Charge transport in graphene oxide

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CHARGE TRANSPORT IN GRAPHENE OXIDE

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CHARGE TRANSPORT IN GRAPHENE OXIDE

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Abstract

The objective of this thesis is to study charge injection across the gold/graphene-oxide (Au/GO) interface and elucidate the charge transport mechanisms in graphene oxide (GO) and lightly reduced GO (RGO). Ballistic electron emission microscopy (BEEM) studies show the Au/GO interface to be non-homogeneous at the nanoscale. In addition, the distribution of electron/hole injection barriers across the Au/GO interface was extracted via ballistic electron/hole emission spectroscopy (BHES/BEES). The heterogeneity of the interface is believed to arise due to the different functional groups on GO, which are known to create defects/traps.

Trap energy levels in GO were extracted via thermally stimulated current (TSC) measurements on graphene oxide devices, fabricated by e-beam lithography. In addition, TSC measurements carried out on RGO showed a decrease in the overall trap density compared to that of GO. However, several states close to the Fermi level are shown to emerge with reduction.

Conventional temperature dependent current-voltage (I - V) measurements on RGO measured down to 12K, showed various charge transport mechanisms such as tunneling, hopping, space charge limited current with exponentially distributed traps (SCLC-EDT), and Poole-Frenkel limited transport, depending on the applied field and temperature. The transport gap in GO/RGO is shown to be of the order of a few meV, resembling an ohmic contact.

Overall, the I - V , BEEM and TSC experiments give a correlated view of the transport in GO/RGO, supporting a multi-energy bandgap. In terms of technology, we find that several issues related to trap states have to be first resolved before GO/RGO could be used either as a dielectric or as a channel material.

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1. “Charge Transport in lightly reduced graphene oxide: A transport energy perspective”, R. S. Kajen, N. Chandrasekhar, K. L. Pey, C. Vijila, M. Jaiswal, S. Saravanan, M. H. Ng, C. P. Wong, K. P. Loh. Journal of Applied Physics. 113, 063710 (2013).
2. “Trap levels in graphene oxide: A thermally stimulated current study”. R. S. Kajen, N. Chandrasekhar, K. L. Pey, C. Vijila, M. Jaiswal, S. Saravanan, M. H. Ng, C. P. Wong, K. P. Loh., ECS Solid State Lett. 2, 2, M17 (2013).
3. “Trap energy levels in graphene oxide determined by ballistic electron emission spectroscopy”, R. S. Kajen, N. Chandrasekhar, K. L. Pey and C. Vijila, ECS. Solid. State. Letters. 1, 5, M27 (2012).
4. “Ballistic Electron Emission Microscopy Study of Charge Transport Across an Au/Graphene-Oxide/Modified-Si Stack”, R. S. Kajen, N. Chandrasekhar, M. H. Ng, S. H. Goh, K. L. Pey and C. Vijila, ECS. Solid. State. Letters. 1, 2, M13 (2012).
5. “Ballistic Electron Emission Microscopy on graphene-oxide/metal interface”, R.S.Kajen, N. Chandrasekhar, K. L. Pey and M. H. Ng, Molecular Materials Meeting 2011 conference.
6. “Vibrational excitations in molecular layers probed by ballistic electron microscopy”, R. S. Kajen, N. Chandrasekhar, X. Feng, K. Mullen and H. Su, Nanotechnology. 22, 435701 (2011).

Chapter 1 Introduction

1.1 Motivation and Objective

Excessive leakage current and increased power dissipation [1] in nanoscale silicon transistors has pushed the microelectronics industry to search for better materials. Graphene [2] (a monolayer of close packed carbon atoms exhibiting exceedingly high mobilities [3-4]) and its variants are justifiably expected to revolutionize VLSI/ULSI technology [5-6]. However the current bottlenecks in graphene transistor technology are large-scale manufacturability and the absence of a finite bandgap (graphene is a semi-metal), which prevents efficient switching on/off of the transistors [7]. One solution to tackle the bandgap problem is to add functional groups such as oxygen onto graphene, thus creating graphene oxide (GO), with a tunable bandgap [8] depending on the sp^2 fraction of carbon bonds in the materials. This gives GO the flexibility to be tuned from an insulator to a semi-metal via chemical/thermal reduction, allowing GO to be used for a whole range of applications ranging from a dielectric [9] to a channel material [10]. It might be even possible to implement both graphene charge transport regions and GO transport barriers on the same graphene sheet [11]. In addition, the heterogeneous electronic and chemical structure of GO, with several types of oxygen-containing functional groups on its basal plane and edges, allows it to interact with a wide range of organic/inorganic materials to form several hybrids with unusual properties [12]. Importantly, GO is solution-processable [13], allowing large scale manufacturing options [14], unlike the case of exfoliated graphene.

In order to practically benefit from the advantages mentioned above, regardless of the application type, an electrical contact has to be made to GO/RGO (reduced GO). The metal/GO contact has been reported to be crucial in controlling the charge transport properties in GO/RGO [15], making the study/characterization of injection/Schottky barriers at the metal/GO interface important. However, with the presence of various functional groups in GO [16], the metal/GO interface is expected to be non-homogeneous. Conventional methods such as current-voltage (I - V) and capacitance-voltage (C - V) measurements give a bulk measurement [17] and are not suitable in mapping out the nanoscale interface heterogeneity at the metal/GO interface. To overcome this, **we propose to use ballistic electron emission microscopy (BEEM) [18-19]; a 3-terminal scanning tunneling microscopy (STM) based technique to probe both the electron and hole injection barriers across an Au/GO interface at the nanoscale. In addition, the BEEM technique characterizes vertical charge transport (perpendicular to the graphene plane) across the Au/GO interface,** which will be a feature of most devices, regardless of their being in a sandwich or planar configuration.

Although the heterogeneous structure of GO has several advantages, defects/traps are created due to the different functional groups in GO, and also during the reduction process to obtain RGO [11]. These defects are likely to play an important role in charge transport/injection into GO/RGO. We believe that a detailed study of the energy levels/density of these traps will give a better understanding of charge transport in GO/RGO. **Therefore we use the thermally stimulated current (TSC) technique [20] to characterize the trap energy levels in GO and study the evolution of these levels with laser induced/thermal reduction of GO [15, 21].**

There have been several studies on the charge transport mechanism in RGO, reporting behaviour varying from Schottky limited [15] to Poole-Frenkel [22], hopping and tunneling [10], space charge limited with exponentially distributed traps (SCLC-EDT) [23] and percolation [8]. Although the level of GO reduction and the experimental conditions were varied throughout the reports, we believe that the root cause of the problem could be more fundamental. Charge carrier injection and transport in disordered organic semiconductors is very different when compared with inorganic semiconductors [24, 25]. Several assumptions made in deriving models for charge transport in inorganic materials may not hold [26] for organic materials. **We propose to perform temperature/field dependent I - V studies on GO/RGO devices coupled with an appropriate transport model for disordered organic semiconductors to elucidate the charge transport mechanism in such devices.**

Hence, in this thesis, we aim to better understand charge injection and transport mechanisms in GO/RGO on the micro and nanoscale. Through BEEM, we will be able to obtain information on the charge injection barrier heterogeneity at the Au/GO interface at the nanoscale. Through TSC, we will be able to characterize various trap/defect energy levels present in GO/RGO and through temperature dependent I - V measurements, we will be able to elucidate on charge transport mechanisms present in RGO. Through an extensive study involving advanced characterization techniques such as BEEM, TSC and I - V , we believe that a comprehensive picture of transport could be obtained, which would give a better understanding of charge transport in GO/RGO.

1.2 Organization of Thesis

The thesis is organized as follows:

Chapter 1 introduces GO/RGO as a material with several application possibilities ranging from a dielectric to a channel material.

Chapter 2 reviews the structural and charge transport properties of GO and provides the motivation for the study of charge injection/transport in GO. It examines the various injection/Schottky barrier theories in common inorganic/organic semiconductors, and lists the reasons for transport in GO being fundamentally different from that seen commonly in inorganic semiconductors.

Chapter 3 presents the TSC work done in this thesis. It first reviews trap theory in inorganic/organic materials followed by TSC theory and its application to GO trap energy level characterization. Thereafter, GO synthesis and GO/RGO device fabrication is described along with preliminary material characterization results from techniques such as Raman spectroscopy and atomic force microscopy (AFM), used to test the integrity of GO. After description of the experimental setup and procedure, the TSC results are presented and analyzed.

Chapter 4 presents the temperature dependent I - V characterization work done in this thesis. The chapter begins with a review of charge transport theory in inorganic/organic materials and the transport models used by various groups before proceeding to analyse the temperature dependent I - V characterization data obtained from the RGO devices, whose fabrication is described in Chapter 3.

Chapter 5 presents the BEEM work done in this thesis. It first reviews the BEEM theory in inorganic semiconductors, and discusses the lack of a BEEM theory for organic materials. The different approaches taken by several groups using BEEM to study metal/organic interfaces is reviewed. A large portion of this chapter concentrates

on the BEEM device fabrication and the BEEM experimental setup, which is crucial in determining the success of the BEEM experiment. Thereafter, BEEM results are analyzed to extract the electron/hole injection barrier distribution, and a resonant tunneling BEEM model is proposed. Next, the feasibility of using the BEEM derivative as a tool to extract the injection barrier heights is discussed/analyzed. The technique of using repetitive spectroscopy at a localized region to map tunnel barriers is also addressed. The chapter finally concludes with a discussion of issues related to determining the Au/GO/Si band diagram and the parameters required to obtain an accurate band alignment diagram.”

Chapter 6 compares the results from the TSC, I - V and BEEM experiments to obtain a correlated view of transport in GO/RGO. The results are compared with the density of states of GO/RGO postulated by theory and obtained through experiment, to give an overall view of charge transport and carrier injection into GO/RGO.

Chapter 7 states the important findings of this thesis, their impact in various device applications and provides recommendations for future work.

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Chapter 2 A review of structural and charge injection/transport properties in graphene oxide

2.1 Structure of graphene oxide

Graphene oxide (GO) is a 2-dimensional material with several functional groups on the basal plane of graphene (a sheet of carbon atoms one atom thick). Recent aberration corrected transmission electron microscopy (TEM) studies have given a clear view on the GO structure as shown in Fig. 2.1 [1]. The following points summarize the salient features of GO structure:

1. Graphitic regions up to 8 nm² remain.
2. Oxidized regions exhibit no order with regards to oxidation, have minimal sp^2 bonding character, and form a continuous network across the GO sheet.
3. Holes are present, usually under 5 nm².
4. Hydroxyls and (1, 2) epoxies are some of the dominant functionalities. Carbonyls likely exist along the edges of the holes.
5. Largely unstrained sp^2 bonds exist between carbons within the core of graphitic regions.

These conclusions from Ref. 1 support the structure of GO proposed by Lerf *et al.* [2] as shown in Fig. 2.2.

Figure 2.1: Aberration-corrected TEM image of a single sheet of suspended GO. The scale bar is 2 nm. Expansion (A/B) shows, from (left to right)/(top to bottom), a 1 nm^2 enlarged oxidized region of the material, a proposed atomic structure of this region with carbon atoms in gray and oxygen atoms in red, and finally the average of a simulated TEM image of the proposed structure. Expansion (B) focuses on the white spot on the graphitic region. Expansion (C) shows a 1 nm^2 graphitic portion from the exit plane wave reconstruction of a focal series of GO and the atomic structure of this region. [1]

Figure 2.2: Structural model of GO proposed by Lerf et al. [2].

2.2 Charge transport in graphene oxide

A simplistic picture of the electronics in graphene oxide would be that sp^3 regions (regions with functional groups attached) act as transport barriers which disrupt the sp^2 delocalised π network present in graphene. These barriers then give rise to a bandgap which makes GO insulating. GO is believed to be partially amorphous with intact sp^2 islands (6 nm^2) [3]. Although, graphene itself has a well defined wave vector, for GO, the random functional groups on the graphene basal plane introduces positional disorder [4] into the system which is likely to also create energetic disorder. To study charge transport in GO, it is necessary to make electrical contacts to GO, using metal contacts for any electrical measurement. This motivates an investigation of the nature of the metal/GO interface. An important transport property of a metal-semiconductor (m-s) interface is its injection barrier or the Schottky-barrier height (SBH) [5]. The SBH is a measure of the energy level mismatch between the metal and the semiconductor and determines transport across the m-s interface. A good SBH theory is needed to understand the physics of practical device operation as well as to provide realistic/reliable parameters for device design. In this section, we will briefly discuss SBH theory and methods used to characterize the SBH in standard inorganic semiconductors. We will also elaborate on how these concepts have to be modified in addressing injection barriers across metal/organic interfaces before motivating a study of charge injection/transport across the metal/graphene-oxide interface.

2.2.1 General charge injection barrier theory

2.2.1.1 Schottky-Mott and Bardeen limits

SBH models could be classified under interacting (interaction between the metal and semiconductor) and non-interacting models. In non-interacting models, charge rearrangement at the m-s interface is assumed to be absent and the thermodynamic aspect [6] of interface formation is ignored. Amongst non-interacting models, the first order theory for the SBH was given by Walter Schottky and Sir Neville Mott where the SBH at an m-s interface is given by the difference between the metal Fermi level and the electron affinity of the semiconductor as shown in Eq. 2.1.

$$\Phi_{B,n}^0 = \phi_M - \chi_S \quad (2.1)$$

Here $\Phi_{B,n}^0$ is the SBH at a metal-n-type semiconductor in the absence of interaction effects as shown in Fig. 2.3, ϕ_M is the Fermi level of the metal, χ_S is the electron affinity of the n-type semiconductor and E_g is the bandgap of the semiconductor. CB and VB denote the semiconductor conduction/valence bands respectively. Equation 2.1 is also known as the Schottky-Mott relationship.

Figure 2.3: Schottky barrier height across a typical metal-n-type semiconductor.

Although the theory predicts a SBH as shown in Eq. 2.1, experimental results have deviated from a metal work-function dependent SBH as predicted by this model [6]. SBHs are very much dependent on the preparation of the m-s interface and hence an interface dependent parameter or S parameter (S_ϕ) was created to quantify the deviation from the standard Schottky-Mott theory (Eq. 2.1) as shown in Eq. 2.2.

$$S_\phi = \frac{\partial \Phi_{B,n}^0}{\partial \phi_M} \leq 1 \quad (2.2)$$

Here, $S_\phi=1$ is the Schottky-Mott limit and, $S_\phi=0$ is known as the Bardeen Limit. The Schottky-Mott limit is reached in the absence of interaction or charge rearrangement at the interface. However such a limit is seldom reached. At real interfaces, significant charge rearrangement occurs at the interface, resulting in the formation of dipoles. Old bonds are broken and new ones formed. At the Bardeen limit, the SBH is insensitive to the metal work function and is determined by the interaction between the metal and semiconductor. The insensitivity of the metal work function in affecting the SBH is also known as “Fermi-level pinning” (FL-pinning). The origin of the FL-pinning phenomenon has been attributed to surface states (caused by termination of a periodic crystal lattice) [7], trap states due to defects or by metal-induced gap states (MIGS) [8]. MIGS are metal states tailing into the semiconductor and creating states in the semiconductor bandgap. For such interfaces with strong FL-pinning, models which account for interaction effects have to be used such as the bond polarization theory, which is based on energy minimisation at the interface (via charge transfer). In the bond polarization model, all interface states (including MIGS) are the result of interaction effects. In summary, to arrive at a reliable/accurate SBH, both Poisson’s equations and thermodynamics have to be taken into account.

2.2.1.2 Schottky/Injection barrier height measurement in inorganic materials

In this sub-section, the various techniques used to measure the SBH in inorganic materials and the assumptions behind such techniques will be discussed. Fig. 2.4 shows a schematic of charge transport via thermionic emission across an arbitrary barrier. It can be observed that only the barrier height ϕ_A measured from the Fermi level (E_F) affects transport and not the shape of the barrier. This is generally the case in homogeneous (on the scale of depletion width of the semiconductor) barriers.

Figure 2.4: Schematic of electron transport from a reservoir (shaded area on the left) across an arbitrary barrier with barrier height Φ_A (measured from the metal Fermi level (E_F)). Only the electrons which have energies surpassing the transport barrier are transported across the barrier (represented by the shaded region on the right). [6]

The overall current through such a barrier is given by Eq. 2.3, below,

$$I_{SB} = I_{Sat} \left(\exp \left(\frac{eV}{k_B T} \right) - 1 \right) \quad (2.3)$$

where I_{Sat} is the reverse bias saturation current given by Eq. 2.4, as:

$$I_{reverse} = I_{Sat} = AA^* T^2 \exp \left(-\frac{\phi_{B,n}}{k_B T} \right) \quad (2.4)$$

where V is the applied bias, A^* is the effective Richardson constant, A the cross sectional area of the barrier, k_B is the Boltzmann constant, e is the electronic charge, $\phi_{B,n}$ is the barrier height (SBH) to be measured and T the absolute temperature in Kelvin. From Eq. 2.3 and 2.4, it seems trivial to extract the barrier height via I - V characterization.

However several factors have to be taken into consideration before extracting the barrier height from I - V :

1. Image force lowering

When an electron approaches a metal surface, it induces a positive charge on the metal surface which then acts like an image charge in the metal. The attraction between the electron and the induced image charge causes a lowering of the Schottky barrier height [5].

2. Series resistance

In real devices, the applied bias does not entirely drop across the m-s interface. Parts of the bias drop across the bulk semiconductor and the Ohmic contact at the back of the semiconductor. Hence the V in Eq. 2.3 has to be replaced by $(V - I_{SB}R_S)$ where R_S is the series resistance (which has been assumed to be independent of the applied bias).

3. Doping level

In highly doped semiconductors, the tunnelling probability of carriers is increased and effectively reduces the SBH.

Only upon resolution of the above mentioned issues, could one use the I - V to extract the SBH. In addition, low SBH patches have been found to dominate transport in inhomogeneous interfaces. [6] In the case of such inhomogeneous interfaces, the situation is far more complicated depending on the length scale at which the SBH varies. Next, thermionic emission theory is only valid for large diodes. A cross over

from thermionic emission to tunnelling has been observed as the diode size is shrunk [9, 10] making Eq. 2.3 irrelevant in such a case. Hence the I - V method has to be used with extreme care in determining the barrier height even in inorganic materials.

