in DI water. These CNPs (3-5 nm) were synthesized by wet chemical methods to create different concentrations of surface valence states. The morphology and microstructure of as synthesized CNPs were examined by transmission electron microscopy (TEM). The high-resolution TEM (HRTEM) images of CNP1 and CNP2, and selected area electron diffraction (SAED) patterns are shown in Figures 7.4 (b) and (c), respectively, which confirmed the nanocrystalline characteristic of the CNP particles (3 to 5 nm).

Figure 7.4 (a) Tapping-mode AFM image of RGO sheets with a height profile indicating majority of the sheets are single layer. The lateral dimension of the GO sheets varied from 0.2 - 2 µm. (b-c) HRTEM micrographs of the CNP1 and CNP2 with sizes of less than 5 nm. The insets of the figures show the corresponding electron diffraction patterns, indicating nanocrystalline fluorite structures of the CNPs.
Anchoring crystalline CNPs onto RGO sheets were obtained by ex-situ synthesis as shown in Figure 7.5 where the reduction of GO to RGO and the decoration of CNP on RGO occur simultaneously. After the reduction and decoration process, the color in the resultant solution was changed from light brown to black.

![Figure 7.5 Synthesis strategy for CNP/RGO hybrids. CNPs and GO sheets were mixed in water and then reduced in hydrazine to obtain CNP/RGO hybrids.](image)

Figure 7.6 shows the TEM images of the synthesized CNP/RGO composites. The RGO sheets and the nano structure of the CNPs are clearly observed. As can be seen in Figures 7.6 (a) and (b), micrographs of the CNP1/RGO hybrids at low and high resolution revealed homogeneous distribution of the CNP1s on RGO. On the other hand, the CNPs in CNP2/RGO hybrids were unevenly decorated [See Figures 7.6 (c) and (d)] compared to CNP1/RGO. The TEM micrographs showed that the particle size and nanocrystalline structure remain the same before and after the decoration and reduction process for both CNP1 and CNP2.
7.3.2.2 X-ray Photoelectron Spectroscopy (XPS)

The chemical state of elements in the CNPs/RGO has been extensively characterized by X-ray photoelectron spectroscopy (XPS). Figure 7.7 shows deconvolution of the C1s’ peak in the XPS spectrum of the GO, RGO, CNP1/RGO and CNP2/RGO, respectively. The four deconvoluted peaks indicate the non-oxygenated C-C at 284.6 ± 0.1 eV and oxygen containing functional groups C-OH at 286.0 ± 0.1 eV, C=O at 287 ± 0.2 eV and O=C-OH at 288.6 ± 0.1 eV. The peaks of oxygen functional groups decrease after the reduction and hybridization process. The percentage of non-oxidized carbon changed from 52 % (GO) to ~ 68 % (CNP/RGO)
hybrids) verifying effective reduction of GO in the hybrids. This reduction efficiency of CNP/RGO hybrids is slightly lower than pure RGO (~73 %) [See Table 7.1], however they are similar to other composite reports.37-38

![Figure 7.7 High resolution XPS of the C1s' peaks (275 to 295 eV: 20 eV scans) of (a) GO, (b) RGO, (c) CNP1/RGO and (d) CNP2/RGO hybrids indicating the reduction of the oxygenated carbon. The peak at 284.6 eV indicates C-C, and the other peaks correspond to the oxygenated carbon groups C-OH at 286.0 ± 0.1 eV, C=O at 287 ± 0.2 eV and O=C-OH at 288.6 ± 0.1 eV. The C1s’ peaks also reveal the general ideas of charge transfer interaction between CNPs and RGO,39-41 If the charge transfer from CNPs to RGO is an electron donor type, then the Fermi level of RGO should shift upward toward the conduction band. This shift would result in an increase in the C1’s binding energy. However, in the present study, I could not see any shift in C-C bond energy (at ~ 284.6 eV) which indicates an electrostatic interaction of CNPs with the RGO surface.11, 37 More detailed analysis of the charge transport in CNP/RGO will be discussed later.

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Table 7.1 The percentages of non-oxidized carbon calculated from the deconvoluted XPS spectra of C1s’ peaks (ratio of C/O), Ce 3d’ peaks (Ce3+ concentration), and O1s’ peaks (ratio of Ce-O/C-O) in the composite.

