Measurement of the Electronic Heat Dissipation Channel in Hydrogenated Graphene

Nicholas Hemsworth



Department of Electrical and Computer Engineering McGill University Montréal, Québec, Canada

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Abstract

The electron cooling power in highly-disordered large-area hydrogenated graphene is measured. Millimeter-scale graphene grown by chemical vapour deposition was hydrogenated through the exposure of the surface to atomic hydrogen under ultrahigh vacuum conditions. Electrical transport measurements were performed on hydrogenated graphene samples at temperatures between 300mK and 2K. The electronic cooling power is shown to scale proportionally to the electron temperature to the fourth power and the coupling constant is shown to be on the order of $0.1 \text{mW/K}^4\text{m}^2$. The coupling is shown to be independent of carrier concentration. Preliminary estimates of bolometric figures of merit for hydrogenated graphene operating as a hot electron bolometer are also reported. The optical voltage responsivity is estimated to be $1.5 \times 10^5 \text{V/W}$. This is comparable to existing hot electron bolometers.

Abrégé

La puissance de refroidissement d'électrons dans graphène hydrogénée est mesurée. Graphène aux échelle de millimètres est développée par dépôt chimique en phase vapeur et a été hydrogéné par l'exposition de la surface d'hydrogène atomique dans des conditions d'ultravide. Les mesures de transport électrique ont été fait sur des échantillons de graphène hydrogénées aux températures entre 300 mK et 2 K. Nous avons observé que la puissance de refroidissement d'électronique est proportionnelle à la température des électrons à la quatrième puissance et la constante de couplage est de l'ordre de 0, 1mW/K⁴m². Le couplage est indépendante de la concentration des porteurs de charge. Nous avons fait les estimations préliminaires des chiffres de mérites bolométriques pour le graphène hydrogénée fonctionnant comme un bolomètre aux électrons chauds. La sensibilité de tension réponse de puissance infra-rouge est estimée $1, 5 \times 10^5$ V/W. Ceci est comparable aux bolomètres des électrons chauds existants.

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Chapter 1

Introduction

1.1 Motivation

Infrared radiation resides in the portion of the electromagnetic spectrum that consists of wavelengths longer than those of visible light. The ability to detect infrared radiation is important in a wide variety of applications and industries. This stems from the important fact that all bodies with nonzero temperature emit radiation in this spectrum–a phenomenon known as blackbody radiation. The blackbody emission power is directly proportional to the body's temperature to the fourth power and the emissivity. The emitted power P in Watts is given by the Stefan-Boltzmann equation:

$$P = A\sigma\epsilon T^4,\tag{1.1}$$

where A is the area of the radiating surface, σ is the Stefan-Boltzmann constant which is equal to $5.67 \times 10^{-8} \text{W/m}^2 \text{K}^4$, ϵ is the emissivity, and T is



Fig. 1.1: The electromagnetic spectrum

the temperature in kelvin.

The spectral distribution of the emitted radiation is also dependent on temperature. Bodies with higher temperature will emit more high frequency radiation than bodies with lower temperature. The peak emission wavelength λ_{max} is related to the temperature T of the radiating body through Wien's displacement law. This relation is as follows:

$$\lambda_{max} = \frac{2.8977 \times 10^{-3}}{T} (\text{Km}) \tag{1.2}$$

At room temperatures, the majority of the emitted radiation resides in the infrared spectrum. The ability to detect this emitted radiation allows for the temperature of objects to be sensed from a distance or simply for the identification of objects which are hot compared to their environment. As such, infrared detectors have found applications in military, medical diagnostics, control systems, telecommunications, astronomy, and verification of chemical and biological agents. These diverse applications have motivated continued work in the field of infrared sensors. In particular infrared sensing has applications in:

- **Thermography** The practice of remotely monitoring an object's temperature. Thermography has found uses in nondestructive testing of buildings and in medical applications.
- **Night vision** In situations where visibility is poor due to limited visible light, the ability to sense blackbody radiation in the infrared range can allow for the detection of objects. This is particularly useful in military or rescue operations.
- **Astronomy** Infrared sensing allows for the detection of stellar objects that are not hot enough to emit visible radiation. The ability to detect cold objects allows for the detection of gas clouds and protostars.
- **Communications** The radiation wavelengths of choice for optical communication lie in the infrared range.
- **Infrared Spectroscopy** The molecular structure of a given chemical compound gives rise to a very specific infrared absorption spectrum. Infrared spectroscopy is the practice of probing a material's absorption spectrum for the identification of various chemical species.