Another popular method is capacitance-voltage (C - V) characterisation [5] which measures the mean SBH. The space charge per unit area due to uncompensated dopants is given by

$$Q_{SC} = eN_D W = \sqrt{2\epsilon_S N_D q (V_{bi} - V - k_B T/q)} \quad (2.5)$$

where N_D is donor density, ϵ_S is the dielectric permittivity of the semiconductor, V_{bi} is the built-in voltage. V is the applied bias and q is the charge. The small signal capacitance for the Schottky diode under measurement is given by Eq. 2.6:

$$C = -\frac{\partial Q_{SC}}{\partial V} = \sqrt{\frac{e^2 \epsilon_S N_D}{2(eV_{bi} - V - k_B T/q)}} \quad (2.6)$$

Rearranging Eq. 2.6, we get Eq. 2.7:

$$\frac{1}{C^2} = \frac{2 \left(V_{bi} - V - \frac{k_B T}{q} \right)}{q \epsilon_S N_D} \quad (2.7)$$

Hence by plotting $1/C^2$ versus V (known as the Mott-Schottky plot) in the case of a constant doping profile, one could extract V_{bi} from the intercept of the plot. Thereafter the barrier height could be calculated using Eq. 2.8.

$$\Phi_{B,n}^0 = eV_{bi} + eV_n + k_B T \quad (2.8)$$

where, eV_n is the depth of the Fermi level below the conduction band. It should be noted that the C - V method is only accurate when the density of traps is low. Similar to the I - V , it is also affected by several factors such as series resistance, leakage current and SBH inhomogeneity [6] which modulates the width of the space charge region.

Both methods (I - V and C - V) are macroscopic in nature and offer no information on the lateral inhomogeneity of the SBH at the nanoscale. Ballistic electron emission

microscopy [11] is a powerful scanning tunnelling microscopy (STM) based technique which is able to resolve the SBH inhomogeneity on the nanoscale. The BEEM technique, due to its scanning ability, gives the entire statistical distribution of barriers. This should be compared to the $C-V$ which gives the mean SBH and $I-V$ which gives the lowest barrier in general. We will describe more of the BEEM technique in Chapter 5.

2.2.1.3 Schottky/Injection barrier height measurement in organic materials

In defect free organic/molecular materials, the transport occurs via the HOMO (highest occupied molecular orbital) for holes and LUMO (lowest unoccupied molecular orbital) for electrons, in general. The terminology of HOMO/LUMO and valence-band/ conduction-band (VB/CB) could be thought to be equivalent, where a carrier needs to be transferred to either the HOMO/LUMO or VB/CB for delocalised transport to take place. However, fundamentally, these terms are not the same. The term “molecular” orbital arises due to sp/sp^2 or sp^3 hybridization of carbon atoms. The overlap between the sp^2 orbitals leads to the sigma (σ -bond) while the overlap between the $2p_z$ orbitals leads to the bonding/anti-bonding π/π^* orbitals respectively. The bandgap of the material is defined by the π - π^* gap and hence the π/π^* states also correspond to states through which hole/electron transport take place.

The HOMO and LUMO are also known as “frontier” orbitals. The extent of spatial overlap of these orbitals between neighbouring sites determines the nature of transport in the organic. A strong coupling of the frontier orbitals allows delocalised transport while poor coupling between the orbitals tends to create localized states which depend on thermally activated hopping as the mechanism for the transport [12].

In the presence of defects/traps, a SBH theory for charge injection across a metal-organic interface is not trivial due to the following reasons:

1. The concept of a wavevector- k is ill-defined in the organic making any k -based transport theory irrelevant, and
2. The presence of defects and localized states near the metal Fermi level provides states at the metal-organic interface for electrons to tunnel into, thereby providing an alternative path for conduction apart from the typical thermionic emission type of transport.

A successful theory for transport across the metal-organic (M-O) interface is a model by Arkhipov *et al.* [13] who proposed charge transport across the M-O interface to consist of hopping injection into a localized state at M-O interface, followed by hopping transport across the M-O barrier. Wulf *et al.* arrived at a similar mechanism via Monte-Carlo simulations [14] studying charge transport from a metal to an organic dielectric with random hopping sites.

2.2.2 Significance of charge injection/transport study in graphene oxide

Wu *et al.* [15] investigated transport through lightly reduced epitaxial GO and attributed the transport mechanism to Schottky emission assuming a 2-DEG (2-dimensional electron gas) formulation. In addition, pure GO was reported to be insulating, since no non-linear I - V could be obtained even for voltages up to 60V. Joung *et al.* [16] showed an exponentially distributed trap space charge limited transport (EDT-SCLC) across reduced GO flakes lined up via dielectrophoresis while Navarro *et al.* [17] pointed towards a hopping limited transport mechanism. Kanamori *et al.* [18] attributed transport vertical to the graphene plane in reduced GO to be via a Poole-Frenkel (PF) mechanism using conductive atomic force microscopy studies. Eda *et al.* [19] showed that the in-plane transport mechanism changes from tunnelling and hopping to percolation as the extent of reduction is increased. What is it that causes such wide spread disagreement about the transport mechanism?

In addition, there has been controversy on the value of GO bandgap, with values ranging from 0.25 eV to 5.4 eV [20-22]. On the surface, the origin of the bandgap variation appears to arise from the difference in experimental conditions, device structure and the extent of reduction. However, the origin of this variance appears to be rooted to a multi-energy bandgap as shown by Bansal [23]. In such a situation, it is likely that different groups have been measuring different transitions within the gap. Lastly, it is also unclear whether traditional k-based theories developed for inorganic semiconductors could be still used for GO or whether should GO be given a disordered organic semiconductor treatment along the lines of the theory developed by Arkhipov [13].

Due to the sheer complexity of the GO structure, in terms of both the energetic and positional disorder present in the system, it becomes interesting in its own right to unravel the dominating transport mechanism in such a material. What is the injection barrier in a metal/GO system? Are there trap/defect levels in such a system? Is transport via delocalized states or via localized ones? These issues make the study of charge transport in GO interesting and will be discussed in detail in the following chapters.

2.3 Summary

In this chapter, we introduced the structure of GO as an amorphous material with nm-sized intact graphene regions and motivated an investigation into the study of charge transport in GO. We pointed out the key differences in defining and measuring injection/Schottky barriers in inorganic/organic materials and specifically GO. We show that GO is a disordered material with energetic and positional disorder, and cannot be compared to traditional inorganic materials. The Schottky/injection barrier theory was reviewed along with the various macro/ nanoscale barrier height extraction techniques (I - V , C - V and BEEM) used for characterizing the metal/inorganic interface. While the metal/inorganic interface could be reasonably understood using existing Schottky barrier height (SBH) theories, the metal/organic interface was shown to be non-trivial due to the absence of a well defined wavevector- k in the organic; which subsequently renders the application of traditional k -based theories invalid for organic materials.

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Chapter 3

Trap energy level measurements by thermally stimulated current

3.1 Introduction

During the oxidation of graphene/graphite, several defects [1] are created in the form of epoxide, hydroxyl, carboxyl and carbonyl groups either on the graphene basal plane or its edges. These defects cause a disruption of the sp^2 π -orbital network across the graphene basal plane and thereby create transport barriers for traversing charge carriers. Capacitive photocurrent spectroscopy measurements [2] suggest several defect/trap states in the π - π^* gap of experimentally determined density of states (DOS) of GO and reduced GO (r-GO) as shown in Fig. 3.1. Some observations can be made from Fig. 3.1:

1. The reduction does not lead to a decrease in the bandgap (π^* - π) during the GO (insulator) to r-GO/graphene transition, but instead leads to additional energy levels within the gap.
2. There is an increase in the density of states in the bandgap after reduction.
3. The charge transport mechanism in GO/r-GO is likely to involve the states in the gap.

Figure 3.1: Evolution of the experimentally [2] obtained density of states during reduction from GO (left) to r-GO (right). Reduction leads to additional levels in the π^* - π gap. The blue lines depict possible transitions from the highest filled electronic level to unfilled levels.

These observations coincide with conclusions from transport experiments on r-GO [3] which show that reduction does not lead to delocalization of carriers but rather leads to an increase of localized states in the gap. In addition, carrier transport in r-GO is likely to be by thermally activated hopping of midgap states. Femto-second transient absorption spectroscopy studies on GO/r-GO [4] have shown that the reduction process is unable to completely heal/remove traps. This work also highlights the fact that electrons are more likely to be trapped and detrapped, rather than holes. With the trap states playing a significant role in carrier transport, it becomes increasingly important that device engineers have a clear picture of the band diagram of GO/RGO with the various trap energy levels. Such a study in GO has been lacking. In this chapter we propose to characterize the trap energy levels in GO and the evolution of such levels with reduction, using the thermally stimulated current [5] (TSC) technique. The following subsections will elaborate further on trap theory, TSC theory, GO synthesis and device fabrication, before moving onto the experimental setup/procedure and results.

3.2 Theory

3.2.1 Trap states

The difference between metals, semi-metals, semiconductors and insulators is determined by the relative positions of the valence band (VB) and the conduction band (CB) as shown in Fig. 3.2. The semiconductor and insulator can be distinguished from the metal/semi-metal by the presence of a bandgap between the valence and conduction bands. This implies that one has to supply external energy to excite an electron from the valence band to the conduction band for conduction to occur.

Figure 3.2: Typical band diagram of metals, semimetals, semiconductors and insulators. The differences between the 4 types of materials depend on the relative positions of the conduction and valence band. In a metal, the VB and CB are overlapped. This allows conduction of charge upon application of an electric field. However in a semi-metal, the band overlap is indirect unlike in the case of a metal and thus requires additional energy from momentum (k -vector) considerations for transition into the CB. In both an insulator and a semiconductor a bandgap exists between the VB/CB. However the bandgap in an insulator is relative larger compared to a semiconductor.

The insulator can be further distinguished from the semiconductor as a material with a large bandgap. The metal however has a direct band overlap, implying that it will conduct once an external field is applied. However in the case of a semi-metal there is an indirect band-overlap. Graphene is such a semi metal, whereas graphene oxide, the material of our study, is an insulator due to the presence of defects in the graphene basal plane and edges. Being an insulator, which has a large bandgap, how is conduction possible? The band gap is “forbidden” only in theory [6]. Realistically, the gap is occupied by several levels which are essential for device applications. Such levels which are able to capture carriers and retain them in a restricted locality are known as traps [7]. Traps originate from microstructural defects and are further classified as trapping levels, if they lie near the conduction/valence band and recombination levels, if they lie close to the midgap. Depending on the external conditions these levels can act in several ways. The various processes [7] involved in both the electron trap (E) and the hole trap (H) are shown in Fig. 3.3. The possible transitions for an electron trap (E) are (as indicated alphabetically):

- a) Filling of trap by capture from conduction band
- b) Emptying of trap by moving into the conduction band
- c) Filling of trap by excitation of carriers from lower energy level.
- d) Emptying of traps to lower levels

Similar processes exist for hole traps as shown in Fig. 3.3.

Figure 3.3: Possible transitions involving electron traps (E) and hole traps (H). The red arrows refer to electron transitions [7]. The processes (a) refers to trap filling by electron capture from CB, (b) refers to trap emptying by transition to CB, (c) refers to trap filling by excitation of electrons from the VB and (d) refers to emptying of traps by moving to the VB. The processes (a') refers to trap filling by hole capture from VB, (b') refers to trap emptying by transition to VB band, (c') refers to trap filling by holes capture from the CB and (d') refers to emptying of traps by hole release into the CB.

Thus, conduction is possible through these trap levels even if the bandgap is large. In the case of organic and disordered materials, the situation becomes even more favourable for transport via trap states due to their large number. Graphene oxide can be treated as amorphous [8]. The band diagram for amorphous materials would differ significantly [9] from crystalline materials, as shown in Fig. 3.4. The density of states (DOS) of the band tail states and the trap states in an amorphous material is approximated to follow an exponential distribution as shown in Fig. 3.4.

Figure 3.4: Energy diagram for an amorphous material. [9] An exponential distribution is assumed for both the band tail states (conductive states) leaking into the bandgap and for the trap states (non-conductive state) which is represented by the various straight lines on a log scale (x-axis) with slopes $1/kT_1$ and $1/kT_2$ respectively.

One can observe that there is a significant amount of trap states in between the band tail states. In such a case, the charge carrier dynamics within the material become a strong function on both the conductive tail states and the trapped states. It should be noted that although the concept of exponential DOS has been used to explain the band diagram of amorphous materials, it has been reported that a Gaussian distribution will better fit the HOMO/LUMO distribution in disordered organic materials [10]. In addition, charge carriers in such materials are believed to be highly localized [11] with molecules or molecular subunits as localization centers (localization radius of the size of the molecule). Fig. 3.5 puts several concepts such as shallow/deep states and extended/tail states into perspective.

Figure 3.5: Schematic of density of states in a typical disordered material. [10] The schematic depicts the presence of both tail states penetrating into the bandgap of the material and several shallow/deep electron/hole trap levels within the bandgap. The mobility edges E_c and E_v demarcate the energy beyond which delocalized transport occurs. Possible transitions for trap release and capture are presented in the schematic.

E_c and E_v are known as the mobility edges which demarcate the border between extended states and localized states. The energy gap between the two is known as the mobility gap. The mobility edges essentially play the role of conduction/valence band. Carriers that reach the extended states are delocalized. However, this only happens at very high temperatures. In most cases, at lower temperatures, the transport is determined by tunnelling/hopping between localized states [10]. Thus, it is of interest to the device engineer to know the position of such localized states in order to better understand transport in GO.

3.2.2 Theory of thermally stimulated current

The thermally stimulated current technique has its origin from glow experiments (thermoluminescence) [13] where the information on charge traps was obtained by measuring the intensity of light generated while heating up a sample to free charges from traps. However this method has a disadvantage. Only electrons which undergo recombination contribute to the glow, whereas any electron which enters the conduction band contributes to the TSC [6]. The TSC experiment involves low temperature optical/electrical filling of traps and subsequent heating at a constant rate under a fixed bias voltage, and measuring the current as carriers are detrapped. It is important that the applied bias be low enough to retain the sample in the Ohmic regime, and serve merely to extract the carriers detrapped by temperature. The current is expected to reach a maximum when all the traps (carriers) have been emptied (detrapped). Thereafter the current will drop back to the intrinsic conduction level of the material. In most real materials, such a simple picture may not suffice. Several competing processes occur such as detrapping, retrapping and recombination of trapped charges. Initial theoretical work [14] assumed high fields, negligible recombination, and was applied to the case of p-n junctions and thin semiconducting/insulating films. However, in the case of disordered materials these assumptions breakdown and one has to incorporate the effect of recombination. Another key assumption in several TSC theories is that conduction is only through delocalized carriers above the mobility edge [15] or the conduction band. While this may be true at high temperatures, transport in disordered semiconductors at low temperature is shown to be via hopping of electrons via localized band tail states [11]. Thus the type of theory applicable may well depend on both the material system and the measurement conditions. A suitable theory for GO is presented below, with minor

modification in the interpretation of the theory given in reference [15]. The theory was developed for a single type of carrier (electrons in this case). A similar treatment can be used for holes and it should be noted that contributions to the TSC arise from both holes and electrons. For a single trap level the rate equation is as follows:

$$\frac{dn_i}{dt} = -e_{ni}n_i + n(N_i - n_i)\sigma_{ni}v_n \quad (3.1)$$

where the index i refers to either a trap center or a recombination center, e_{ni} is electron emission rate at the center i to the conduction band, n_i is the number of occupied centers at level i , n is the free electron concentration, N_i is the total number of centers at level i , σ_{ni} is the electron capture cross section and v_n is the mean thermal electron velocity. By summing across all recombination/trapping centers, we get:

$$\frac{dn}{dt} = \sum_i e_{ni}n_i - n \sum_i \sigma_{ni}v_n(N_i - n_i) \quad (3.2)$$

We now make an assumption that there is only one trap and the rest of the levels are recombination centers. Then we could lump the total effect of all the recombination centers into a single parameter τ_n , the recombination lifetime as shown below.

$$\tau_n^{-1} = \sum_{j.recomb.centers} \sigma_{nj}v_n(N_j - n_j) \quad (3.3)$$

With this, Eq. 3.2 could be written as follows:

$$\frac{dn}{dt} = e_{ni}n_i - n\sigma_{ni}v_n(N_i - n_i) - \frac{n}{\tau_n} \quad (3.4)$$

where the index i now refers to a particular trap of interest. The equation now accounts for detrapping, retrapping and recombination. During the TSC experiment, the material is optically excited at low temperature to fill the trap states. Thereafter the temperature is ramped up at a constant rate such that $dT = a dt$, where a is the heating rate. Here, we make the important assumption that retrapping is negligible. The

justification for our assumption lies in the results of our TSC spectra, to be discussed later. For a system with significant retrapping, the fall (in time and hence temperature due to a constant heating rate) of the TSC curve will be significantly reduced, compared to the rise. However in our case, the rise and fall of the TSC current are similar as we will show in the results section. Thus we assume that:

$$\tau_n^{-1} \gg (N_i - n_i)\sigma_{ni}v_n \quad (3.5)$$

Hence, the rate equation for a particular trap level is:

$$\frac{dn_i}{dt} = a \frac{dn_i}{dT} = -e_{ni}(T)n_i(T) \quad (3.6)$$

The solution to this is given by,

$$n_i(T) = n_i(T_o) \exp\left(\int_{T_o}^T -\frac{e_{ni}}{a} dT\right) \quad (3.7)$$

Under the same assumption of negligible retrapping, we could rewrite Eq. 3.4 as:

$$\frac{dn}{dt} = a \frac{dn}{dT} = e_{ni}n_i - \frac{n}{\tau_n} \quad (3.8)$$

The solution for Eq. 3.8 is explained in detail in Ref. 15. For brevity we state the results below.

$$n = n_{i0}\tau_n e_{ni} \exp\left(-\int_{T_0}^T \frac{e_{ni}}{a} dT'\right) \quad (3.9)$$

where, n_{i0} is the intrinsic carrier concentration at the beginning of the scan. Since the emission rate e_{ni} is an increasing function with temperature, n will reach a maximum.