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<td>52</td>
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<td>-</td>
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<tr>
<td>RGO</td>
<td>73</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>RGO/CNP1</td>
<td>68.5</td>
<td>78</td>
<td>45</td>
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<tr>
<td>RGO/CNP2</td>
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In order to see the surface properties of CNPs before and after incorporation into RGO, Cerium 3d (Ce 3d) spectra of CNPs and CNP/hybrids were analyzed. The peaks of v’ (at ~ 885 eV) and u’ (at ~ 900.5 eV) corresponding to the Ce$^{3+}$ ions are clearly observed in CNP1/RGO (Figure 7.8 (a) red line). The peaks of v (at ~ 882 eV), v’’ (at ~ 888.1 eV), v’’’(at ~ 897.9 eV), u (at ~900.8 eV), u’’ (at ~ 906.8 eV) and u’’’ (at ~916.4 eV) corresponding to 4+ ions in CNP2/RGO are also observed (Figure 7.8 (a) green line). Comparison of these peaks to the as synthesized CNP1 and CNP2 (Figure 7.8 (b)) showed no changes in the Ce 3d peaks. It is noted that although the surface properties of the CNPs are very sensitive to various factors such as synthesis route, size, functional groups, dopants, oxygen partial pressures and temperature, in the present study, ex-situ methods strongly conserved the surface properties of the CNPs.
Figure 7.8 (a) Red line indicates Ce 3d spectra of XPS for CNP1/RGO, showing majority of the Ce$^{3+}$ peaks in hybrid. It is also confirm that the oxidation state (3+) in cerium oxide NP surface was not affected by the reduction of CNP1/GO in to CNP1/RGO hybrid. Green line indicates CNP2/RGO, showing the majority of the 4+ oxidation state. The presence of peak at 916.4 ± 0.2 eV indicates the contribution of 4+ oxidation state. (b) XPS of Ce 3d showing high resolution spectra of the as-synthesized CNP1 (predominantly trivalent state of Ce) and CNP2 (predominantly tetravalent state of Ce) particles with the Ce 3d$\text{5/2,3/2}$ energy profile. Line $v'$ and $u'$ correspond to the Ce$^{3+}$, while $v$, $v''$, $v'''$, $u$, $u''$ and $u'''$ are characteristics of Ce$^{4+}$ ions.

Cerium oxide has a fluorite crystal structure, in which Ce$^{4+}$ cation is surrounded by eight O$^{2-}$ anions in a cube, with each O$^{2-}$ coordinated to four Ce$^{4+}$ cations. The change in the valence state from Ce$^{4+}$ to Ce$^{3+}$ introduces oxygen vacancies into the crystal lattice. Thus, the presence of Ce$^{3+}$ indirectly indicates the oxygen vacancies in the lattice. For the quantitative calculations of Ce$^{3+}$ concentration in hybrids, high resolution XPS spectra of Ce 3d were deconvoluted (Figure 7.9). Then, the Ce$^{3+}$ concentration was calculated by taking the ratio of the integrated peak areas corresponding to Ce$^{3+}$ to the total area under the XPS spectrum. Concentration of Ce$^{3+}$ is expressed as:

$$\text{Ce}^{3+} = \frac{v_0 + v' + u_0 + u'}{v_0 + v' + u_0 + u + v + v' + v'' + u + u'' + u'''}.$$

(7.1)
Figure 7.9. Deconvolution of cerium 3d peaks for (a) CNP1/RGO, (b) CNP2/RGO hybrids. (a) and (b) show the Ce 3d_{5/2} and Ce 3d_{3/2} spectra. The symbols represent the experimental points while the red line is a fit to the data and green line represents deconvoluted peaks.

Second column of Table 7.1 shows the calculated concentration of Ce$^{3+}$ on the surface of the particles in the hybrids. The higher concentration of Ce$^{3+}$ (78%) in CNP1/RGO compared to CNP2/RGO (12%) was observed which indicates that the surface oxidation state of the CNP1/RGO contains much higher density of oxygen vacancies compared to CNP2/RGO.

Figure 7.10 shows comparison of XPS O1s spectra of GO before and after the reduction and hybridization. It shows a decrease in the carboxylate and carbonyl groups (C-OH at ~ 533.4 eV and O=C-OH at 528.4 eV) from GO which is consistent with the XPS of C1s spectra results and a new peak that evolves at 529.8 ± 0.1 eV corresponding to the Ce-O bond. The area peak ratios of ~ Ce-O/C-O (peak at 532.2 eV) were calculated and shown in the third column of Table 7.1. The lower ratio (20 %) of CNP2/RGO compared to CNP1/RGO (45 %) indicates the lower particle fraction attached on the RGO surfaces which is consistent with the TEM studies. I speculate that the oxygen vacancies interacted more with the oxidized domains of RGO.
compared to the carbon atom which was confirmed by the absence of any substantial shift in the C1s’ peaks.