The two primary classes of infrared detectors are photon detectors and thermal detectors. Photon detectors rely on photoconduction in order to detect radiation. Thermal detectors rely on an induced temperature change to detect radiation. One particular type of thermal detector called a bolometer relies on an induced temperature change to produce a change in resistance which can then be measured by external circuitry. The operating principles of bolometers are discussed in chapter 2.

Recent studies on hot electrons in graphene have shown that graphene is a promising candidate material for bolometery. The particular type of bolometer envisioned for graphene is called a hot electron bolometer (HEB). This device uses the electrons within a material as the absorbing medium. A hot electron bolometer would exploit the relatively weak electron-phonon coupling in graphene along with the small electronic heat capacity in order to make a very sensitive and fast thermal detector. A drawback associated with using graphene though is the very weak temperature dependence of the material's resistance over a very wide range of temperatures. In the last few years, multiple graphene-based bolometers have been reported. One such device was constructed from bilayer graphene. The inferred noise-equivalent power for this device was very low $(33 \text{fW}/\sqrt{\text{Hz}} \text{ at } 5\text{K})$ and the inferred response time (0.2ns at 5K) is superior to commercial silicon bolometers and transition edge sensors by three to five orders of magnitude at similar temperatures [2]. A second device made from disordered graphene has been reported. This device has a measured electrical responsivity of $6 \times 10^6 V/W$ at 1.5K and an inferred optical noise-equivalent power of $44 \text{fW}/\sqrt{\text{Hz}}$ [3]. Due to the promise of recent devices, further investigation into graphene as a potential material for bolometry is of scientific interest. In this work, we consider heavily-disordered hydrogenated graphene as a candidate material for hot-electron bolometers.

1.2 Hydrogenated Graphene

The weak temperature dependence of the resistance in graphene limits the suitability of the material for use in bolometers. This necessitates the addition of disorder. The resistance of disordered materials typically depends very strongly on temperature. One means of inducing disorder is through the random hydrogenation of the surface of graphene to produce hydrogenated graphene.

Hydrogenated graphene is pristine graphene that has had atomic hydrogen covalently bonded to its surface. This material was first reported on in 2009 where the discovery was interpreted as evidence for graphane–graphene that has had its surface completely covered with hydrogen [4]. Hydrogenation transforms graphene from a highly conductive semimetal into an insulator. Partial hydrogenation has been shown to open a bandgap in graphene. This fact has been verified with scanning tunneling microscopy (STM) and angle-resolved photoemission spectroscopy (ARPES) measurements [5]. The hexagonal lattice structure is retained with a reduced lattice constant. This process has been shown to be completely reversible: annealing can be used to completely restore the semimetallic state, the original lattice constant, and the quantum hall effect [4].

This material is expected to be of great interest in bolometry as it will allow the weak electron-phonon coupling and small electronic heat capacity of graphene to be harnessed without being impeded by the weak temperature



Fig. 1.2: Hydrogenated graphene

dependence of the resistance.

1.3 Thesis Contributions

We have performed electrical transport measurements on large-area hydrogenated graphene. The results of the electrical transport measurements were analyzed to determine the dominant electronic heat dissipation mechanism and the parameters critical to hot-electron bolometers such as thermal resistance and the temperature coefficient of resistance. The graphene was grown by chemical vapour deposition at L'Université de Québec à Montréal. The graphene was transferred to the target substrate using the cleanroom facilities at McGill and the hydrogenation was performed using the facilities over at L'Université de Montréal. Contributions of our work to the field of 2D materials and bolometry include:

1. Determination of the electron temperature dependence on the input power in highly-disordered large-area hydrogenated graphene. The coupling strength was found to be on the order of $0.1 \text{mW/K}^4\text{m}^2$ and the exponent was found to be 4.