Setting the derivative of Eq. 3.9 to zero, we obtain:

$$\frac{dn}{dT} = n_{i0}\tau_n \left(e^{-\int (e_{ni}/a) dT'} - e_{ni} \frac{e_{ni}}{a} e^{-\int (e_{ni}/a) dT'}\right) = 0 \quad (3.10)$$

$$de_{ni}/dT = e_{ni}^2/a \text{ at } T = T_m \quad (3.11)$$

It can be shown that the electron emission rate e_{ni} could be written as

$$e_{ni} = D_i T^2 \exp(-E_{i0}/k_B T) \quad (3.12)$$

Where,

$$D_i = (16\pi m_n^* k_B^2 / \hbar^3) (g_{i0}/g_{i1}) \sigma_{ni}(\infty) e^{\alpha_i/K_B} \quad (3.13)$$

The terms m_n^* refers to effective mass of electrons in the material, k_B is the Boltzmann constant, $\hbar$ is Planck's constant, g_{i0}/g_{i1} the bound-state degeneracy factor, $\sigma_{ni}(\infty)$ the coefficient for a thermally activated capture cross section, α_i the reduced Fermi energy and finally E_{i0} the ionization energy of a trap. From the above relationships we get:

$$\left(2T_m + \frac{E_{i0}}{k_B}\right) = \frac{D_i}{a} T_m^4 e^{-E_{i0}/k_B T_m} \quad (3.14)$$

Here we assume σ_{ni} is temperature independent and that $E_{i0}/K_B \gg 2T_m$. Therefore:

$$E_{i0} = k_B T_m \ln \frac{16\pi m_n^* k_B^3 (g_{i0}/g_{i1}) \sigma_{ni} e^{\alpha_i/k_B} T_m^4}{\hbar^3 a E_{i0}} \quad (3.15)$$

This can be rewritten as:

$$\frac{E_{i0}}{k_B T_m} = \ln \frac{T_m^4}{a} + \ln \frac{16\pi m_n^* k_B^3 \sigma_{ni} (g_{i0}/g_{i1}) e^{\alpha_i/k_B}}{\hbar^3 E_{i0}} \quad (3.16)$$

Thus, one could solve for E_{i0} graphically/iteratively. We now assign values for the parameters as follows: $(g_{i0}/g_{i1}) = 1$, $m_n^* = m_0$, $\alpha_i \approx 0$, $\sigma_{ni} = 10^{-14} \text{ cm}^2$ [4], $a = 1/60 \text{ K/s}$ and the standard values for $\hbar$ and k to get the second term as $\ln(44/E_{i0})$ where E_{i0} is in eV. Assuming that $T_m = 10 \text{ K}$ the first term gives $\ln(600000)$. Even if the ionization energy was about 0.01 eV, the second term will still be very small compared to the first term. Hence, for our range of temperatures we can approximate E_{i0} as:

$$E_{i0} = k_B T_m \ln \frac{T_m^4}{a} \quad (3.17)$$

While Eq. 3.17 has been derived to account for transport through delocalised states, the formula is still applicable to a disordered material such as GO, where charge transport is expected to take place through hopping transport across defect states near the Fermi level. Arkhipov *et al.* had shown that the hopping transport in a disordered

material could be mapped into a multiple trap and release problem with the transport energy level playing the role of the mobility edge/ conduction band [12]. We utilize this concept to investigate charge detrapping from GO defect states to the transport energy level in TSC experiments. The transport gap in graphene oxide (with minimal reduction) was found by Eda *et al.* to be of the order of only a few tenths of meV [3]. The transport gap indicates the energy for a carrier to gain in order for it to enter the transport energy level where hopping transport occurs. Hence in our work, we approximate the GO Fermi level to represent the transport energy level. E_{i0} in Eq. 3.17 would then correspond to the energy between the GO trapped/defect levels and the GO Fermi level.

3.3 Experimental

3.3.1 General considerations

Device design and fabrication for thermally stimulated current experiments depend on several factors. The crucial ones are listed as follows:

1. Measurand (the quantity to be measured) - Trap energy levels in GO and r-GO.

Traps have been characterized [16] by temperature dependent current voltage characteristics (I - V) on r-GO. However the measurements have been made on a film of r-GO sheets lined up via dielectrophoresis between two electrodes. An inherent problem with this method is that additional defects are being generated due to transport barriers between sheets/flakes, and may differ from trap studies across a single sheet of GO. To reduce such effects, devices with contacts on a single sheet of GO is essential.

2. Material considerations-1- High Resistivity of GO

Unlike r-GO, which is a semiconductor, GO is insulating with resistances in the tera-ohm range. This not only makes it difficult to study traps by conventional temperature dependent I - V , but also prevents the use of standard experimental tools such as deep level transient spectroscopy (DLTS) or capacitance-voltage (C - V) measurements. Hence, the TSC technique which is capable of measuring trap information even in insulators is proposed to measure the trap levels in highly resistive unreduced GO.

3. Material considerations-2- Sensitivity of GO to laser irradiation.

Laser irradiation [17] is known to reduce GO. Therefore, the optical method for trap filling in the TSC technique should be avoided.

4. Material considerations-3- GO flake size

GO flakes obtained from solution based chemical exfoliation certainly seem to be a better alternative for higher throughput fabrication, as compared to the mechanically exfoliated method to obtain graphene from graphite and its subsequent oxidization to get GO. However, the GO flakes that are produced by this route have to be synthesized optimally, to get dimensions of at least a few microns. The GO flake size will also determine the type of lithography to be used; e-beam lithography in this case, as the line width of optical lithography is limited to 2 μm in our lab.

5. Device design- Top or bottom contacts

The advantage of bottom contacts is that one could pattern an array of electrodes and then simply deposit the graphene oxide above. This method certainly saves on fabrication and cost. However it has been found that bottom contacts have an effect of causing significant bending [18] of the GO sheets at

the electrode edges and hence are likely to add to the defect density in GO. To circumvent this, a top contact should be employed.

From the above considerations, it is clear that the device should preferably be fabricated on a single flake of GO with top metal contacts using e-beam lithography. In addition, an alternative to the optical method should be used for trap filling.

3.3.2 GO synthesis and AFM characterization

Graphene oxide flakes can vary in size from a few nm to a few 100 microns depending on the synthesis conditions. By carefully controlling oxidation process and sonication of the flakes in solution, one is able to get big-sized graphene oxide (BSGO) [19]. It is also possible to vary the synthesis conditions to get a higher distribution of single layer BSGO flakes. Such BSGO flakes will have fewer defects as compared to a thin film constructed from a network of smaller sized flakes due to the smaller number of sheet to sheet junctions. BSGO flakes were obtained from Prof Loh Kian Ping's group (NUS Chemistry) who synthesized the flakes using recipe from Ref. 19 as follows:

“1.5 g of graphite, 1.5 g of NaNO_3 and 69 ml of H_2SO_4 were first mixed and stirred in an ice bath. Next, 9 g of KMnO_4 was slowly added. The solution was kept in room temperature and stirred for 1 h. After which, 100 ml of water was added and the temperature was increased to 90 °C. After 30 mins, 300 ml of water followed by 10 ml of H_2O_2 were slowly added. The resultant mixture was filtered and washed by water until the solution pH was about 6. The synthesized GO sheets were dispersed in water: methanol (1:5) mixture and purified with 3 repeated centrifugation steps at 12,000 rpm for 30 mins. The purified sample was centrifuged at 8 krpm for 30 min to remove the smaller sized GO sheets. Then the remaining solution was redispersed in water/methanol mixture with the ratio of 1:5 and centrifuged at 2,500 rpm to recover the big sized graphite oxide (BSGO) sheets.”

The BSGO sheets were then spin-coated on to a pre-diced 1 cm by 1 cm Si/SiO₂ (300 nm) substrate. It has been reported, that flakes of sizes up to several microns were obtained by this method, with a high percentage of single/double layer flakes. To characterize the flakes, an atomic force microscopy (AFM) study was carried out using a multi mode-Digital Instruments system in the tapping mode. Fig. 3.6 (a) presents a 10 μm by 10 μm scan region which confirm the presence of large flakes (extending beyond the scan limits). To determine the number of layers for the flakes, a line profile was taken along a possible single/double layer region, as shown by the dotted line in Fig. 3.6 (a). The analysis of the line profile as shown in Fig. 3.6 (b) confirms the presence of single/double layers from their respective heights of 1 nm and 2.1 nm respectively [1].

Figure 3.6: (a) AFM image of GO. It is clear that the lateral sizes are much larger than the scanning range of the AFM (10 μm in our case). (b) AFM line profile of the dotted line in (a). The line profile confirms the presence [1] of both single layer and double layer GO given by their respective thicknesses of 1 nm and 2.1 nm.

3.3.3 GO device fabrication

The major challenge in graphene related devices is to be able to find the GO/graphene flake on the substrate, pattern electrodes on them and etch the area in-between the adjacent electrodes outside the device area (to prevent stray conduction paths). This process requires the following steps:

1. Premark the wafer with coordinates (requires 1 mask) before spin coating GO.
2. Record the specific coordinates of flakes.
3. Use E-Beam lithography to make electrode patterns.
4. Repeat process on every device.

This method is extremely tedious, and the process was made more tedious by the poor optical contrast of GO compared to graphene (which makes it difficult to pin the coordinates down). Instead we propose and use the following method:

1. Randomly pattern an array of electrodes using a mask with several devices
2. Use Raman spectroscopy to pick up the devices that contain GO
3. Continue processing only on the selected devices.

The process flow is as follows. A 100 μL 4% polymethylmethacrylate (PMMA) (MicroChem, MW: 495 K) anisole solution was spin coated on substrates at 4000 rpm and baked at 120°C for 2 min. The source/drain electrodes were patterned by electron beam lithography (FEI/Sirion), and this was followed by the development of PMMA with a methyl isobutylketone (MIBK) and isopropyl alcohol (1:1) solution. Fig. 3.7(a) is a schematic of a few elements in the array of devices. Each element in the array consists of 2 hall-bar devices and one 4-terminal device as shown in Fig. 3.7(b). Fig. 3.7(c) shows a zoomed-in view of the 2 type of devices.

Figure 3.7: (a) Schematic of a section of the array of elements on a chip. In each chip, 9 elements were present. Here we show only 4 for clarity of detail. (b) A 10x zoom of each element in the array which consists of electrodes connecting 2 hall-bar (6-terminal) devices and one 4-terminal device. (c) 100x zoom of (a) showing one hall bar and one 4-terminal device.

After development, thermal evaporation of 5 nm Cr/35 nm Au is performed in vacuum at 10^{-5} Pa. The sample is then left in acetone overnight before performing liftoff. The samples are then blown dry with N_2 . At this juncture Raman spectroscopy [20], was carried out to pick the devices with GO in the active device region, using a 488 nm laser of spot size $1 \mu m$. Devices with GO gave strong D ($1350 cm^{-1}$) and G peaks ($1600 cm^{-1}$) as shown in Fig. 3.8. The presence of the 2D peak $\sim 2700 cm^{-1}$ corresponds to the presence of unreduced/intact sp^2 regions.

Figure 3.8: Strong D and G peaks confirm the presence of GO.

As we can observe from Fig. 3.7(c), the electrodes are connected outside the central device area by unwanted/stray GO. This is likely to create additional conduction paths between electrodes, instead of exclusively measuring the device under test. Therefore, it is important to etch away the intermediate graphene oxide regions and isolate the electrodes external to the device area. Therefore, another step of E-Beam patterning (using alignment marks from previous patterning) was done to pattern the etch mask before using oxygen plasma (20 W, 20 sccm oxygen plasma (RIE NTI-2312) for 40 s) to etch away the unwanted GO areas. The device after isolation is pictured in Fig. 3.9(a) and (b), by SEM and optical imaging respectively. The etched GO-free areas are shown in Fig. 3.9(a) in between the metal electrodes. The etched areas show the underlying SiO_2 area, which provide a good contrast between the areas with GO present (darker areas). Care was taken to obtain the SEM images only after all measurements are completed, since e-beam irradiation has been reported to reduce GO [21]. After the final etch step, the sample was left overnight in acetone to remove the resist. Thereafter the samples were cleaned with IPA and blown dry with N_2 . Electrodes were wire-bonded (as shown in Fig. 3.9(c)) to a chip carrier after gluing the sample with silver paint to the chip carrier, which was then mounted on a chip socket and placed in a cryostat for measurement.

Figure 3.9: (a) SEM image of a typical 4-terminal GO-device. The etched GO-free areas serve as isolation against stray conduction between adjacent electrodes. The distance between the outer-most electrodes is approximately 5 μm . The red arrow points towards a typical device active area used for 2 terminal I - V measurements. (b) Optical image showing zoom out of (a). Each element in the array consists of electrodes connecting 2 hall-bar devices and one 4-terminal device. The purple lines serve to isolate the electrodes (orange) from one another outside the device area. (c) SEM image of wire bonding to a typical 4-terminal device.

The device process flow is summarized in Fig. 3.10.

Figure 3.10: Process flow for making graphene oxide devices.

3.3.4 TSC Experimental setup

The experimental setup consists of the following equipment.

1. Vacuum closed cycle refrigerator

(Janis-model CCS-450K with working range between 12K-500K).

2. Lakeshore temperature controller (model 331) with variable heating rate options.

3. Keithley sub-femto-ammeter (model 6430) with remote pre-amplifier to reduce noise.

The general experimental setup is shown in Fig. 3.11. The cryostat is cooled down to 12 K via the helium compressor at a vacuum level of 10^{-1} Pa. The temperature in the cryostat is monitored via a Lakeshore 331 controller. The laser source was not used during the TSC, since GO is expected to reduce under laser irradiation as explained earlier. I - V measurements were taken via the Keithley 6430 ammeter.

Figure 3.11 Schematic of general experimental setup for TSC experiment.

Fig 3.12 and Fig 3.13, show photographs of the sample mounted on the sample holder and the position of the temperature sensor behind the sample mounting plate respectively. The sample is glued using silver paint to the chip holder, which is in turn placed in a chip socket. The electrodes are wire bonded to the chip holder which is then connected electrically to the chip socket. The chip socket is mounted on a PCB by soldering (beneath the PCB). To electrically isolate the soldering bit beneath the PCB from the cryostat sample holder, a thin glass slide is placed on two sides, below the PCB to elevate the PCB just enough to avoid contact with the cryostat sample holder. The cryostat sample holder is designed such that it has 8 pins. The pins are present on either side, but are electrically isolated from the cryostat sample holder by a teflon cylindrical shield which runs in between the pin and the cryostat sample holder.

Figure 3.12: Photograph of sample mounted on cryostat sample holder.

Figure 3.13: Photograph of sample holder mounting plate.

One end of the pin is connected to the PCB which links all the way to the device. The other end is connected to the cryostat wiring which terminates on a 10-pin connector (one end in the cryostat and the other end in ambient). From the ambient end connector, the signals are wired to a signal box with BNC connectors. The Keithley femto-ammeter (model-6430) is then connected to these BNC connectors via a remote pre-amplifier from which voltage could be sourced and the current measured. All measurements were taken in the dark by covering all apertures of the cryostat with aluminium foil. In the cryostat, the samples were shielded using radiation and vacuum shrouds.

3.3.5 GO TSC Experimental procedure

The TSC experiment was modified to suit GO. Laser irradiation is known to reduce GO. Therefore, it is not feasible to fill the traps by the optical method and still retain unreduced GO. We could alternatively use the electrical method to fill the traps [9]. This requires one to know clearly the surface potential and band bending at the metal-GO interface. But getting such information is difficult in an insulating material which shows linear I - V characteristics even up to 60 V [21]. Fortunately, in the case of GO, trap states below the GO Fermi level are likely to be already filled as shown in the experimental DOS of Ref. 2, and hence we exploit this advantage in our experiment. This then allows us to bypass the optical trap filling step. As the temperature is ramped up, carriers are detrapped from filled trap levels below the GO Fermi level (in the case of electrons) to the GO Fermi level and contribute to the TSC current.

The sample was first heated to about 325 K and maintained at this temperature for 30 minutes to drive off any water vapour on the sample. Care was taken not to heat GO beyond 353 K at which GO will start to reduce [1]. After the initial heating process, the sample was cooled down to 12 K. A bias of 60 V was applied and the sample was heated at a rate of 1 K/min after the initial transient stabilized. During the heating procedure, the thermally stimulated current through the device was measured. It should be noted that unreduced GO did not show any semiconducting behaviour [21] even when biased up to 60 V. Thus we chose 60 V in order to give a higher TSC (tens of picoamps as compared to the noise fluctuations which were of the order of femtoamps). As the sample is heated, electrons will be thermally detrapped and will contribute to the TSC current.

3.3.6 RGO TSC Experimental procedure

To study the effect of reduction on modification of the trap states, the GO sample was irradiated with a 1 mW 630-670 nm (1 mm spot size) solid state laser for one minute. Laser irradiation is known to induce local heating of GO and hence reduce the material [17]. After irradiation, the resistance of the material dropped from tera-ohms to a 100 giga-ohms. Furthermore, a non linear I - V characteristic (discussed in Chapter 4) was obtained at room temperature, unlike the linear curve for unreduced GO. The sample was heated at 423 K for 2 hours thereafter to further reduce the sample resistance before carrying out the TSC experiment. However, the decrease in the sample resistance at room temperature was negligible compared to the decrease caused by the laser irradiation. We shall term the sample with laser irradiation and 2 hours of heating as RGO-1 whereas the unreduced GO will be known as GO. TSC experiments were carried out on RGO-1 after cooling the sample down to 12 K. A bias of 20 V was used, based on the I - V of RGO-1 (discussed in the following chapter). The bias voltage was chosen to be lower than the take-off voltage (voltage at which non-linearity of I - V begins, slightly above 30V) of RGO-1. To find out whether further heating would heal the traps or add more states in the gap, RGO-1 was heated at 445 K for 2 hours to form RGO-2 and for another 14 hours at 445 K (16 hours in total) to form RGO-3. The reduced GO devices were all measured at a bias of 20 V. All measurements were repeated several times on many devices to ensure repeatability/consistency.

3.4 Results and analysis

The TSC results are subjective, in the sense that the conclusions will depend on the interpretation [11] of the TSC curve. The TSC analysis for GO is certainly not as trivial as that of crystalline materials, where the only upward transition in the case of electrons is to enter the conduction band. In a disordered material such as GO, several possible things can take place:

1. Transition of carriers from a trap state to the mobility-edge via thermal excitation and hence giving rise to transport.
2. Transition of carriers from Fermi level to trap states or from trap states to the tail states/transport energy level from which transport will be via thermally assisted hopping.
3. Trapped electron could recombine with a hole.

If the density of localized states is large enough, there will be a high probability of hopping transport. Else, thermal excitation to the conduction/valence band will be the dominant form of transport. Therefore, the position of the Fermi level and density of states becomes very important in determining the nature of transport and the origin of the TSC current.

3.4.1 GO TSC results and analysis

Fig. 3.14 shows the TSC results obtained from the GO samples. Several peaks could be observed between 31K and 307K. By inspection, it is clear that the rise and fall of the current in the vicinity of each peak is almost symmetrical, implying that the retrapping phenomena are weak or negligible as we have assumed in the TSC theory section in the derivation of Eq. 3.17. This justifies our assumption. Using Eq. 3.17 we obtain a wide range of trap energies for GO between 47.6 meV and 0.71 eV.

Figure 3.14: Thermally stimulated current in Graphene Oxide. Various peaks in the TSC indicate temperatures at which detrapping occurs.

We also observe that, the current level decreases with an increase in temperature. We believe that the origin of this phenomenon arises due to charge detrapping or electron-phonon coupling [22] which could cause a drop in the conduction as the temperature is raised. Had it been just purely tunnelling, a temperature-independent intrinsic current level (horizontal-line) would have been observed as the background on which the TSC peaks appear.