Figure 7.10 Comparison of XPS high resolution spectra of O1s’ peaks (524 to 540 eV) of GO before (a) and after (b) hydrazine reduction. CNP/RGO hybrids XPS spectra show two peaks after deconvolution indicating the O-Ce (529.7 eV) and C-O (532.2 eV) for (c) CNP1/RGO and (d) CNP2/RGO.

7.3.2.3 Raman Spectra

Figure 7.11 shows Raman spectra of the pure RGO (black line), CNP1/RGO (red line), and CNP2/RGO (blue line). In pure RGO, the three peaks are attributed to the G band at 1593.9 cm\(^{-1}\), D band at 1329.3 cm\(^{-1}\) and 2D band at 2638 cm\(^{-1}\), respectively. An additional peak at ~ 450 cm\(^{-1}\) is observed in the CNP/RGO hybrids and is attributed to the presence of ceria peak. The G band is related to in-plane vibration of \(sp^2\) C atom, while the D band is disordered defects such as
bond-angle disorder, bond length disorder and hybridization.\textsuperscript{42-43} The 2D band is related to the number of layers and chemical doping.\textsuperscript{44-45} The intensity ratios of D to G ($I_D/I_G$) band can be used to estimate the size of $sp^2$ graphitic region by using Tunistra - Koening relation.\textsuperscript{46-47} The ratio of $I_D/I_G$ (~ 1.2) is almost the same for all materials with size of $sp^2$ graphitic region of ~ 4.5 nm, indicating that the anchoring of CNP with RGO does not affect (deteriorate) the crystalline $sp^2$ region which is consistent with the XPS C1s spectra. G band of CNP1 and CNP2 hybrids are up shifted by 9.3 and 3.1 cm\textsuperscript{-1}, respectively. There are several factors affecting the shifting of the G band, such as defects, strains and doping.\textsuperscript{47-49} $I_{2D}/I_G$ intensity ratio is very sensitive to doping and related to Dirac point.\textsuperscript{46} The ratios are increased for CNP1 and CNP2 hybrid by 0.03 and 0.01, respectively. The changed ratio of more than 1 has been observed for molecular charge doping in other reports.\textsuperscript{50-51} However, in this study, only a small fluctuation was observed, indicating that the effect of charge doping can be ignored. Therefore, the up shifting of G band, in this case, was mainly caused by stress from oxygen states of CNPs.

![Raman spectra](image)

Figure 7.11 Raman spectra of the CNP1/RGO (red line), and CNP2/RGO (blue line), and pure RGO sheets (black line).
7.3.3 N-type Field Effect Transistor Properties of RGO/CeO2

To explore how oxygen vacancies on the CNPs affect the electronic transport properties of RGO sheets, I have measured room temperature electronic transport properties in backgated field effect transistor (FET) configuration. The CNPs/RGO hybrids were assembled via dielectrophoretic (DEP) between the prefabricated gold source and the drain electrodes. The channel width and length were 3 µm and 25 µm, respectively. Figure 7.12 (a) shows schematic illustration of the fabricated device along with the electrical transport measurement setup.

Figure 7.12 (b) shows the current (I)-voltage (V) characteristics of one of the CNP1/RGO devices in the range of -5 V and 5 V with \( V_g = 0 \) in air and vacuum condition. In air, the \( I-V \) curve of a forward sweep (red solid line with voltage range of -5 V to +5 V) and a reverse sweep (black solid line with voltage range of +5 V to -5 V) show hysteresis with non-linear behavior. In contrast, highly symmetric with no hysteresis behaviors of \( I-V \) curve was observed in the vacuum condition (blue curve). I attribute the marked difference in the \( I-V \) characteristics between the two conditions to the fluctuations in oxygen vacancy density in the ambient condition which occurs due to the continuous reaction of the vacancies with \( O_2 \) and/or \( H_2O \). This is further supported by the fact that the CNP2 hybrids, which have far less number of oxygen vacancies than CNP1, did not exhibit such a hysteresis in the ambient measurements.