- 2. Evidence suggesting that the dominant electronic heat dissipation mechanism in hydrogenated graphene consists of phonon emission into the substrate.
- 3. Determination of the thermal resistance, the temperature coefficient of resistance, and other preliminary bolometric parameters for hydrogenated graphene serving as a hot electron bolometer.

This thesis will adopt the following the structure:

Chapter 2:

The basic operating principles of bolometers will be introduced followed by an overview of the important figures of merit associated with said devices. The various types of bolometers as well as the typical figures of merit associated with each type will be covered.

Chapter 3:

An introduction to hot electron effects in 2D materials will be presented. The basic physics of hot electrons will be covered as well as the possible electronic heat dissipation mechanisms.

Chapter 4:

The details through which the graphene was prepared will be outlined. The structure of hydrogenated graphene will be discussed and the exact process through which graphene in this project was hydrogenated is detailed. The physics of Raman spectroscopy is introduced and its utility of quantifying the level of disorder in hydrogenated graphene is justified. The Raman data for the measured samples is presented.

Chapter 5:

Electrical transport theories are introduced. The experimental setup used to conduct electrical transport experiments is detailed and the transport results are presented. The electron temperature vs applied power and temperature is extracted and these relations are used to quantify the electron coupling to the environment. Preliminary bolometric figures of merit are presented.

Chapter 2

Bolometers

This chapter will review the operating principles of bolometers and provide an overview of the main types of bolometers. This will serve to further motivate the project and introduce the particular type of bolometer envisioned for hdyrogenated graphene. This section will serve as a brief introduction to the topic. Refer to Rogalski for a more detailed discussion [6].

2.1 Operating Principles

Bolometers are a particular type of thermal detector that are commonly used for sensing radiation in the infrared range. They consist of an absorbing medium that is thermally connected to the environment through a thermal link. Radiation is absorbed by the absorbing medium which raises the medium's temperature above that of the environment. An equilibrium temperature is established once the rate of energy entering the absorbing body is equal to the energy leaving the absorbing body through the thermal link. The resulting temperature is sensed through the use of a temperature transducer (a thermometer). Bolometers in which the absorbing medium and the temperature transducer are the same are called monolithic. Bolometers in which they are different are called composite.

The simplest thermal models for bolometers consist solely of a thermal capacitance which models the heat capacity of the absorbing medium and a thermal resistance which models the thermal impedance between the absorbing body and the environment. The thermal model is shown in Figure 2.1.



Fig. 2.1: Thermal model for a generalized bolometer

The equilibrium temperature of the absorbing medium for a given incident infrared (IR) optical power can be expressed in terms of the heat capacity and the thermal resistance as follows:

$$\Delta T = \frac{\epsilon \Phi_0 R_{th}}{(1 + \omega^2 R_{th}^2 C_{th}^2)^{\frac{1}{2}}},$$
(2.1)

where ϵ is the emissivity of the absorbing body, Φ_0 is the incident IR optical power, R_{th} is the thermal resistance, ω is the angular frequency at which the IR optical power is modulated, and C_{th} is the heat capacity.

The simple thermal model gives rise to a characteristic thermal time constant defined as:

$$\tau = \frac{C_{th}}{G_{th}} = C_{th} R_{th} \tag{2.2}$$

The induced temperature change of the absorbing body can be related to a change in the electrical output signal through the expression:

$$\Delta V = K \Delta T, \tag{2.3}$$

where the parameter K encapsulates the temperature dependence of the electrical read out system and is a function of both temperature and input power.