3.4.2 RGO TSC results and analysis

The TSC spectrum for RGO-1 is shown in Fig 3.15.

Figure 3.15: TSC spectrum for RGO-1 showing 4 distinct peaks.

The TSC spectrum of RGO-1 has several differences as compared to that of GO shown in Fig. 3.14. These are listed below:

1. The peaks are of a higher intensity and are more pronounced as compared to that of GO.
2. There are fewer peaks observed in RGO-1.
3. The shape of the peak is asymmetrical.
4. The current increases rapidly after approximately 225K (crossover point).

We believe that the higher intensity TSC current is caused by the laser irradiation, which not only reduced the GO, but also populated more states as compared to the

method without any prior illumination. It is possible that there may be other peaks under each of the 4 peaks. Thus an overlap of two or more peaks could give rise to a super-peak. This could also help us understand the asymmetry. But for our analysis we simply considered the 4 peaks and extracted the trap energies from Eq. 3.17 using the characteristic peak temperatures. The extracted energies are at 0.189 eV, 0.396 eV, 0.593 eV and 0.678 eV from the GO Fermi level. There could be other trap energies at higher temperatures, which could have been masked by the high intrinsic conduction. After 293 K, kinks in the TSC at 320 K and 340 K could be observed. We are not entirely sure whether these are TSC peaks. If they are, then the other possible trap levels would correspond to 0.75 eV and 0.803 eV from the Fermi level. Lastly, we believe that the crossover point demarcates a crossover from a tunneling limited intrinsic conduction to a hopping limited intrinsic conduction mechanism. Figs 3.16 and 3.17 show the TSC spectra for RGO-2 and RGO-3.

Figure 3.16: TSC spectra for RGO-2.

Upon analysis of TSC spectra for RGO-2, we find the following features:

1. The TSC current levels have dropped as compared to RGO-1.
2. Several additional peaks appear, when compared to RGO-1.
3. The area under the peaks has reduced.
4. The peaks near 290 K remain.
5. The current takes off after about 175 K as compared to 225K in RGO-1

After the TSC experiment with RGO-1, the additional charges in various trap levels as a result of laser illumination would have been detrapped. Hence a smaller number of charges (based on the original DOS of the material) are expected to be trapped and detrapped. This accounts for the drop in the peak intensities. The presence of a strong peak at 290 K suggests that traps further away from the Fermi level are hardly removed/healed by reduction since this trap energy has remained both in GO and RGO-1. Lastly, as RGO-1 is further reduced, activation energy for hopping conduction is expected to decrease [3] leading to the manifestation of a quicker onset of hopping limited intrinsic transport mechanism (175 K for RGO-2 as compared to 225 K for RGO-1).

Figure 3.17: TSC spectra for RGO-3.

From TSC spectra of RGO-3, the following observations could be made:

1. The cross-over point moves to even lower temperatures (64K in RGO-3).
2. The areas under the peaks have reduced compared to RGO-2.
3. The higher temperature peaks still remain. However the trap density has reduced.
4. Some new peaks appear.

The movement of the cross-over point towards a lower temperature is an indication of further GO reduction. Thermal annealing is useful in reducing the defect density, since the area under the peaks has reduced. However, the persistent presence of trap levels further away from the Fermi level show that, they are not completely removed by heating, in agreement with findings from Ref. 4. To have an overview of the trap levels in GO, RGO-1, 2 and 3, the peak temperatures from the respective TSC spectra

are plotted in Fig. 3.18. We find that the peaks at approximately 92 K, 187 K, 254 K and 290 K are present in all four devices. The peak at 130 K disappears in RGO-1, but reappears in RGO-2 and RGO-3. We speculate that this could be due to laser-induced depopulation of traps states at the 130 K (0.264 eV from the GO Fermi level).

From work by *Bansal et al.*, we understand that the presence of defects cause several discontinuities in the graphene density of states, resulting in the emergence of localized band tail states even up to the Fermi level. Hence, we believe that it is the emergence of states near the Fermi level (corresponding to the low temperature TSC peaks) which are responsible for conduction in RGO. This interpretation is also supported by work by *Eda et al.*, who showed that the transport in RGO is by hopping transport via mid-gap states (near the Fermi level) for lightly reduced GO [3].

Figure 3.18: Comparison of peaks in GO, RGO-1, RGO-2, RGO-3 shown in Fig. 3.14, 3.15, 3.16 and 3.17 respectively. The lines in red indicate common peaks.

3.5 Summary

In this chapter, we have reviewed the theory of carrier traps in crystalline, amorphous and disordered material along with a suitable TSC theory to analyze the GO TSC data. The GO synthesis and device fabrication process were discussed after explaining various experimental considerations and sample requirements that need to be fulfilled. The TSC analysis of GO showed the presence of several electronic traps in the GO bandgap between 47 meV and 0.94 eV from GO Fermi level. To investigate the effect of reduction on the trap level/density, the GO was reduced by laser irradiation and different heat treatments. Reduction helps to lower trap density. However, traps further away from the GO Fermi level persist despite reduction with the emergence of trap states closer to the Fermi level. We find trap levels at 0.189 eV, 0.396 eV, 0.593 eV and 0.678 eV from the GO Fermi level for GO and RGO-1-3 in general. We believe that the transport gap of GO will depend on the relative density of states available at each of these energy levels. With reduction, the appearance of low temperature peaks, points to an increase of states near the Fermi level available for hopping conduction. This effectively translates into a decrease in the GO transport gap by reduction or simply be the emergence of new states for conduction with as GO is reduced [2, 3].

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Chapter 4

Temperature dependent current-voltage characterization

4.1 Introduction

Several groups have studied charge transport in reduced GO by current-voltage (I - V) characteristics [1-6], proposing various transport models ranging from tunneling, Schottky, variable range hopping, space charge limited current with exponentially distributed traps, Poole-Frenkel (PF), and percolation models. Clearly, there is no consensus on a specific charge transport model. This could be due to the wide variation in parameters, such as reduction method, single flake or thin film, and on whether top or bottom contact is employed. In the case of pure GO, little is known. This could be due to its insulating nature, [3] with no semiconducting behaviour (non-linear I - V) seen even up to 60V. It then becomes necessary to apply some sort of reduction technique to obtain any useful I - V results. In our work, we use laser irradiation and thermal heating/annealing to form lightly reduced GO. We believe that investigating lightly reduced GO will give some insight into transport in GO. In this chapter, several transport models will be presented and their suitability discussed, for describing charge transport in RGO-1-3 at various bias and temperature regimes. Such charge transport models have been traditionally used for inorganic materials. However, in the case of organic materials, several of the assumptions made in deriving the models are violated. The principal reason for this is the generally non-crystalline nature of organic materials, making k (wave/momentum vector) for charge carriers an invalid quantum number. The situation for GO is not entirely clear since graphene is

crystalline and carriers could possess a well defined k vector. In contrast, GO is found to be predominantly amorphous [7] due the high proportion of sp^3 C-O bonds. Reduced GO lies somewhere in between graphene and GO. We will discuss the various transport models and the main assumptions made in deriving each of the models in the following section. We will also review some of the models used in describing charge transport in organics generally, and applied to the case of reduced GO specifically.

4.2 Theory

4.2.1 Traditional methods

Charge transport models [8] have been generally classified as either bulk or electrode/injection limited. Common injection limited models would include Schottky limited and Fowler-Nordheim (FN) model. If the energy of the electrons is large enough to launch them across the metal-semiconductor or metal/insulator Schottky barrier, the Schottky current due to such electrons could be modelled using the Schottky current formula in Eq. 4.1.

$$J = \frac{4\pi m^* q k_B^2 T^2}{h^3} \exp\left(-\frac{q\phi}{k_B T}\right) \exp\left(\frac{q}{k_B T} \sqrt{\frac{qE}{4\pi\epsilon_0\epsilon_r}}\right) \quad (4.1)$$

Where, m^* is the effective mass of the electron, $q\phi$ the barrier height, E the applied electric field, ϵ_0 the vacuum dielectric permittivity, ϵ_r the relative permittivity of the semiconductor, k_B is Boltzmann's constant and h is Planck's constant.

Alternatively, even when the energy of the electron is lower than the Schottky barrier, under high applied fields, electrons could quantum mechanically tunnel across the barrier depending on the tunnelling probability. The FN tunneling current in such a case is described by Eq. 4.2.

$$J \propto E^2 \exp\left(\frac{-4\sqrt{2m^*}}{3\hbar qE}[(q\phi - E_F)^{3/2}]\right) \quad (4.2)$$

Where, E_F is the metal Fermi energy level and $\hbar$ is the reduced Planck's constant. It is clear from the above equations that the Schottky model has very strong temperature dependence whereas the tunneling model is independent of temperature. When the injection rate is higher than what the semiconductor/insulator could accommodate, a space charge limited current (SCLC) arises as described in Eq. 4.3.

$$J = \frac{8}{9} \cdot \mu \cdot \frac{\epsilon_0 \epsilon_r}{d^3} \cdot V^2 \quad (4.3)$$

where, d is the distance between the electrodes and μ is the carrier mobility. At low fields the I - V is expected to be ohmic. In deriving this Eq. 4.3, the effect of traps has been neglected. In the case of exponentially distributed traps (trap states tailing exponentially in the gap) this is modified, as described in Eq. 4.4:

$$h(E) = \frac{H_t}{E_t} \exp\left(\frac{-E}{E_t}\right) \quad (4.4)$$

where, H_t is the trap density, E_t is the characteristic energy (for detrapping) of the distribution and $h(E)$ is the trap distribution function. Upon integration of $h(E)$ in energy, the trap density in the region of integration is obtained. The SCLC current [9] in the presence of exponentially distributed traps (SCLC-EDT) gets modified as shown in Eq. 4.5.

$$J = q^{1-l} \mu N \left(\frac{2l+1}{l+1}\right)^{l+1} \left(\frac{l}{l+1} \frac{\epsilon_s \epsilon_0}{H_t}\right)^l \frac{V^{l+1}}{d^{2l+1}} \quad (4.5)$$

where $l = T_C / T$. Here k_B is the Boltzmann constant and $k_B T_C$ gives the characteristic energy (E_t) of the trap. H_t is the trap density. N is the density of states in the valence/conduction band depending on the trap type. The exponent l could be obtained from the gradient of the $\log I$ versus $\log V$ curve. Further manipulation of Eq. 4.5 leads to Eq. 4.6:

$$J = \left(\frac{\mu_p N_V q V}{d} \right) f(l) \exp \left[-\frac{E_t}{k_B T} \ln \left(\frac{q H_t d^2}{2 \epsilon_s \epsilon_0 V} \right) \right] \quad (4.6)$$

where,

$$f(l) = \left(\frac{2l+1}{l+1} \right)^{l+1} \left(\frac{1}{l+1} \right)^l \frac{1}{2^l} \quad (4.7)$$

the function $f(l)$ could be approximated as 0.5 for $l > 2$, hence giving Eq. 4.8:

$$J = \left(\frac{\mu_p N_V q V}{2d} \right) \exp \left[-\frac{E_t}{k_B T} \ln \left(\frac{q H_t d^2}{2 \epsilon_s \epsilon_0 V} \right) \right] \quad (4.8)$$

The trap density could be calculated from $\ln J$ versus $1/T$ plots. Another method lies in observing that at a cross-over voltage V_C , the $\ln$ term tends to zero giving a temperature independent current. V_C could be extracted by extrapolating the $\log I$ versus $\log V$ curves at different temperatures. The point, at which the different curves meet, will be the cross-over voltage. Thereafter, the trap density H_t could be calculated using the following equation:

$$V_c = \frac{q H_t d^2}{2 \epsilon_s \epsilon_0} \quad (4.9)$$

In semiconductors with defects, localized charged trapping centers are created in the bandgap of the material, which trap charges passing in their vicinity. While thermal energy is required to detrapp the trapped carrier, under the influence of an electric field, the potential seen by the trapped carriers in the direction of the field is reduced and the carrier is detrapped with a smaller amount of energy than what was required earlier in the absence of a field. This phenomena is well described by the Poole-Frenkel (PF) model which describes field enhanced thermal excitation of trapped electrons into the conduction band as shown in Eq. 4.10.

$$J = q \cdot N_c \cdot \mu_e \cdot E \cdot \exp \left(-\frac{q \phi}{k_B T} \right) \cdot \exp \left(\sqrt{\frac{q}{\pi \cdot \epsilon_0 \epsilon_r}} \frac{q \sqrt{E}}{k_B T} \right) \quad (4.10)$$

A similar formula could be also used for hole traps.

4.2.2 Modifications of traditional models to describe organic materials

The methods used in the preceding section were derived for inorganic materials. In dealing with organic materials, various modifications to the traditional methods have been made by different groups. A 2-dimensional electron gas treatment (2-DEG) was applied for charge transport across an epitaxial graphene/graphene oxide interface by Wu *et al.* [3]. In doing so, the Schottky formula was modified as described in Ref. 3. We find that such an assumption may not be suitable in our case, as a 2 DEG system requires a critical density of carriers for transport/conduction, whereas in GO the intrinsic carrier density is expected to be lower than this due to its insulating/semiconducting nature. Barth *et al.* showed that the T^2 term in the Schottky formula could be dropped, as integration across k-space in an organic material is illegitimate [10]. Arkhipov *et al.* pointed out that carrier injection into the organic is a two-step process [11]. Charge carriers first jump from the Fermi surface of a metal to localized states in the organic near the Fermi level. Thereafter the carriers will either flow back to the metal or keep hopping forward with the assistance of an external field [12]. The hopping injection current formula in such a situation is significantly different as compared to the standard Schottky formula as shown below:

$$J = ev \frac{\int_a^\infty dx_0 \exp(-2\gamma x_0) \int_{-\infty}^\infty dE \text{Bol}(E) g[E - U(x_0)] \int_a^{x_0} dx \exp\left[-\frac{e}{k_B T} \left(F_0 x + \frac{e}{16\pi\epsilon_0 \epsilon x}\right)\right]}{\int_a^\infty dx \exp\left[-\frac{e}{k_B T} \left(F_0 x + \frac{e}{16\pi\epsilon_0 \epsilon x}\right)\right]} \quad (4.11)$$

where v is the attempt-to-jump frequency of carriers from the metal contact, γ is the inverse localization radius, a is the distance from the electrode to the nearest hopping

site, $g(E)$ is the density of states, T is the absolute temperature, k_B is the Boltzmann constant, e is the elementary charge and $U(x)$ is the energy barrier for carrier injection formed by the superposition of the field, F_0 and the coulomb field of the image charge as shown below:

$$U(x) = \Delta - \frac{e^2}{16\pi\epsilon_0\epsilon x} - eF_0x \quad (4.12)$$

where, Δ is the zero-field barrier height, ϵ_0 is the permittivity and ϵ is the dielectric constant. Lastly the function $Bol(E)$ is defined as:

$$Bol(E) = \begin{cases} \exp\left(-\frac{E}{k_B T}\right), & E > 0 \\ 1, & E < 0 \end{cases} \quad (4.13)$$

In addition, Arkhipov *et al.* showed that even for barriers as large as 1 eV, the injection mechanism is by hopping injection and not thermionic injection, thereby leading to an ohmic contact [11].

4.2.3 General approach to transport modelling in organic materials

While it is usual to model transport in inorganic materials by a one-electron (band-structure) approach [13], several complications arise in the case of organic materials where electron-phonon and electron-electron interactions have to be considered. The complexity further increases with any energetic or positional disorder. Various reviews [13-16] have appeared regarding charge transport in organic materials. The general view on charge transport in organic materials is to use either polaronic models or disorder based models. In most polaronic models, one assumes that the material is

defect free and transport is limited by the dynamic disorder arising from electron-phonon coupling. However in the case of GO, such a model may not be entirely suitable. GO is a material with several types of defects caused by different functional groups randomly positioned on the graphene basal plane, leading to both positional and energetic disorder. Hence, disorder based models may be better suited for GO. In several disordered materials where transport through delocalized states is limited, the transport occurs through localized states through a hopping transport process. Carriers hop from one localized state to another based on the hopping probability which is a function of the energy difference and physical distance between the initial and target state. Wulf *et al.* used Monte Carlo (MC) simulations to model charge transport in disordered organic materials [17]. In such a simulation one of the important parameters to be fed into the simulator is the hopping rate of carriers, which is given by Miller-Abraham's model (a single phonon supplies the energy for hopping and transport is limited by the most difficult hop) or the Marcus expression (similar to the Miller-Abraham's model, but takes entropy into consideration) [13]. Although a full MC simulation is best suited for such problems, analytical formulae are preferred to get a feeling for the parameters that limit transport in such materials. Eq. 4.14 describes the hopping current through a material as a function of temperature.

$$I \propto \exp(T/T_0)^{-1/n} \quad (4.14)$$

Where, n takes an integer value between 1 and 4 [5, 18]. Such analytical formulae are often arrived at after simplifying assumptions such as the most meaningful (contributing to overall current) hop being an upward jump (in energy) and hops occur near the vicinity of the Fermi energy level.

In the presence of energetic disorder, the MC results show PF dependence, with the electric field lowering the energy barrier for upward hops [13]. Another way of

looking at transport is via trapping/detrapping of charges. Several states exist in the gap due to pseudo-exponentially distributed traps (caused by the tail ends of states at the HOMO/LUMO) and by the presence of chemical impurities and defects [16]. These traps could lead to a SCLC-EDT current as described in Eq. 4.5. In such a scheme, the carriers are thermally activated from the trap states to the transport band, where they diffuse for a while before being retrapped.

4.3 Results and analysis

4.3.1 Transport in RGO-1

The RGO-1, RGO-2 and RGO-3 samples described in chapter 3 were used for the electrical characterization. Temperature dependent I - V on RGO-1 shows a monotonously increasing current with temperature (Fig. 4.1). However, the dependence of the current on temperature appears to be much weaker below 110K signifying the absence of thermally activated processes affecting transport.

Figure 4.1: Temperature dependent I - V characteristics of the RGO-1 device.

From the I - V alone, it is difficult to ascertain whether the current is bulk or injection limited. Although the responses look symmetrical on both the positive and negative axes, we have to keep in mind that both electrodes are of the same material. This means that the current could essentially consist of both electrons and holes, unlike in the case with dissimilar electrodes where a certain carrier type could be effectively blocked. Hence, based on the symmetric linear I - V alone, one cannot discern the relevant injection model. One method is to extract the dielectric constant from the injection limited and bulk limited models and compare them with dielectric constant measurements [18]. Dielectric constant measurements of GO have yielded a relative permittivity between 3 and 12 for GO depending on the level of humidity [19]. Figs. 4.2 and 4.3 show the Schottky and PF fits respectively for RGO-1 data shown in Fig. 4.1. Both models appear to fit well away from the low field regions. However, upon extracting the dielectric constant values from both models (by equating the gradients of the curves at high electric fields in Fig. 4.2 and Fig. 4.3 with the Schottky/PF equations respectively), we find that the PF model fits better for temperatures above 230K whereas the Schottky model fits better in the range 110K-170K. Between 170K and 230K there appears to be a mixture of both Schottky and PF limited behaviour. Below 110K both models fail to give a reasonable value for the dielectric constant. Hence, we observe a possible transition from injection limited to bulk limited transport above 200K (averaged value between 170/230K). Using the PF model, the relative dielectric constant for GO was extracted to be 10.8. As the temperature is increased, detrapping becomes easier, making the effective space charge (that impedes carrier injection) lower. At even higher temperatures, space charge is irrelevant, and transport is limited by traps (PF).