Figure 7.12 (c) shows the FET characteristics of the hybrids. To avoid the complication from physisorbed oxygen on CNP/RGO hybrids in the air, all FET characteristics were measured in the vacuum condition. The backgate voltages \( (V_g) \) were swept from -100 to +100 V with a constant bias voltage of 1 V. As seen in Figure 7.12 (c), the CNP1/RGO shows \( n \)-type and the CNP2/RGO shows ambipolar properties. In general, RGO and RGO hybrids with other material
exhibited a “V” shaped ambipolar or $p$-type FET behaviors.\textsuperscript{52-55} However, it is important to note that due to the influence of high density surface oxygen vacancies on the electronic transport properties, the ceria incorporated RGO hybrids show $n$-type FET behavior. On the other hand, the CNP2/RGO (blue line), which has lower density of oxygen vacancy, shows ambipolar FET behavior.
Figure 7.12 (a) Schematic diagram of RGO/CNP FET device structure. The SEM image of the CNPs decorated on RGO sheets shown in between Au electrodes. (b) Current ($I$) – voltage ($V$) curves of RGO/CNP1. The red line is swept from -5 to 5 V (forward sweep), while black line is swept from 5 to -5 V (backward sweep) in ambient condition. The blue line represents the forward and backward sweeps of $I$-$V$ curves in vacuum. (c) Current ($I$) as a function of gate voltage ($V_g$) with $V= 1$ V for CNP1/RGO (black line) showing $n$-type property, $I$-$V_g$ for CNP2/RGO (blue line) showing ambipolar property. (d) Schematic illustration of the effects of oxygen vacancies created from CNP on RGO sheets. The mobile holes in RGO sheets are trapped with oxygen vacancies in CNPs, while the mobile electrons transport along the sheets.

This phenomenon can be explained by the hole trapping by the localized electrons at the oxygen vacancies of CNP1 surfaces. The mobile holes in the RGO sheets recombine with the localized electrons in CNP1. The schematic illustration of the hole trapping mechanism is shown in Figure 7.12 (d). In CNP, oxygen has a formal valence of 2- ($O^{2-}$), and when an oxygen
vacancy is created, two electrons are left at the vacancy site of the CNPs.56-57 These electrons remain localized in the $f$-level of two Ce atoms which accordingly change their formal valence from $+4$ to $+3$ states, while the reverse process occurs during oxidation.29-31 When CNPs are anchored on RGO sheets, the mobile holes in the RGO interact with the localized electron on CNPs via Coulomb interaction resulting in hole trapping at the vacancy site. This hole-capturing primarily occurs at the interface between the CNPs and the RGO sheets. In addition, this hole-trapping process effectively transforms the ambipolar RGO into $n$-type. As a result, the CNP1/RGO, which contains much more oxygen vacant sites than the CNP2/RGO, exhibits enhanced $n$-type properties.

7.4 Conclusion

In this chapter, I demonstrated the RGO/ NPs composite and studied transport properties of the composites. First, I synthesized RGO/CdS via one step solvothermal reduction methods. The RGO/CdS showed $p$-type FET property at room temperature. However, its mobility value is lower than RGO only sheet. Using low temperature transport measurement, I found that the ohmic regime vanishes at very high temperature (~ 225 K) compared to RGO only sheet (~ 40K). Further analysis with SCLC mechanism found high defects with defect density of $8 \times 10^{16}$ cm$^{-3}$, which is 4 times higher than RGO only sheets. The CdS QD may create additional trap state of charge. Second, I synthesized RGO/CeO$_2$ composite with chemical hydrazine reduction methods. By increasing the density of the oxygen vacancies on CeO$_2$, I observed interaction of mobile holes in the RGO and the localized electrons in the CNPs resulting in an $n$-type RGO/ CeO$_2$ composites.
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8 CONCLUSION

8.1 Summary

In this dissertation, solution based chemically derived reduced graphene oxide (RGO) sheets with AC dielectrophoresis (DEP) were utilized to fabricate 100% assembly yield graphene based field effect transistor (FET) and study their detailed electronic transport properties. Chapters 1 through 3 included an overview of the basic concepts of graphene and device fabrication techniques relevant to the experiments described in Chapters 4 through 7.

In Chapter 4, I demonstrated the first ever high yield fabrication of FET using RGO sheets. The RGO sheets, suspended in water, were assembled between prefabricated gold source and drain electrodes using AC DEP. All of the devices showed FET behavior with the application of a gate bias, with the majority of them demonstrating ambipolar behavior. In addition, I elucidated on the nature and density of defects in RGO sheets by using space charge limited conduction (SCLC) model. I estimated an average trap density of $1.75 \times 10^{16}$ cm$^{-3}$.