Figure 4.2: Schottky plots of temperature dependent I-V data shown in Fig. 4.1.

Figure 4.3: Poole-Frenkel plots of temperature dependent I-V data shown in Fig. 4.1.

To further investigate the I - V characteristics, the $\log I$ versus $\log V$ was analyzed as shown in Fig. 4.4. Significant hysteresis could be observed between the forward and backward sweeps of the I - V characteristics on such log scale. The upward sweep starts with a sub-linear slope (gradient $m < 1$) attributed to charge trapping, and progresses into the space charge limited current with exponentially distributed trap (SCLC-EDT) regime beyond a critical voltage. From the slope of curves in Fig. 4.4, an m value (gradient) is obtained to be between 4.8 and 6.1 for temperatures ranging between 350K and 12K (not shown in Fig 4.4). The downward sweep however ends with an ohmic regime ($m=1$), signifying that negligible trapping occurs. To calculate the trap density in RGO-1, the cross over voltage was extracted to be 164V by extrapolating the curves in the SCLC-EDT regime as shown in Fig. 4.5. Only three of the curves have been shown for clarity. The trap density in RGO-1 was estimated to be $1.54 \times 10^{17} \text{ cm}^{-3}$, assuming that the relative dielectric permittivity of RGO-1 is approximately 10.8 at 290K (extracted from the PF plot shown in Fig. 4.3). The trap energy was estimated to be 0.113 eV (from the conduction band/mobility edge) using the SCLC-EDT theory discussed earlier.

Figure 4.4: Temperature dependent $\log I$ versus $\log V$ characteristics showing hysteresis between upward and downward sweep due to charge trapping. The oval regions denote the various regimes present in the sweep: Ohmic, sub-linear (charge trapping) and SCLC-EDT.

Figure 4.5: Depiction of crossover voltage extraction from the SCLC-EDT characteristics in Fig. 4.4. Only three curves have been shown for clarity.

Figure 4.6: Temperature dependent Fowler Nordheim (FN) plots of the RGO-1 results shown in Fig. 4.1.

FN plots in Fig. 4.6 show that the transport is limited by FN tunneling only at very high fields and low temperatures. Even at very high fields, there is significant temperature dependence for the higher temperature curves in the FN plot. From the FN plot at 12K, an injection barrier height of 0.127 eV was obtained. To have a better understanding of the various types of field/temperature dependent transport mechanisms present in RGO, a $\ln J$ versus $1/T$ curve is plotted as shown in Fig. 4.7. It is clear that below 110K (as shown on the right of the dotted line) the transport appears to be temperature independent thus suggesting a tunneling mechanism.

Figure 4.7: $\ln J$ versus $1/T$ curves at various fields. The dotted line demarcates the temperature dependent regime from the temperature independent tunneling regime.

We now consider the effect of traps. From the slopes of Fig 4.7 at moderate fields (60V) and higher temperatures ($>230K$), a barrier height of 0.215 eV is obtained for the PF model. From the same curve at moderate temperatures, a thermal activation

energy of 8.6 meV was obtained for hopping transport from Eq. 4.15, which describes the current density for a thermally activated process involving carrier hopping from one isolated state to another [23].

$$J = CE \exp\left(-\frac{q\phi}{k_B T}\right) \quad (4.15)$$

Where ϕ is the activation energy, J is the current density, C is a constant and E the electric field across the device.

The findings for transport in RGO-1 are summarized as follows.

1. FN tunneling limited transport was observed at low temperature and high fields.
2. Schottky limited transport was found approximately below 200K and at moderate fields.
3. PF limited transport was observed above approximately 200K and at moderate fields.
4. Ohmic transport was found at low fields and moderate temperatures.
5. SCLC-EDT transport was determined at moderate temperatures and fields.

At this point it seems confusing that so many mechanisms are simultaneously present in the same material. Especially, with an obvious contradiction between the Schottky model (injection limited) and the SCLC model (bulk limited) which appear to be present in the same regime (moderate fields and $T < 200\text{K}$). Also, why is the thermal activation energy so low? To analyze these phenomena and better understand the details, one has to appreciate that all the models investigated so far have been originally proposed to explain transport in inorganic semiconductors. To what extent these models could be used for organic materials is debatable. We discuss these issues below. Charge transport across a metal-organic interface is a 2-step process as pointed

out by Arkhipov *et al.* [11], consisting of charge injection into a localized state at the interface near the metal Fermi energy level followed by hopping across the potential barrier. Hence injection across a metal/organic interface is significantly different from that of common thermionic injection seen across metal/inorganic interfaces. Therefore, it is very likely that charge injection in GO is via hopping injection rather than thermionic injection. Hence, it is possible that the Schottky fit at $T < 200\text{K}$ is likely to be accidental. Another subtle point is that if the carriers are injected into states that lie near the Fermi level of the metal, then very little energy is required to overcome the metal/organic barrier at the interface, thus mimicking an Ohmic character across the interface, albeit with a high characteristic resistance. This is consistent with the linear I-V's up to high fields. In this light, a low thermal activation energy for hopping is no surprise. Above 200K we have SCLC-EDT and PF models which are both bulk limited models. It might be difficult to distinguish the dominant mechanism between the two at this stage. In an organic material, the HOMO and LUMO follow a Gaussian distribution. The deep end of the Gaussian distribution could be approximated by a pseudo-exponential distribution, which leads to states in the gap. In addition, there could be chemical impurities and other microstructural defects (vacancies etc) leading to further states in the gap. This then leads to a PF type of field dependent transport. It is however unclear whether the PF dependence arises from conventional detrapping of carriers into the conduction band or due to the field dependent lowering of the hopping energy barrier [13]. Horowitz [20] suggested that the PF behaviour arises due to modification of the Coulombic potential near localized states, leading to an increase in the tunnel transfer rate between sites. Transport thus appears to be a combination of tunnelling, hopping and detrapping processes. To summarize, we observe regimes for electron transport in RGO-1 as shown in Fig. 4.8. At low temperatures, the thermal

energy will not be enough for hopping transport to occur. Hence the electrons are likely to be transported purely by a tunneling mechanism. This essentially involves tunneling across the metal-organic interface and then tunneling through the bulk RGO-1 material. Tunneling through a channel length of $1\mu\text{m}$ may seem difficult. However, tunneling in RGO-1 is facilitated by intact conductive sp^2 graphene regions which did not get oxidized. The electrons could then tunnel from one graphene island to another and finally to the electrode. In this manner, the effective tunneling length becomes very much reduced, allowing a conduction path across the two electrodes. At moderate temperatures, the electrons possess enough thermal energy for hopping transport. The electrons are likely to hop across the metal-organic barrier, and continue hopping across the bulk. Here, the transport is dependent on the ease of hopping through RGO-1. At even higher temperatures, the electrons possess enough thermal energy to detrapp from trapped states or tunnel across a lowered Couloubic potential (between localized states) as evaluated from the PF field dependence.

Figure 4.8: Transport regimes in RGO-1 as a function of temperature. The red line (Poole-Frenkel regime), blue line (hopping regime) and the black line (tunneling regime) have been drawn to clearly distinguish the various transport regimes. Green triangles indicate experimental data points.

4.3.2 Transport in RGO-2

I-V characteristics of the RGO-2 (RGO-1 heated/reduced at 445K for 2hrs), shown in Fig. 4.9 appear very similar to those seen in RGO-1 (Fig. 4.1). Both SCLC-EDT and PF limited transport were observed as shown in Fig 4.10 and Fig. 4.11, respectively. However, the extracted parameters were significantly different. From the PF plots (Fig. 4.11), the RGO-2 relative dielectric constant at 290K dropped to 8.39 as compared to 10.8 in RGO-1. The trap density/energy of $1.45 \times 10^{17} \text{ cm}^{-3}$ and 0.1 eV were extracted from the SCLC-EDT plots (Fig. 4.8b). From the FN plots (Fig. 4.12), a barrier height of 0.119 eV was obtained. The $\ln J$ versus $1/T$ plots (Fig. 4.13) showed a similar tunneling-hopping-PF transition as seen in RGO-1, however with lower thermal activation energy of 5 meV (extracted from the hopping regime of the $\ln J-1/T$ curve) as compared to 8.6 meV in RGO-1. In addition, the trap barrier was extracted to be 0.23 eV from the slope of the PF region in the $\ln J-1/T$ curve.

Figure 4.9: Temperature dependent I-V characteristics of RGO-2.

Figure 4.10: Temperature dependent $\log I$ versus $\log V$ characterization of RGO-2 showing an ohmic to SCLC-EDT transition with increasing field.

Figure 4.11: Temperature dependent Poole-Frenkel plots of RGO-2, data shown in Fig. 4.9.

Figure 4.12: Temperature dependent Fowler Nordheim plots of RGO-2, data shown in Fig. 4.9.

Figure 4.13: $\ln J$ versus $1/T$ plots at different applied fields for RGO-2, data shown in Fig. 4.9.

4.3.3 Transport in RGO-3

RGO-3 was obtained after 16 hrs of heating/reduction of RGO-1 at 445 K. The linear I - V (Fig. 4.14) looks qualitatively similar to that of RGO-1/2. SCLC-EDT and P-F behaviour is observed, as shown in Fig 4.15 and Fig. 4.16 respectively. The wiggles in the low voltage regions are due to noise, which could be eliminated by standard averaging techniques (not described here). From the PF-plot (Fig. 4.16) slope at 290 K, a relative dielectric constant of 7.33 is obtained for RGO-3. The trap density/energy was extracted from the SCLC-EDT curves (Fig. 4.15) at 290 K to be $9.97 \times 10^{16} \text{ cm}^{-3}$ and 0.115 eV respectively. From the FN plots (Fig. 4.17) a barrier height of 0.118 eV ($T=12\text{K}$) was obtained. Analysis of the $\ln J-1/T$ (Fig. 4.18) curves gives hopping activation energy of 1.3 meV and a barrier height of 0.256 eV. A barrier height of 0.118 eV was obtained from the FN plots at 12 K. $\ln R$ versus $1/T$ curve shows a monotonic decrease in the resistance with increasing temperature (Fig. 4.19).

Figure 4.14: Temperature dependent linear I - V characterization of RGO-3.

Figure 4.15: Temperature dependent log-I versus log-V curves for RGO-3, data shown in Fig. 4.14.

Figure 4.16: Temperature dependent Poole-Frenkel plots for RGO-3 data, shown in Fig. 4.14.

Figure 4.17: Temperature dependent Fowler-Nordheim plots for RGO-3 data, shown in Fig. 4.14.

Figure 4.18: $\ln J$ versus $1/T$ plots at different applied fields for RGO-3 data, shown in Fig. 4.14.

Figure 4.19: In Resistance versus 1/T curves showing a decreasing resistance with temperature.

4.4 Discussion and conclusion

Table 4.1 summarizes the extracted transport parameters for devices RGO-1 to RGO-3.

Sample	ϵ_{r-290K}	$PF_{T=290K}$	$FN_{T=12K}$	E_A	Trap density	Trap energy
		Barrier-eV		meV	cm ⁻³	eV
RGO-1	10.8	0.215	0.127	8.6	$1.54e^{17}$	0.113
RGO-2	8.39	0.23	0.119	5	$1.45e^{17}$	0.1
RGO-3	7.33	0.256	0.118	1.3	$9.97e^{16}$	0.115

Table 4.1: Summary of extracted transport parameters from RGO-1-3.

The relative dielectric constant, activation energy for hopping and trap density reduces with the extent of reduction from RGO-1 to RGO-3. However the trap energy stays constant around 0.11 eV. From Table 4.1 we observe that there is a close correlation between the SCLC-EDT trap energy and the FN barrier. If the trap states are caused by microstructural defects, it is reasonable that the trap energy stays constant; while the

trap occupancy changes as the oxidation state is modified. This may give us some confidence about the trap energy level being at 0.11 eV. However, there is no indication of a 0.11 eV peak from the RGO TSC results in Chapter 3. This puts forth a clear contradiction.

By analyzing the density of states (DOS) in RGO by Bansal *et al.*, we find that there are several localized states in the RGO DOS between the π - π^* gap on either side of the Fermi level as shown in Chapter 3 (Fig. 3.1) [21]. With a high density of localized states, it is difficult to expect conduction to be via carriers that enter the conduction band, especially when the Fermi level is approximately 2 eV away from the π^* orbital. Next, Mattevi *et al.* developed a structural model for RGO describing the distribution of sp^2 clusters at various temperatures (levels of reduction) (shown in Fig. 4.20) [22].

Figure 4.20: Structural model of GO at different stages of reduction by thermal annealing at: a) room temperature; b) 100°C; c) 220°C; d) 500°C. The dark gray areas represent sp^2 carbon clusters and the light gray areas represent sp^3 carbon bonded to oxygen groups (represented by small dots). At 220°C, the percolation among the sp^2 clusters initiates (corresponding to sp^2 fraction of 0.6). [22]

Between panels a-d, we can observe that the dark areas (conductive sp^2 regions) are disconnected from each other at lower temperatures until a percolation threshold is reached at 220 degrees. The light grey dots represent the oxygen atoms, while the light grey area represents the sp^3 (insulating regions). For our work we do not expect to have reached the percolation threshold (220°C), as we annealed only till a maximum temperature of 445K (172°C). Hence, we are still within the hopping/tunneling regime

(where carriers have to hop between the sp^2 sites). Coupled with the view from Arkhipov *et al.* view (hopping injection across a metal/organic interface [11]) and Eda *et al.* (transport in RGO is through hopping via localized midgap states), we are led to believe that transport in GO occurs due to injection into states near the Fermi level and the subsequent hopping of carriers across localized states. The FN tunneling and SCLC-EDT current are calculated from the number of carriers that make it to the conduction band. Therefore, even though the SCLC-EDT and the FN model give consistent barrier heights, we believe that they do not capture the essential physics of transport in RGO. Thus, the trap density and energies obtained from these two models have to be viewed with caution.

Next, we discuss the (0.215-0.256 eV) barriers evaluated from the PF-field dependence in RGO-1 to RGO-3. These barriers correlate well with the TSC results in Chapter 3 (peaks at 0.19 eV and 0.26 eV). The PF barrier could also be viewed as the columbic potential seen by carriers tunneling between localized sites as proposed by Horowitz *et al.*, rather than the typical detrapping energy to launch carriers into the conduction band energy [20].

Finally, transport measurements by Eda *et al.*, suggest the presence of 2 activation energies in RGO [1] (A low activation energy (about 50 meV) for transport near the Fermi level and possibly a higher activation energy (0.2-0.5 eV) for transitions away from the Fermi Level). We believe that in our work, owing to the low level of GO reduction (sample resistance is still in the order of $>100G\Omega$ as seen in Fig. 4.19), we may not have reached the higher activation regime mentioned in Ref.1; We extract an activation energy of only 47 meV (from our high temperature regime) and interestingly an even lower activation energy of 1.3 meV (from the intermediate temperature regime) for RGO-3 from the $\ln J$ versus $1/T$ curve shown in Fig 4.18. We

propose that our measured hopping barriers from the intermediate region in Fig 4.8 could be indicative of the true transport gap near the Fermi level for the following reason: In [1], the tunneling regime had not been demonstrated. This could be due to the fact that their least reduced RGO had a resistance of approximately $10\text{G}\Omega$. In comparison, all our samples had resistances higher than $100\text{G}\Omega$. Hence, we believe that the authors of Ref. 1 did not observe a transition between tunneling and hopping, since the tunneling regime might have existed at very low temperatures (below the lowest temperature of 78 K that was reported). Without analyzing the transition regime, we cannot be sure whether lower barriers indeed exist. In our work, we clearly demonstrate the departure from the tunneling regime and claim an ultra low hopping barrier of below 10 meV to be representative of the transport gap near the Fermi level. The higher hopping barrier extracted from the “high” temperature regime in our work would then correspond to other transitions away from the Fermi level. The decrease in the hopping activation energy from RGO-1 to RGO-3 gives us confidence that, there indeed exists a lower barrier than that reported by Eda *et al.* The ultra-low hopping activation energy matches well with the picture of an ohmic contact advocated by Arkhipov *et al.* [11]. In addition, the concept of multiple activation energies also fits well with the multi-energy bandgap picture [21].

Hence, by applying two different models (hopping and PF), from the same regime, we extract two different parameters (hopping activation energy and a tunneling activation energy). We believe that both hopping and tunneling processes co-exist in RGO.

4.5 Summary

In this chapter, temperature dependent current-voltage (I - V) was used to characterize charge transport in RGO with various degrees of reduction. In summary, we believe that although several models such as the SCLC-EDT/FN and the Schottky models fit our experimental data in various temperature/field regimes, they do not contain the necessary/correct physics to explain transport via localized states, which fill up the entire π - π^* gap as observed from photocapacitive measurements by Bansal *et al.* [21]. Due to the lack of several parameters required to solve the hopping SCLC equation (Eq. 4.11), we cannot solve the equation to extract unknowns.

However, from the temperature dependence of the current density, charge transport is found to be dominated by tunneling transport below 110 K, hopping transport with a low activation energy (<10 meV) between 110 K-200 K, and a higher activation energy (~ 50 meV) between 200 K and 350 K. We also postulate that the lower activation energy could pass undetected in samples where the level of reduction is high. The extracted low thermal activation energy is reminiscent of an ohmic contact, consistent with the theory by Arkhipov *et al.* who treated transport across the metal-organic interface through hopping injection rather than by thermionic injection [11].

We also report on a Poole-Frenkel (PF) field dependence at moderate temperatures and moderate-high fields. We believe that the origin of the PF dependence is due to the lowering of the Coulombic potential between localized states, which cause the tunnel transfer rate to increase, rather than the detrapping energy required to release a trapped electron into the conduction band.

We show that that the dielectric constant and the lowest hopping energy of RGO decreases with the extent of reduction. However the PF barrier appears to have changed very little with the extent of reduction within experimental errors. In order to

probe any further into transport in this material, one needs to obtain several parameters, (density of states, inverse localization radius and attempt to escape frequency) which are required to solve Arkhipov's equation (Eq. 4.11). We also propose/suggest a theoretical Monte-Carlo (MC) study, with variations of various parameters, which would give more insight into transport in RGO.

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Chapter 5

Ballistic electron emission microscopy study of the Au/GO barrier

5.1 Introduction

In the previous chapters, macroscopic methods such as I - V and TSC have been used to characterize traps and charge transport in GO respectively. Though such methods help to extract important parameters determining charge transport, these are spatially averaged values. Charge injection/Schottky barrier inhomogeneity on the nanoscale is completely masked by the nature of such macroscopic measurements. GO is a non-stoichiometric material with several types of terminal groups attached to its basal plane/edge and consequently is chemically non-homogeneous. GO can also exist in the form of single, double or multi-layer. Hence, a non-homogeneous interface is expected to form when Au is deposited onto GO. Probing such interfaces requires techniques with nanoscale resolution. Surface techniques such as ultraviolet photoelectron spectroscopy (PES) and inverse photoemission spectroscopy (IPES) have a better spatial resolution than I - V , but such techniques are only able to probe the interfacial properties in the thin-film limit (metal coverage of a few atomic layers). It is unclear whether such measurements are representative of practical devices with thicker metal film (tens of nm). In addition, there are several issues that need to be considered in probing the metal-molecule interfaces [1], such as microstructure of metal contact, lattice matching of metal/semiconductor and post-metal evaporation organic integrity, which by itself could cause interface inhomogeneity.

In our work, we use ballistic electron emission microscopy (BEEM) [2-3] which leverages on the nanometer-scale imaging capability of scanning tunneling microscopy (STM) to obtain high spatial resolution images of the local Schottky barrier across the Au/GO interface. Such a technique allows characterization of areas with different electronic structure in the presence of interface heterogeneity. BEEM is a three-terminal STM with top metal (base) grounded, and a back (ohmic) contact to the semiconductor (collector) as shown in Fig. 5.1. The base is connected to a STM circuit while the collector is connected to the same ground through an extra current amplifier (BEEM Femto amplifier).

Figure 5.1: Schematic of BEEM setup. [4]

When a negatively biased STM tip is brought within tunneling distance (a few angstroms-Å) to the metal film, electronic wavefunctions of the tip and the metal overlap and a tunneling current is injected from the STM tip to the grounded metal (base) as shown in Fig. 5.2. At energies sufficiently higher than the metal Fermi energy, the injected electrons traverse the metal film ballistically, before reaching the

metal/semiconductor interface. If the energy of the electrons is sufficient to overcome the local band offset or the Schottky/injection barrier ϕ_{Bn} , the electrons would then cross the metal semiconductor interface into the semiconductor (collector) and be collected as BEEM current via the ohmic contact at the back of the semiconductor.

Figure 5.2: Energy level diagram in a BEEM experiment. $E_{F-Tip}/E_{F-Metal}$ is the Fermi energy of the tip and metal respectively, V_T is the applied tip bias, ϕ_{Bn} is the metal-semiconductor Schottky barrier for electrons to be extracted and E_C is the conduction band of the semiconductor.

This procedure of extracting the barrier height is known as ballistic electron emission spectroscopy or BEES. The same procedure could be applied to extract the hole barrier by applying a positive tip bias, and the procedure for hole spectroscopy is known as ballistic hole emission spectroscopy or BHES. By maintaining a constant bias, and tunneling current, the tip can be used to scan the metal surface to give a spatial/lateral map of the Schottky barriers in a certain region. Hence BEEM/BEES could be used both as a nanoscale microscopy and a spectroscopy tool. In addition, the potential across the BEEM device is effectively zero since the base is grounded and the collector is at virtual ground. This feature allows barrier height measurements with minimum perturbation to the system. Having a thin organic layer, a small bias itself

could cause huge fields across a device, which could create shorts or lead to the vibrational Stark effect [5]. BEEM avoids this problem completely. BEEM provides nanoscale spatial resolution and an energy resolution typically about 10-20 meV at liquid nitrogen temperatures, but depending on the sample and the signal to noise ratio, it can be as low as ~5 meV [6]. The BEEM ultimate lateral resolution is determined by the spreading of the carriers in the metal film due to mutual Coulomb repulsion and interaction with the Fermi sea. [1]

5.2 Theory

5.2.1 BEEM on metal/inorganic semiconductors

Prietsch [7] and Narayanamurti [8] have extensively reviewed BEEM transport in metal semiconductor/insulator interfaces. In these reports, a generalized description is given for a typical BEEM process:

1. Tunneling of carriers from tip to metal base layer.
2. Hot electron transport through the metal base layer.
3. Transmission across the metal-semiconductor (m-s) interface.
4. Transport inside the semiconductor.

Out of several models, the Bell-Kaiser (B-K) model [3] is based on a planar electrode tunneling formalism which has a simple analytic relationship for extracting the barrier height near the threshold voltage (onset of BEEM current) as shown in Eq. 5.1.

$$I_B(V_T) \propto (V_T - V_0)^2 \quad (5.1)$$

Where, V_0 is the threshold voltage to be extracted, V_T is the tip bias voltage and I_B is the BEEM current. The barrier height will simply be eV_0 .

It has to be noted that several assumptions have been made in arriving at such a model.

1. The transport in the metal is ballistic.
2. There is transverse momentum conservation at the m-s interface, where the momentum k of an injected electron is conserved in the semiconductor.
3. A constant transmission coefficient is assumed (normally it is a function of energy).

Most importantly, the B-K relationship is only valid near the BEEM threshold region. At higher voltages, carrier scattering in the metal overlayer and semiconductor, impact ionization in the semiconductor, and several other factors cause a severe deviation from the B-K model [8] towards higher powers.

5.2.2 BEEM on metal/organic semiconductors

There is a key difference between transport in organic materials and in inorganic materials. Electron waves in inorganic materials are delocalized and can be described by a wave vector k . However, in organic materials, charge transport occurs through localized states where k no longer a good quantum number. With a valid wave vector k , it is possible to formulate k -dependent (and consequently energy or bias dependent models, permitting limited scattering) BEEM theories. Therefore, in the strictest sense, neither the Bell-Kaiser, nor k -dependent BEEM theories can be directly applied for an organic material where k is not a good number. In the absence of a BEEM theory for organic materials the next best option is to read off the threshold from the point where the BEEM current deviates from zero [4] (inspection method). This can be described scientifically/ graphically as inferring the barrier height to be the intersection point between the subthreshold baseline BEEM current level or $I_{\text{BEEM}}=0$ (in the presence of no BEEM offset current) line and the tangent of the BEEM curve near the onset of BEEM current. We will term this method as the ‘intersection method’ hereafter.

Lastly, the first derivative of the BEEM spectra has also been used [9] to extract the injection barriers in an organic material.

5.3 Experimental

Although the BEEM technique has evolved from a pure research tool to an application-oriented technique, it is still far from becoming a “push button” technique as it requires a fair bit of experimental skill and knowledge to operate [7]. Hence, this section is devoted to bridge the gap between BEEM theory and BEEM experiments which involves sensitive current measurements of the order of a few pA. The measurement techniques for such low-level signals depend very much on the sample preparation, experimental setup/conditions and noise reduction methods. We will cover all the above aspects in this chapter.

5.3.1 General requirements

The BEEM equipment does not come ready-made/is not a plug and play, and has to be home assembled. The common starting point would be a commercially available STM system, which has to be modified to measure BEEM current. In order to do BEEM experiments with an STM instrument, the following additional requirements have to be met [7].

1. The base (Au) is to be grounded by a BEEM electrode. This ensures that the bias across the BEEM device is zero as depicted in Fig. 5.3(a). The separate BEEM electrode is controlled by a Kleindiek micromanipulator as shown in the photograph in Fig. 5.3(b). Lastly the tunneling current is to be measured by the biased tip itself. To enable BEEM measurements, noise levels must be below 1pA. Methods to reduce the BEEM noise include the use of electrical

shielding and the placement of the current amplifier close to the collector to prevent electrical pickup noise.

Figure 5.3: (a) Experiment schematic, and BEEM connectivity diagram. The buried Au/GO interface is studied. The Au metal is grounded while the APTES-modified silicon collector is connected through a current amplifier to the same ground. (b) View of tip and BEEM electrodes at a typical Au/Si diode viewed by an optical microscope. The image at the bottom is due to the reflection of the tip and electrode at the Au/silicon surface (Courtesy of Dr. Cedric Troade from IMRE). The BEEM electrode grounds the base/metal while the ohmic contact is made by arsenic implantation and thermal annealing at the back of the n-Si wafer.

2. To achieve nanoscale resolution there must be sufficient vibration isolation. Mechanical vibrations yield strong tunnel-current variations due to the exponential dependence of tunneling current distance. To circumvent this problem, the BEEM system is placed on top of a vibration isolation table.
3. The BEEM measurement has to be carried out in complete darkness. The faintest source of light may lead to photocurrents, which can easily saturate the current amplifier. Therefore all viewports must be covered during measurement.

5.3.2 Sample Requirements

For accurate and reliable BEEM measurements, the GO BEEM sample has to meet certain stringent criteria [7].

1. High input resistance and low output resistance

For an Au/GO/Si device, there are two resistances to take note of; the input resistance caused by the Schottky contact between Au/GO barrier and the output resistance caused by the back ohmic contact at the collector. It must be borne in mind that the field across the device is zero since Au and Si are technically grounded. It is possible for the electrons that enter GO to return back to the metal if the Au/GO barrier is lower than the Si/back-contact barrier. Having two paths for the BEEM current, the current would be split according to the ratio of the resistances at either barrier. This may not affect the barrier height directly, but limits the BEEM current magnitude and hence resolution. Having a high output resistance means that a smaller proportion of the BEEM current is able to reach the I - V converter. If the BEEM current falls way below noise levels, the BEEM signal will be masked by noise and may pass undetected. Therefore, it is important that the Au/GO input impedance be much higher than the output resistance. To achieve this, the silicon substrate back contact is made Ohmic. This ensures that most of the BEEM current is collected. To increase the input resistance, smaller diameter diodes could be used or/and the experiment could be carried out at lower temperatures.

2. Sufficient metal coverage and proper grounding

The metal coverage should be thick enough and continuous to ensure that there is proper grounding. On the other hand, the film thickness should be within the mean free path of the electron in the metal (Au), which is reported to be in the range 10-25nm [10-11] at room temperature. Only then ballistic transport is possible. Otherwise

scattering in the metal may prevent the electron from going across the Schottky barrier. In our experiment we choose a conservative film thickness of 10nm Au.

3. GO flake size

Deposition of thicker carbon particles present in the GO solution on the silicon surface may create a discontinuity in the metal film coverage, causing improper grounding which may lead to a tip crash. In addition, the presence of larger granules on the surface could be detrimental by providing a leakage path and thereby render any BEEM measurement impossible. These issues had to be rectified by fine-tuning the GO layer deposition process.

5.3.3 Graphene oxide synthesis

A modified Hummers method was used for graphene oxide production as described in Ref [12]:

“Graphite powder (NGS Naturgraphite GmbH, carbon content: 80%–99.5%, flake size: >0.85 mm) was added to concentrated sulfuric acid. The mixture was heated for 4.5 h at 80 °C. The mixture was cooled to room temperature and sonicated (at 300 W) in a water-bath for 6 h to break down the graphite into smaller and thinner flakes. The solution was then diluted with 0.5 l of de-ionized (DI) water and was left overnight to allow graphite to be fully oxidized. The suspension was filtered and washed with DI water using a 0.2 µm nylon filter. The obtained solids were left to dry for 24 h under room temperature and pressure. The dried solids were then stirred with potassium permanganate (KMnO₄) in concentrated sulfuric acid while being placed in an ice bath to limit the temperature rise and to allow for completion of the reaction. Subsequently, a 30% hydrogen peroxide solution (H₂O₂) was added to the mixture. Instantly, the mixture color turned bright yellow. The mixture was then left overnight and then filtered and washed with diluted hydrochloric acid (HCl 1:10). Once this was

accomplished, the residue was dissolved in DI water, followed by filtering. The GO powder was obtained after drying the residue at ambient temperature for 1 day. The GO solution was then prepared by sonicating the obtained powder in DI water for 20 min.'

5.3.4 BEEM sample preparation

An n-type Si (111) wafer doped with phosphorous at 10^{15} cm^{-3} was ion-implanted with arsenic at the back of the wafer. The wafer was then subjected to a rapid thermal annealing (RTA) process at 1000°C for 3 s to activate the implanted ions thus forming the necessary back ohmic contact. The wafer was then diced into $6 \times 6 \text{ mm}^2$ square samples (the piezo range for stage control is only 6mm per axis) and cleaned by acetone for 10 minutes followed by an IPA (iso-propyl alcohol) clean for 10 minutes. Thereafter the samples were subjected to a 20 s dip in 7% buffered Hydro-Fluoric acid (HF) followed by a dip into deionised (DI) water to check for hydrophobicity. The cleaned sample was then dipped in a 2% aqueous amino-propyl-triethoxy-silane (APTES) solution for 2 minutes, rinsed in DI water and blown dry with N_2 . APTES was used as an adhesion promoter to bind the GO flakes onto the hydrophobic Si surface. Previous attempts to transfer GO without using APTES had led to very low coverage by GO on the Si surface (checked via microscope). FTIR results (as shown in Fig. 5.4) confirm the presence of APTES on the hydrophobic Si surface. In addition, we expect only a monolayer [13] of APTES to form as a result of the short sample immersion duration in APTES. This results in a modified silicon surface for GO to be transferred onto. Hereafter we will refer to the APTES modified silicon surface as m-Si. The GO solution was drop-casted onto m-Si. After 1 min, the samples were quickly rinsed in DI water, blown-dry with nitrogen gas, immediately transferred into a thermal evaporator and placed under vacuum conditions. The rinse step is extremely

important since it helps to remove larger particles that could otherwise affect the BEEM experiment. A 10 nm thick layer of gold (99.9% purity) was thermally evaporated at 10^{-5} Pa at a deposition rate of $0.1 \text{ \AA/s}$ through a shadow mask (5x5 arrays of holes with diameter of 0.5mm) to form the final Au/GO/m-Si device for the BEEM study. In addition, Au/Si diodes and Au/m-Si diodes were also fabricated to be studied as control experiments for the Au/GO/m-Si BEEM study. The control devices were fabricated in the same manner as the Au/GO/m-Si device except that the gold evaporation took place immediately after the HF cleaning step for the Au/Si device and before the GO drop-casting step for the Au/m-Si devices respectively.

Figure 5.4: FTIR spectrum at 45° for APTES modified silicon surface.

5.3.5 AFM and Raman characterization

Atomic force microscopy (AFM) measurements were performed using a Digital Instruments system in the tapping mode to characterize the GO layers obtained from the solution. The GO solution was drop-casted on a Si sample with a layer of 300 nm thick SiO_2 pre-treated with APTES to promote adhesion of the GO-flakes. Coarse inspection of the presence of GO flakes was carried out via an optical microscope. Thereafter, the sample was analyzed by AFM. Fig. 5.5 shows the position of GO flakes in a $10\ \mu\text{m}$ by $10\ \mu\text{m}$ area. To verify the existence of single/double layer GO flakes, a line profile (see vertical dashed line) over a selected region (circled in red) was taken, as shown in the inset of Fig. 5.5. The heights of the single and double flakes were measured to be 0.8 and 1.7 nm, respectively. The measured heights are in good agreement with reported results found in the literature [14].

Figure 5.5: Atomic force microscopy image of GO on 300 nm SiO_2/Si . The presence of single/double layer GO was confirmed with the height profile (see inset) along the dashed line within the circled GO region.

Raman spectroscopy (WITec CRM200 system with wavelength 488 nm and spot size $\sim 0.5 \mu\text{m}$) was used to verify the presence of graphene oxide. Fig. 5.6 is the Raman spectrum obtained from a GO coating patterned onto a $2 \mu\text{m}$ grating. Three peaks were observed at 1354 cm^{-1} , 1595 cm^{-1} and 2700 cm^{-1} from the spectra (see inset for close up view). These peaks represent the D, G and 2D peaks respectively, validating the presence of GO [15] in the solution used for coating.

Figure 5.6: Raman spectroscopy analysis on a GO coating detects the D, G and 2D peaks. A zoomed-in view of the 2D peak is shown in the inset for clarity.

5.3.6 BEEM experimental setup

The BEEM measurements were performed in a home-built BEEM–STM system comprising a modified Molecular Imaging STM head, a XYZ Attocube stage for sample placement (sample stage coarse positioning). A Kleindiek micromanipulator is used as the BEEM electrode, to gently ground the base with a $50 \mu\text{m}$ Au wire. A Nanonis controller (signal processing unit) maintains 2-way communication with the

computer-user interface. The system can be operated in air or in low vacuum at ambient temperature. The back ohmic contact to the Si wafer is directly in contact with the conducting sample stage, which acts as the collector for the BEEM current (connected to a FEMTO amplifier). Mechanically cut 0.25 mm diameter PtIr (90% Pt, 10% Ir) tips were used for the BEEM–STM measurements carried out in the constant tunneling current mode.

5.4 Results and Analysis

5.4.1 BEEM study on Au/Si

We present the results of the BEEM study of the Au/Si interface (shown in Fig. 5.7) which will serve as the first of our control experiments for the main BEEM study on GO. STM imaging of the Au surface at a constant tunneling current of 1 nA and bias - 1.2 V showed the polycrystalline nature of the Au films deposited by thermal evaporation as depicted in Fig. 5.7 (a). BEEM on the Au/Si interface, was done simultaneously (on the same area at the same time) with STM, under the same conditions as those used for the STM imaging. This showed a non-homogeneous barrier as shown in Fig. 5.7 (b). The lighter regions represent higher BEEM current while the darker region represents lower BEEM current. Fig. 5.7 (c) depicts the Bell-Kaiser (B-K) fit to the experimental data (9 spectra average). An electron injection barrier height of 0.8 eV was obtained from the B-K fit for the Au/Si system. No significant barrier height differences were observed (by fitting the BEES spectra at the dark/light regions with the B-K fit) between the dark/light regions suggesting that the difference in BEEM current is likely due to the spatial inhomogeneity in the transmission factor across the Au/Si interface.

Figure 5.7: STM image of the top gold surface at a tip bias of -1.2 V and 1 nA tunneling current. BEEM image of the Au/Si interface on a $100 \times 100 \text{ nm}^2$ area (acquired on the same area as that used in the STM scan) scanned at a constant tip bias of -1.2 V. The lighter areas correspond to higher BEEM current and darker areas to lower BEEM current. (c) BEES spectra (9 spectra average) at a constant tunneling current of 1 nA. An electron barrier height of 0.8 eV is obtained using the Bell-Kaiser (B-K) fit (red curve) to the experimental data.