In Chapter 5, I presented significant new understanding of the electron transport properties of RGO using low temperature electron transport measurements and showed that the properties of RGO sheets can be described as graphene quantum dot (GQD) arrays where graphene domains act like QDs while oxidized domains behave like tunnel barriers between QDs. I obtained the GQD sizes to vary from 5 to 8 nm, in excellent agreement with previous transmission electron microscopy (TEM) studies. I also demonstrated Efros-Shklovskii variable range hopping (ES VRH) in RGO sheets of varying carbon $sp^2$ fractions, both in Ohmic and non-Ohmic regimes. From the estimated localization length (from 0.5 to 3.4 nm), I calculated a
bandgap variation of the RGO from 1.43 to 0.21 eV with increasing \( sp^2 \) fraction from 55 to 80 % which agrees remarkably well with theoretical prediction. By extrapolating the data to 100 % \( sp^2 \) fraction, I concluded that Mott VRH may not be observed in the chemically reduced RGO sheets. I also reported on tunable Coulomb blockade (CB) in RGO sheets of varying carbon \( sp^2 \). At very low temperature, CB is observed for all RGO sheets at below \( V_t \). The scaling parameter (\( \alpha \)) increases from 2.1 to 3.5 with increasing carbon \( sp^2 \) fractions from 55 to 80 % due to increases of topological defects.

In Chapter 6, I reported on the electron transport properties of RGO nanoribbon (RGONR) made by lithographical fabrication of RGO sheets. Temperature dependent resistance of all RGONR shows Ohmic ES VRH and is independent of size or dimension of RGONR. At low temperature and high electric field (high bias regime and non-Ohmic), the data can be explained with field dependent ES VRH, providing further evidence of ES VRH in RGONRs. I also observed CB in RGONR. From temperature dependent \( V_t \), I observed sub linear behavior where at lower temperature, \( V_t(T) \) slope is linear, however as the temperature further increased, the slope of \( V_t(T) \) is reduced. This sub linear behavior is a signature of 1D array system. However, the scaling factor \( \alpha \) (> 2.5) is not in agreement with its theoretical 1D array system. This may be due to additional trap state, which is created at the edge of the RGONRs.

In Chapter 7, I elucidated on the low mobility and density of charge traps in RGO/CdS composite by measuring and analyzing temperature dependent current-voltage characteristics. The Ohmic regime is vanished at very high temperature (~ 225 K) compared to RGO only (~ 40K) with similar carbon \( sp^2 \) fraction of RGO sheets for both. I found that the transport of the composite follows SCLC and estimated the trap density of \( 8 \times 10^{16} \text{ cm}^{-3} \), which is 4 times higher.
than RGO only sheets. The cadmium sulfide (CdS) QD may create additional trap state of charge. Additionally, RGO/cerium oxide (CeO$_2$) composites with different amounts of oxygen vacancies were synthesized. By increasing the density of the oxygen vacancies on CeO$_2$, I observed interaction of mobile holes in the RGO and the localized electrons in the CeO$_2$, resulting in an $n$-type RGO/CeO$_2$ composites.

8.2 Future Directions

Graphene is a potential material for the future generation electronic devices. However, it suffers from zero bandgap even at the charge neutrality point, which is one of the hurdles for graphene to be an useful digital electronic device application. For example, in graphene-based field effect transistor (FET), the zero bandgap does not allow its use in logic applications, which require frequent on/off switching. Reduced graphene oxide (RGO) has provided a potential in obtaining a band gap in graphene and thereby tuning the electrical properties from semimetal to insulator. However, its electronic device performance is not enough to for device application due to residual defects. Specifically, the presence of topological defects could make additional trapped charges on the sheets, which is a major problem for high quality graphene based electronics through RGO sheets. These defects are created mostly during the reduction of both chemical and thermal methods. Therefore, new development of reduction methods is essential to improve their electrical performance.

On the other hand, incorporation of RGO with nanoparticle composites has shown an opportunity to tune electrical properties of RGO. However, enhancing electronic properties is yet
to be established. Therefore, developments on new functional materials need to be addressed such as magnetic and metal nanoparticles.
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3. Name of author
   Daeha Joung, A.Chunder, Lei Zhai and Saiful I. Khondaker.

4. Volume number, page number (or article identifier), year
   Volume 21, Number 16, Page 165202

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License Number: 3027161334606
Order Date: Nov 13, 2012
Publisher: American Institute of Physics
Publication: Applied Physics Letters
Article Title: Space charge limited conduction with exponential trap distribution in reduced graphene oxide sheets
Author: Daeha Joun, A. Chunder, Lei Zhai, Safiul I. Khondaker et al.
Online Publication Date: Sep 1, 2010
Volume number: 97
Issue number: 9
Type of Use: Thesis/Dissertation
Requestor type: Author (original article)
Format: Print and electronic
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Number of figures/tables: 4
Title of your thesis / dissertation: Electronic Transport Investigation of Chemically Derived Reduced Graphene Oxide Sheets
Expected completion date: Nov 2012
Estimated size (number of pages): 200
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APPENDIX H:
LIST OF RELEVANT PUBLICATIONS
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