5.4.2 BEEM study on Au/m-Si

We present the results of the BEEM study of the Au/APTES-modified-Si (Au/m-Si) interface (shown in Fig. 5.8) which will serve as the second of our control experiments for the main BEEM study on GO. Fig. 5.8 (a) shows the STM image while the BEEM image on Fig. 5.8 (b) shows the Au/m-Si interface to be non-homogenous. Both the STM and BEEM images were taken simultaneously across a 100 nm X 60 nm area under a tip bias voltage of -1.2 V and 1 nA tunneling current. An electron injection barrier height of 0.8 eV is obtained from the B-K fit (red curve) to the averaged experimental BEES spectra (9 spectra average) on Fig 5.8 (c). No significant barrier height difference was observed between the dark/light regions. From the BEEM results from the Au/Si and Au/m-Si systems we find that no additional barriers are created by the incorporation of the APTES modification of the Si surface and hence infer that the APTES layer merely acts as an adhesion layer for the incorporation of GO onto the Si substrate.

In addition, density functional theory calculations were carried out on the APTES molecule to compute the molecular HOMO and LUMO bandgap shown in Fig. 5.9. DFT calculations were done using Gaussian 98 at B3LYP1 level implemented in the Firefly Quantum Chemical package [16], which is partially based on the GAMESS (US) [17] source code. APTES has a large bandgap of 7 eV, which is expected of small sized molecules. Thus, if the APTES layer with its large bandgap indeed blocked transport, then absolutely no BEEM current would have emerged. However due to the thickness of the APTES layer which is only a few angstroms, electrons will simply tunnel through the APTES layer. Therefore, the APTES layer mainly forms an adhesion layer for our work, and has no influence on transport. We do not discount the possibility that there could be a little attenuation across a thin tunneling barrier.

Electrons exiting from the GO can easily get into the n-Si conduction band and be collected as BEEM current.

Figure 5.8: STM image of the top gold surface at a tip bias of -1.2 V and 1 nA tunneling current. BEEM image of the Au/m-Si interface on a 100 X 60 nm² area (acquired on the same area as that used in the STM scan) scanned at a constant tip bias of -1.2 V. The darker areas correspond to higher BEEM current and lighter areas to lower BEEM current. (c) BEES spectra (9 spectra average) at a constant tunneling current of 1nA. An electron barrier height of 0.8 eV is obtained using the Bell-Kaiser (B-K) fit (red curve) to the experimental data.

Figure 5.9: DFT calculations depicting the HOMO and LUMO in APTES.

5.4.3 BEEM study of the Au/GO interface

BEEM on the Au/GO interface, was done simultaneously with STM (see Figure 5.10), under the same conditions as those used for the STM imaging (-1.2 V tip bias voltage and 1 nA tunneling current). This showed a non-homogeneous barrier as in Fig. 5.11. Three distinct types of regions marked 1-3 for lightest to darkest were found to exist in the BEEM image. The darker region represents lower BEEM current while the lighter regions represent higher BEEM current. It is not to be assumed that higher BEEM current refers to a lower injection barrier although that possibility does exist. Hence, we directly probed each of the 3 regions to extract the barrier heights using BEES (at a constant tunneling current of 1 nA), as shown in Fig. 5.11. Barrier heights of 0.8 eV and 0.9 eV and 1.02 eV, were obtained, respectively for regions 1-3 using the B-K fit (as shown in red) in Fig. 5.12. The B-K results coincided well with the barrier height extraction using the intersection method as shown in Fig. 5.13.

However, to assume that the B-K theory is appropriate simply because the model fits the data would be a leap of imagination. There are several issues here. First, since B-K is a k -dependent theory, it may not apply in our case since k would not be a valid quantum number in GO due to lattice mismatch. Secondly, the data in the BEEM spectrum has a significant amount of noise which causes uncertainty in determining the barrier height. It almost appears that the B-K model will appear to fit at least in the range chosen (within 100 meV-200 meV from the barrier height energy).

Figure 5.10: Scanning tunneling microscopy image of the top gold surface at a tip bias of -1.2 V and 1 nA tunneling current.

Figure 5.11: BEEM image of the Au/GO interface on a $100 \times 100 \text{ nm}^2$ area (acquired on the same area as that used in the STM scan) scanned at a constant tip bias of -1.2 V. The darker areas correspond to lower BEEM current and lighter areas to higher BEEM current. Three distinct regions labelled 1-3 have been found.

Figure 5.12: BEES at the 3 regions shown in Fig. 5.11 show the existence of three different barrier heights. The barrier heights range from 0.8 to 1 eV for the three regions 1-3 (top to bottom). Bell-Kaiser fit to the BEES spectra is shown as the red curve. The spectroscopy is in agreement with the barrier height trend observed from imaging thus confirming the presence of 3 distinct barrier heights at the interface.

Figure 5.13: Barrier height extraction using the intersection method for the BEES spectra at regions 1 to 3 respectively (shown in Fig. 5.11). The obtained barrier heights correlate well with the results obtained in Fig 5.12 using the B-K method.

Therefore, to determine the injection barriers for Au/GO, a statistical approach has to be taken to remove noise in the data. Ideally one should take several BEEM spectra on each region and average it to remove noise in the data. However, there is always a finite sample drift (sample moves laterally relative to the tip) which means that the next time one probes the surface, it may be at a different spot. Thus, it is advised that one should wait long enough until the sample drift is stabilized. However working in the ambient has shown device degradation to occur with time [18]. Hence it is certainly challenging to get good, stable BEEM spectra and images in such situations. There is little that one could do to rectify the problem as far as imaging is concerned apart from working in UHV and low temperatures. However as far spectroscopy is concerned one could resort to statistical averaging to get a distribution of the barrier heights as shown in Fig. 5.14. More than 50 BEEM samples were measured. Each sample had 25 devices. For each sample a brief period of time (about 1 hour) was allocated to allow the sample drift to stabilize to a very low value while scanning the surface. Thereafter, the BEEM spectra were taken at various locations in each device of the sample. The barrier heights were extracted using the B-K fit. The B-K fits however were carried out very close to the threshold in order to converge with the barrier heights that were extracted using the intersection method. In all cases, the intersection method was found to be the most appropriate for determining the barrier height.

Figure 5.14: Distribution of electron injection barriers across the Au/GO interface of over 100 samples.

The extracted barrier heights show a main peak at 1 eV and other subsidiary peaks around 1.2 eV and 1.35 eV. It has to be noted that during the initial few hours of probing, only barriers below 1.13 eV were observed. The barriers above 1.13 eV only started to appear later in the experiment after repeated probing at the same location. This issue will be discussed later in this chapter. Another issue here is the concept of STM induced photocurrent or STM-PC [19] which will give a current of the same order of magnitude as the BEEM current, at the bandgap of the collector (1.1 eV for silicon in our case). Thus, when an injection barrier was obtained at around 1.1 eV, care was taken to immediately reverse the polarity of the tip and carry out ballistic hole emission spectroscopy (BHES) to check the presence of STM-PC if any. If the origin of the current was indeed STM-PC then the barrier height via BEES and BHES will match the silicon bandgap. In which case, one can easily conclude that the

measured barrier height is not indicative of the injection barrier. However in our work we did not encounter any such case. We will first try to characterize the lower barrier by cropping away the barriers above 1.13 eV as shown in Fig. 5.15. The observed distribution of measured hole injection barriers using BHES is in Fig. 5.16.

Figure 5.15: Distribution of Au/GO electron injection barrier heights below 1.13 eV. The distribution shows a central peak near 1.0 eV for the given range.

Figure 5.16: Distribution of hole injection barrier heights across the Au/GO interface. The distribution shows a central peak near 0.5 eV for the given range.

From both distributions it is evident that the electron/hole barrier is centered at 1 eV/0.5 eV with tails running down on either side of the peaks. However, it is not clear what the origin of this distribution or tail is. We list a few possibilities below.

1. Finite density of states in the organic HOMO-LUMO gap (difference in the energy between the highest occupied molecular orbital and the lowest unoccupied molecular orbital)

It is possible that in an organic material, the BEEM current arises due to electron resonant tunneling (residence of the electron for a finite time in an intermediate state) through the organic instead of the usual Schottky emission process across the metal/inorganic-semiconductor. If there are available states in the HOMO-LUMO gap of the organic and if the energy of the incoming electron is larger than the n-Si conduction band, the BEEM current will be observed as a consequence of resonant tunneling through the gap states. This is shown schematically in Fig. 5.17. In such a

case the barrier height will certainly depend strongly on the distribution of states in the HOMO-LUMO gap of GO.

Figure 5.17: Resonant tunneling BEEM model.

2. Different thickness of GO

During transfer of GO flakes from the solution onto m-Si, one does not have control on the thickness of the GO flakes. We have no control on whether a single/double or multi layer GO is being probed at any one instance. It is possible to attribute the largest barrier to single layer and intermediate barriers to double layer and finally the lowest barrier to multi-layer GO. Such an inference is justifiable from a tight binding perspective [20] which states that the bandgap reduces as the number of atoms/layers increases, and from the existence of such layers as characterized by AFM. The presence of three such distinct regions could cause a distribution of barrier heights.

3. Different functional groups on GO

Theoretical calculations [21] show that different chemical groups such as O, OH and COOH, could lead to completely different electronic structures with states in the HOMO-LUMO gap depending on the functionalization. Thus, each block of data in the histogram could correspond to a specifically functionalized GO. For example a GO with two OH groups will behave differently from that which has only one OH. This gives permutations of functionalized GO with each structure having its own injection barrier.

From the above, it should be clear that it is extremely difficult to pinpoint the cause of the distribution of barriers. We can only speculate on the origin of the distribution of barriers. Next, to extract a single parameter as an injection barrier one would need to analyze an averaged BEES/BHES curve as shown in Fig. 5.18. Both spectra have been averaged over 9 or more spectra, all taken at a constant tunneling current of 0.5 nA. Special care was taken not to use high tunneling currents which could modify the surface and thereby give an unrepresentative barrier height. We immediately observe that the noise level has dropped significantly as compared to the single spectrum BEEM in Fig. 5.12. It almost appears that the B-K model will appear to fit at least in the range chosen (within 100 meV-200 meV from the barrier height energy). Even then the fit does not seem satisfactory. An exponent of 5.5 can be used instead of 2 to fit the electron injection barrier using a power law model, like the B-K model, all the way up to 1.4 V. But it eventually gave unphysical injection barrier values, such as 0.3 eV. The best course is use the intersection method, which gives an electron/hole injection barrier of 1.0 eV/0.5 eV respectively.

Figure 5.18: Raw experimental BEES (left) and BHES (right) spectra (9 or more spectra) at a constant tunneling current of 1 nA. The red curves on both the BEES/BHES represent the B-K fit to averaged spectra (see top inset for BEES averaged spectra and bottom inset for BHES averaged spectra). The B-K fits extracted the electron/hole barrier heights to be 1.0 eV / 0.5 eV respectively. The insets also depict the barrier extraction through the intersection method (depicted by the intersection point of the 2 red lines in the inset). Both methods gave similar barrier heights.

We have also used the derivative method [9] on the BEES/BHES curves to mark out the barriers. The derivative of the averaged/smoothed BEES/BHES shown in Fig. 5.18 is given in Fig. 5.19 and 5.20. Using the intersection method (intersection between the baseline dI/dV curve and the tangent to the curve above the threshold voltage), a 1.0/0.5 eV barrier from the BEES/BHES derivative is obtained respectively (shown in the inset of Fig. 5.19/5.20 respectively). In addition, step-like features are also observed at different voltages which are believed to be injection barriers [9]. Such features have been observed in inorganic materials such as GaAs and also in organics

like p-phenylene. Using the BEES derivative, additional barriers apart from the 1 eV barrier appear at 1.12 eV, 1.2 eV, 1.26 eV and 1.35 eV. By comparing the barriers extracted from the derivative method with the histogram in Fig. 5.13, we find that there is a close correlation especially with the histogram peaks near 1.35 eV and 1.2 eV. Thus, we believe that the barriers above the 1 eV barrier could indeed be higher energy states through which conduction could take place.

Figure 5.19: Derivative of BEES curve (shown in Fig. 5.18) showing step like-features. The inset shows the extraction of the 1.0 eV barrier using the intersection method.

Figure 5.20: Derivative of BHES curve (shown in Fig. 5.18) showing step like-features. The inset shows the extraction of the -0.5 eV barrier using the intersection method.

As mentioned earlier, the barriers above 1.13 eV only appeared later in the experiment as a result of repeated probing at the same location and were never been observed in the first instance. Having established that there could be higher energy states above 1 eV which are available for conduction, it is interesting to investigate the origin for the initial non-appearance of the higher energy barriers.

Such a phenomenon can be linked to charge trapping in graphene oxide [22]. Vertical transport through GO (1-2 nm thickness) is likely to be via resonant tunneling as depicted in Fig. 5.17. Thus, there will be a finite residence time for electrons traversing GO, depending on the difference in the energy of the incoming electron and a specific resonant level. Hence, at any instance, it is possible that the resonant level is occupied by an electron, and the next incoming electron has to tunnel via higher energy states. This process could be repeated and each newer incoming electron will

be forced to tunnel via a higher state than the preceding electron. A similar analogy could also be used for hole transport. Such levels appear in the spectra because the acquisition time is sufficiently large to average over all such events.

This theory could then account for all the observed barriers across the entire histogram. We therefore suggest that BEES/BHES could be used as nanoscale density of states peak energy level extraction tool in an ultra-thin organic material by repeated spectroscopy on a specific location. Such a method would certainly depend on the residence time of charges in the material to be investigated. However further work needs to be done to validate the idea both experimentally and theoretically. Having extracted the injection barriers across the Au/GO interface, we will next discuss the construction of a band energy level diagram for the Au/GO/m-Si system and the necessary parameters that are required to be measured in order to construct the band diagram.

5.4.4 Building the Au/GO/m-Si band diagram

The band diagram for organic charge transport is very different from that seen in the inorganic case. Extensive work has been done by the Kahn group [23-24] with metal on organic and organic on metal interfaces. Fig. 5.21 (a) shows a typical metal-organic interface, where the vacuum level is denoted by E_{VAC} , Fermi energy level by E_{F} , metal work function by ϕ_{M} , electron/hole injection into the LUMO/HOMO by $\phi_{\text{Bn}}/\phi_{\text{Bp}}$ respectively, charge neutrality level of the interface states by E_{CNL} , electron affinity and ionization energy by EA and IE respectively and the dipole by Δ . If the interface Fermi energy is above/below E_{CNL} , the net charge in the interface states is negative/positive and one gets a dipole with a corresponding sign at the interface [24]. The parameters mentioned above are typically measured with ultraviolet-photoelectron spectroscopy and inverse photoemission spectroscopy as shown in Fig 5.21 (b).

Figure 5.21: (a) Band energy level diagram across a metal-organic interface which shows the presence of a vacuum level shift, interface dipole and interface charge neutrality level. (b) Typical UPS/IPES measurements on an organic material showing the necessary parameters for drawing of a band diagram such as in (a) [24].

Thus, one needs to have a complete set of parameters discussed above in order to get a band diagram for the Au/GO interface. Furthermore several other factors need to be considered.

1. Metal deposition on organic or organic deposition on metal [24]

Interfaces have been classified by the ability of interface states to pin the Fermi level down via a parameter S (between 0 and 1). Those interfaces which are least influenced by the interface states are said to approach the Schottky-Mott limit ($S=1$) whereas the other extreme at $S=0$ would be the Bardeen limit as discussed in Chapters 2/3. Organics deposited on metals exposed to the ambient, generally form interfaces that approach the Schottky-Mott limit. In other words, such an interface will not have a dipole or any vacuum level shift and the barrier heights can be determined by the metal work function and the organic electron affinity. The work function of metals exposed in the ambient could vary significantly as compared to atomically clean metal

prepared in UHV. Metals exposed to the ambient get passivated by atmospheric gases and hence “contaminated”. The contamination acts like a separation and effectively increases the metal-organic distance reducing the interaction between the metal and the organic layer, and decoupling the organic film from the continuum of metal states. This causes a significant reduction in the density of interface states/dipole and in the limiting case reaches the Schottky-Mott limit where the vacuum levels align. However, if the processing was under ultra high vacuum conditions, a strong departure from the Schottky-Mott limit is expected due to much stronger metal-organic interactions. Under such conditions, vacuum level shifts and interface dipole need to be measured in order to construct the band diagram.

2. Orientation of organic layer

Next, the orientation of the organic will govern the strength of the metal-organic interaction. Flat lying molecules in general would have a larger part of its pi-orbitals interacting with the metal wave-function. In the case of GO, although it is likely to lie flat, the pi orbital overlap in the molecule itself is very much diminished due to several terminal groups disrupting the pi-orbital network for lateral transport. In the vertical case, the amount of interaction between GO and metal needs to be investigated.

3. Metal diffusion into organic layer

Au is also known to diffuse into the organic matrix and act as a doping center. Whether this will occur in GO and whether it will affect the Au/GO interaction needs to be investigated. It is only known that Au will not penetrate the graphene plane as it is impermeable to helium [25].

Hence, in order to build a band diagram for Au/GO, IPES and UPS experiments have to be carried and necessary parameters extracted.

5.5 Summary

In this chapter, we have discussed nanoscale investigation of vertical charge transport across a non-homogeneous Au/GO interface. This is a necessary step regardless of the device structure being either of a planar or sandwich configuration, since charge injection into GO is necessary in both cases. The BEEM theory for inorganic materials was briefly discussed and the invalidity of k-based theories for BEEM on organic surfaces was pointed out. The Au/GO interface was mapped on the nanoscale using BEEM and an average electron/hole injection barrier of 1.0/0.5 eV was statistically determined. Several additional injection barriers were observed from the derivative of the BEES/BHES spectra which are believed to be additional states in the gap available for charge injection. We believe that the appearance of such states with repeated BEEM spectroscopy on a local area is related to charge trapping within the GO, and/or resonant tunneling via higher energy available states. If this is indeed the case, BEEM can be a useful nanoscale probe of the peaks in the density of states at the interface. Further work however needs to be done to verify such a theory on other materials, along with an appropriate theory for such transitions in a metal-organic interface. The constraints in building a band diagram for a metal/organic interface due to the departure of interface properties from the ideal Schottky-Mott limit were presented. The charge transport is proposed to involve ballistic transport in Au, injection across the Au/GO interface and finally resonant tunneling through the GO layer into the modified silicon layer before being collected as BEEM current.

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Chapter 6

Correlation between TSC, IV, BEEM and density of states in GO

Three techniques have been used in Chapters 3-5 to study various transport related parameters in GO. In Chapter 3, the trap levels in GO and RGO-1-3 were determined by the thermally stimulated current (TSC) technique. In Chapter 4, temperature dependent current-voltage (I - V) characterisation was used to investigate the transport mechanism in RGO. In Chapter 5, ballistic electron emission microscopy (BEEM) was used to study the nanoscale lateral injection barrier inhomogeneity and extract the electron/hole barriers in GO. Based on the results obtained from the various experiments, is it possible to form a cohesive picture of the transport in GO or in RGO? Do the different techniques give a synchronous view of transport? What is the origin of the transport barrier that is seen? These questions form the central theme of this chapter.

6.1 Density of states in GO

GO being an insulating material, has a very low intrinsic carrier density and only injected carriers contribute to transport. However, the injected carriers can only be accommodated if there are available states in GO. This makes the analysis of the density of states (DOS) in GO important. Theoretical DOS and experimentally derived DOS [1, 2] both show the presence of several states in the π - π^* gap as shown in Figs. 6.1 and 6.2 respectively.

Figure 6.1: Carbon 2p partial DOS calculated for graphene (black line), for C atom of graphene faraway from O (blue line) and for carbon atom bonded to O (red line). [1]

Figure 6.2: Evolution of the experimentally obtained density of states during reduction from GO (left) to r-GO (right). Reduction leads to additional levels in the π^* - π gap. The blue lines depict possible transitions from the highest filled electronic level to unfilled levels. [2]

In both figures, the π - π^* gap varies between 4.4 eV-6 eV. We had independently carried out electron energy loss spectroscopy (EELS) (Courtesy of Dr. Michel Bosman) and observed a peak at 5.45 eV (not shown here) which is indicative of interband transitions [1] (π - π^*). It is however very unlikely that the regimes of transport studied in this thesis for GO, involve such huge transitions. This makes the analysis of states within the gap important. The various peaks in the density of the states, above the Fermi level, from DOS-1 and DOS-2 (Fig. 6.1 and 6.2 respectively) are tabulated below in Table. 6.1, and are explained in detail below.

DOS-1-GO-a	-0.1	-0.67	-1.1	-1.45	-1.93			-2.4
	0.21	0.61	1.03	1.42				2.01
DOS-1-GO-b	-0.4	-0.67	-1.07	-1.48	-2			-2.48
	-0.4	-0.67						
	0.21	0.61	1.21	1.54				2.01
DOS-2-GO	-0.5							-2.33
	0.2	0.39	0.72	1.08	1.28	2.31		2.59
DOS-2-RGO	-0.13	-0.59	-1.02	-1.34	-1.67	-1.9		-2.47
	0.2	0.4	0.85	1.05	1.28	1.71	2.28	2.62
	0.2							

Table 6.1: Comparison of DOS peaks from references 1 and 2, with data measured in this thesis. The boxes shaded in light grey/yellow/green correspond to the values that were measured by TSC/BEEM and I - V respectively.

In Table 6.1, DOS-1 refers to the theoretical DOS and DOS-2 refers to the experimentally extracted DOS. DOS-1-GO-a is the DOS for the C atom of graphene faraway from O and DOS-1-GO-b for the carbon atom that is bonded to O. DOS-2-GO

is the experimentally extracted DOS of GO, while DOS-2-RGO is the experimentally extracted DOS for reduced GO. The boxes shaded in light grey/yellow/green correspond to the values that were measured by TSC/BEEM and I - V respectively. The numbers in parentheses indicate the detrapping energies from the trap energy level to the π^* level. Several of the peaks in DOS-1 match those observed in DOS-2. As GO is reduced, several other peaks appear [2]. From the DOS in Figs. 6.1 and 6.2, it seems clear that the addition of O groups onto the graphene plane causes discontinuities in the DOS of graphene, resulting in gaps in the DOS. Conversely, the act of reduction creates new states in the DOS of GO, attempting to link back these discontinuities/gaps. However, the continuous DOS seen in graphene is not retrieved. The above mentioned phenomena have been partly observed in TSC, (through an increase in the number of peaks at lower energy levels as GO is reduced) discussed in Chapter 3, and in the I - V characteristics discussed in Chapter 4 (as a drop in the activation energy with the extent of reduction signifying that the transport gap is narrowing down to reach the case of graphene which has a zero gap).

Another observation is that the effect of bonding an O atom to C seems to diminish the number of states available for conduction at most energy levels of interest as shown in DOS-1. From these observations it appears that the origin for a transport gap in GO is likely to be the incorporation of defects onto the graphene plane, specifically the O group. While the main reason for the DOS structure is likely to be due to defects, the impact of metal induced gap states (MIGS) on altering the DOS should not be discounted. Recent work by Liang *et al.* [3] shows that MIGS appear inside the bandgap of graphene nano-ribbons (GNR), near the middle. In addition, MIGS are broadened in energy due to the coupling with states of the metal contact.

6.2 Correlation between I - V , TSC and BEEM

Although the three methods (I - V , TSC and BEEM) probe various trap levels in GO/RGO, there are some fundamental differences between the techniques.

In BEEM, one can measure the entire distribution of trap levels, since BEEM can distinguish between states below and above the Fermi level. This is generally not possible in I - V or TSC, unless different electrode materials are used to specifically block a certain carrier type (electron or hole). However, the range of trap energies measured by BEEM is limited by the collector material (silicon). For injection barriers lower than that of the Au/Si system, the Au/Si system will be the controlling factor. In other words, barriers below 0.8 eV for electrons and 0.3 eV for holes cannot be measured by BEEM using silicon (bandgap 1.1 eV) as the collector. This is where the TSC and I - V technique will prove to be useful in extracting the GO trap energy levels.

Hence, we find that the three techniques complement each other and will next discuss the correlation between the three techniques and the density of states (DOS) in detail. We first start with a correlation of the BEEM results with the DOS. This will enable us to locate the metal Fermi level unambiguously. After this, correlation of the I - V and TSC results becomes easier.

6.2.1 BEEM results

The BEEM results could be separated into BEES and BHES results. We will first discuss the BEES results. From the BEES histogram in Fig. 6.3, we find a multi-modal distribution of barriers with several peaks between 1.0 eV and 1.4 eV. The important point to note is that the peak at 1 eV has a large spectral weight compared to the one at 1.4 eV. The BHES histogram in Fig. 6.5 shows a distribution of barriers between 0.3-0.7 eV, with a large spectral weight at 0.5 eV. Therefore, the metal Fermi level is to be

located between a DOS electron peak and a DOS hole peak, at 1 eV and 0.5 eV from the metal Fermi level respectively. Upon careful observation of DOS-2, the location of the metal Fermi level turns out to be very close to the Fermi level of GO shown in Fig. 6.2. This is fortuitous, making our work of correlation easy. Were it otherwise, correlation would have been quite difficult. Our observation is well supported by the literature on graphene workfunction [4] of 4.5 eV, which coincides with the workfunction of Au in contact with a π -conjugated polymer [5].

6.2.1.1 BEES

In BEES, the spectroscopy is purely due to electrons. Such a condition cannot be met in TSC or in conventional I - V while using similar electrodes. Hence, in BEES, only the electronic states above the Fermi level in the GO DOS are accessed.

These values are very closely related to the DOS peaks:

- 1) 1.03 eV and 1.42 eV in DOS-1-GO-a,
- 2) 1.21 eV in DOS-1-GO-b
- 3) 1.08 eV and 1.28 eV in DOS-2-GO.

In addition a revisit of the BEES derivative as shown in Fig. 6.4 shows remarkable correlation to the corresponding DOS peaks.

Figure 6.3: Distribution of electron injection barriers across the Au/GO electron injection barrier obtained from BEES.

Figure 6.4: BEES derivative curve showing step like-features.

6.2.1.2 BHES

The BHES histogram in Fig. 6.5 shows a distribution of barriers between 0.3-0.7 eV.

Figure 6.5: Distribution of hole injection barrier heights across the Au/GO interface obtained from BHES. The distribution shows a central peak near 0.5 eV.

The observed barriers are correlated to the following DOS peaks:

- 1) -0.67 eV in DOS-1-GO-a
- 2) -0.4 eV and -0.67 eV in DOS-1-GO-b and
- 3) -0.5 eV in DOS-2-GO.

Although the kinks seen in the BHES derivative shown in Fig. 6.6 show several states between 0.78 eV and 0.95 eV, they do not coincide with the DOS peaks. However, we believe that these states could have been enveloped within the tail of the -1 eV state in DOS-1-GO-a and b.

Figure 6.6: BHES derivative curve showing step like-features.

6.2.2 I - V results

From the I - V results in Chapter 4, we extracted activation energies for RGO in the order of a few meV. We also extracted a barrier of 0.23 eV from the Poole-Frenkel field dependence. DOS-2-RGO supports both findings through the presence of unoccupied states close to the Fermi level and through the 0.2 eV state. Thus, the extracted low activation energy likely corresponds to transport through the tail states near the Fermi level. These low barriers however remain invisible to BEEM due to the Si collector blocking effect (The Si bandgap blocks/prevents carriers with insufficient energy to enter the Si conduction/valence band and hence do not contribute to the overall BEEM current). Coincidentally, we also measured detrapping energies of 0.19 eV (98K) and 0.264 eV (130K) using TSC which correlate well the I - V results.

6.2.3 TSC results

The main peaks for TSC on GO and RGO-1-3 are seen at 0.19 eV, 0.264 eV, 0.396 eV, 0.593 eV and 0.678 eV. The TSC peaks are shown to correlate extremely well with the DOS/BEEM and the I-V results as shown below:

- 1) 0.19 eV - This level has been observed and is well correlated to the DOS-1-GO-a/b as the 0.21 eV state and to the DOS-2-GO/RGO as the 0.2 eV state. We also believe that this level is related to the 0.23 eV barrier extracted from the I - V results.
- 2) 0.264 eV - This level correlates to the 0.23 eV state extracted from I - V .
- 3) 0.396 eV - This level is well correlated with the -0.4 eV state in DOS-1-GO-b, 0.39 eV state in DOS-2-GO and the 0.4 eV state in DOS-2-RGO.
- 4) 0.593 eV – This level matches well with the 0.61 eV state in DOS-1-GO-a/b and the -0.59 eV state in DOS-2-RGO.
- 5) 0.678 eV- This level is well correlated with the -0.67 eV state in both DOS-1-GO-a/b.

We also believe that the 0.396 eV and 0.593 eV levels are likely to be related to the -0.5 eV level (within the tail of the distribution in energy as seen in Fig 6.5) extracted from BHES.

6.3 Summary

I - V , TSC and BEEM have been found to complement each other, using the DOS of GO/RGO as the reference. The correlation between the three techniques and the density of states has been discussed in detail. From I - V , the lowest barriers are well correlated with the RGO DOS (activation energy of less than 10meV and the existence of a 0.23eV state/energy barrier). Although TSC helps to map out the distribution of traps with several peaks at 0.19eV, 0.264eV, 0.396eV, 0.593eV and 0.678eV from the GO Fermi level, it is generally not possible to resolve with confidence whether the states accessed are below or above the Fermi level (for simplicity, we have assumed that only electron traps are involved in GO [7]). It is only possible using BHES/BEES. The existence of states with peak energy levels of -0.5 eV, 1.0 eV, 1.26 eV and 1.35 eV were determined, and were found to conform to the GO DOS. In addition, the 1.35 eV state was also detected simultaneously using TSC, exhibiting the synergy between the techniques. However, BEEM does suffer a setback where the collector material presents a lower limit on the barriers/trap levels that are measured, due to the blocking effect of the collector.

To summarize, the lowest barriers were found by I - V , the intermediate barriers by TSC and the entire distribution (including higher barriers) by BEEM. From our results, we are able to confirm/support the findings of Bansal *et al.*, confirming that GO/RGO has a multi-energy bandgap [2]. We also believe that the origin of the transport gap in GO is due to a combination of defects on the graphene plane and metal induced gap states (MIGS).

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Chapter 7 Conclusions

7.1 Summary

This thesis presented a combination of thermally stimulated current (TSC) measurements, current-voltage (I - V) measurements and ballistic electron emission microscopy/spectroscopy (BEEM/S) measurements to understand charge transport in GO/RGO.

TSC measurements on GO devices fabricated using e-beam lithography, and contacted by thermally evaporated top gold contacts revealed the presence of several shallow/deep traps in the GO bandgap. Laser irradiation and thermal heating were employed to evaluate the impact of GO reduction in modifying the trap states and thereby the overall transport. Reduction of GO led to an overall decrease in trap density. However, traps states further away from the Fermi level could not be completely removed. In addition, several new states were found in the GO bandgap close to the Fermi level after reduction. The decrease in the trap density is counter-intuitive, since a lower density of trap states would imply a reduced level of hopping conduction via these traps states. However, we believe that transport is likely to be controlled by states closer to the Fermi energy level, which have been observed to increase with reduction.

To investigate the dominant charge transport mechanism in GO/RGO, I - V measurements were carried out. While GO remained insulating as expected, the charge transport in RGO was observed to be a combination of tunneling and hopping via localized trap states in the GO bandgap. Temperature/field dependent I - V measurements revealed the presence of several different transport mechanisms in RGO, each dominant in a specific temperature/field regime. Tunneling transport was found to be dominating below 110K (i.e., down to the limit of our experiment, 12K),

hopping transport between 110K-200K and an exponentially-distributed-trap space charge limited current (EDT-SCLC)/Poole-Frenkel (PF) mechanism from 200K-350K. A trap energy of 0.23eV was extracted from the PF field dependence which correlated well with the TSC measurements and the density of states (DOS). A possible reason for the PF field dependence in RGO could be the modification of the Coulombic potential near localized states, which leads to an increase in the tunnel transfer rate between sites. However, we do not discount the possibility of field induced charge detrapping into localized states for hopping conduction. We also wish to point out that the PF field dependence has been observed by several other groups as a general transport phenomenon of disordered semiconductors rather than conventional charge detrapping into delocalized states. At very high fields and low temperatures, Fowler-Nordheim tunneling was observed to be the dominant mechanism, whereas at high fields and high temperatures, we expect a decrease in the hopping activation energy as a result of further RGO reduction. We found the existence of two sets of hopping energies (a hopping energy of the order of a few meV at lower temperatures and a hopping activation energy of the order of about 50 meV at higher temperatures. The lower activation energy is believed to correspond to transport near the Fermi level, while the higher activation energy corresponds to transport away from the Fermi level. The hopping activation energy was shown to reduce with the extent of reduction, thus narrowing the transport gap. The extracted low activation energy of RGO (a few meV) is indicative of an Ohmic contact rather than a Schottky contact.

We find that the spread in the conduction mechanisms in RGO found in the literature is due to more than just processing conditions. GO being an amorphous material with positional disorder, should be treated as a disordered organic material in our opinion. We believe that the large variance in observed optical-gaps/transport-bandgap by

several groups is a manifestation of the several possible combinations of “inter-state” transitions in the “multi-energy” bandgap of GO/RGO. This issue is further complicated by the preparation and processing conditions of GO. Nevertheless, we conclude from our experiments that reduction of GO provides enhanced conduction, through a decrease in the transport gap rather than a decrease in the GO bandgap (i.e., gap between the HOMO and LUMO).

The states in the GO bandgap arise mainly due to the HOMO/LUMO states tailing into the gap. We infer that the oxygen-based functional groups on GO cause discontinuities in the density of states (DOS) of the underlying graphene plane, resulting in a transport gap. In addition, we also believe that metal induced gap states (MIGS) are likely to broaden the DOS and modify charge transport in GO by decreasing the transport gap. From our measurements, it is difficult to quantify the contribution of this effect. Experiments with metals of different work functions, and with different surface electronic states (s versus d, for instance) may help in quantifying this contribution.

Ballistic electron emission microscopy across the Au/GO interface showed a non-homogeneous interface at the nanoscale, with a distribution of electron/hole injection barrier with a mean of 1.0/0.5 eV. We believe that the origin of this inhomogeneity/distribution is due to the various functional groups attached onto the graphene basal plane, although other possibilities such as distribution in the GO thickness could also contribute. We postulate that transport in the vertical direction in the Au/GO/Si BEEM samples is likely due to a resonant tunnelling process, where the incoming ballistic electrons tunnel via a defect state in the GO bandgap instead of conventional “over the barrier” type of transport. The derivative of the BEES spectra are shown to contain information on the various barriers present at the Au/GO interface. We also present repeated spectroscopy at a particular location as a method to

yield higher energy barriers in GO, which correlates well with the barriers found by using the BEES derivative and the GO DOS. In addition, we attribute this phenomenon to charge trapping (i.e., due to finite residence time in GO) at lower energy levels, thereby forcing the injected electrons from subsequent BEES runs, to be transported by resonant tunneling through higher energy states.

The TSC, I - V and BEEM techniques complement each other in giving a consistent and correlated view of transport in GO/RGO. From our results, we support the “multi-energy” bandgap model for GO. Although the transport gap is only of the order of a few meV, transport is severely limited to tunneling and hopping between defects caused by both the functional groups on GO and by those created during GO reduction. For the use of RGO as a channel material, studies on tailoring of states in the GO bandgap to improve channel mobility are required. This would require determination of processing-electronic property correlations. In addition, methods to remove traps further away from the GO Fermi level have to be found. On the other hand, the transport gap has to be sufficiently widened to prevent stray conduction through the GO layer for dielectric applications.

7.2 Recommendations

Although BEEM is a very powerful technique to probe organic interfaces and even single molecules, the lack of a BEEM theory for injection into the organic has kept the field at a standstill. BEEM theory for disordered semiconductors like GO is expected to be even more challenging. We therefore recommend a theoretical study of BEEM across organic/metal and disordered semiconductor/metal interfaces. Next, the BEEM experiment could be repeated with a different collector material, preferably a lower bandgap material than silicon, which will allow carriers with lower energies to be detected. This requires working in ultra-high vacuum (UHV) and at cryogenic

temperatures. However, one has to be mindful of changes to the GO HOMO/LUMO levels arising from the replacement of Si with a new material. In such a case, it would be a good idea to also carry out inverse photoelectron spectroscopy and ultraviolet photoelectron spectroscopy to obtain information on the HOMO/LUMO levels of GO. In addition, one could also carry out a series of BEEM experiments on the Au/RGO interface as a function of the extent of GO reduction.

Another area worth exploring is the fabrication and characterization of devices in the planar/sandwich configuration with dissimilar metals, which selectively favour either hole or electron transport. Such experiments will give a clearer picture on both out-of-plane and in-plane transport properties in GO/RGO. The effect of reducing electrode dimensions in influencing charge carrier injection and transport could also be investigated. In addition, I - V and R - T should be carried out over a larger range of temperatures in order to unravel new transport related phenomena. It will be also interesting to study the effect of the number of layers of GO/RGO in modifying transport properties. Such a study will help to understand the coupling between the layers and transport perpendicular to the graphene plane better.

We believe that the ultimate challenge is to carry out defect engineering on the graphene plane in order to give a specific DOS, and thereby desired transport properties. On the other hand, with advances in scanning probe microscopy and atom manipulation techniques, such a feat may not be too far away.