The temperature of the absorbing medium is read out resistively. The temperature dependence of the thermometer is typically characterized by the temperature coefficient of resistance which is given by:

$$\alpha = \frac{1}{R} \frac{dR}{dT} \tag{2.4}$$

In the case of a constant-current biased bolometer, the parameter K will be equal to $IR\alpha$ and the change in the output voltage can be expressed as:

$$\Delta V = IR\alpha\Delta T \tag{2.5}$$

2.2 Figures of Merit

The performance of bolometers is typically assessed through four figures of merit: the responsivity, the noise equivalent power, the detectivity, and the response time.

2.2.1 Responsivity

The responsivity is a measure of how large of an electrical signal is produced for a given amount of optical input power. The voltage responsivity is defined as the amplitude of the electrical output signal to the amplitude of the input radiation power. Voltage responsivity in units of (V/W) is given by the following expression:

$$R_v = \frac{IR\alpha\epsilon R_{th}}{(1+\omega^2\tau^2)^{\frac{1}{2}}}$$
(2.6)

2.2.2 Noise Equivalent Power

The noise equivalent power is the input power required to produce an output signal with a signal-to-noise ratio of 1 over a 1Hz bandwidth. The value of the noise equivalent power depends largely on the dominant noise mechanism within the detector. There are four main sources of noise: Johnson noise, flicker noise, background fluctuation noise, and thermal fluctuation noise. Thermal detectors are typically limited by thermal fluctuation noise [7]. Should a detector be limited by thermal fluctuation noise the noise equivalent power will take the form:

$$NEP = \sqrt{\frac{16A\sigma K_b T^5}{\epsilon}},\tag{2.7}$$

where A is the area of the detector, σ is the Stefan-Boltzmann constant, K_b is the Boltzmann constant, T is the temperature, and ϵ is the emissivity of the detector active area [6].

2.2.3 Detectivity

The detectivity is the reciprocal of the noise equivalent power.

$$D = \frac{1}{NEP} \tag{2.8}$$

A useful variation of this metric is the specific detectivity which includes information concerning the area of the absorber of the device. It is defined as follows:

$$D^* = \frac{\sqrt{A\Delta f}}{NEP},\tag{2.9}$$

where A is the area of the absorbing medium and Δf is the detector bandwidth. Values for D^* are typically expressed in units of cmHz⁻¹W⁻¹ also known as the Jones.

2.2.4 Response Time

The speed of a detector is characterised through the response time. This metric can be determined from the thermal resistance and the heat capacity using equation 2.2.

2.3 Types of Bolometers

2.3.1 Metal Bolometers

Metal bolometers were the first bolometers to be used with the first device being reported in 1881 [8]. These devices use metal as the absorbing medium and can operate at room temperature. Typically, the metal is kept very thin to keep the heat capacity down in order to improve the responsivity. The typical thickness of the metal film is between 10 and 50 nm. Metal bolometers typically exhibit positive temperature coefficient of resistance values between 0.3 and 0.4 %/K. Responsivities have been reported of 4 V/W and with a response time of 16 milliseconds. These devices are limited by Johnson noise and have noise equivalent powers on the order of 10^{-9} W [9].

2.3.2 Thermistor Bolometers

Thermistor bolometers are very similar to metal bolometers in terms of how the devices operate but with a different material for the absorbing medium. Thermistor bolometers utilize a thin flake of semiconductor material as the absorbing medium. Typically mixtures of oxides of manganese, nickel, and cobalt are used. These materials have negative temperature coefficient of resistance values around 4 %/K—much higher than those of metal bolometers. These detectors offer good responsivity for wavelengths between 1 and 15 μ m and exhibit response times on the order of several milliseconds [6].

2.3.3 Semiconductor Bolometers

Semiconductor bolometers exploit the strong temperature dependence of the electrical resistance of doped semiconductors at low temperatures to achieve very high levels of sensitivity. The sensitivity of semiconductor bolometers can be orders of magnitude higher than that of room temperature devices and are the detectors of choice for many infrared and submillimiter applications [6]. Conduction at operating temperatures in semiconductor bolometers occurs through variable range hopping. Variable range hopping is very sensitive to the exact doping profile of the semiconductor which places very stringent demands on uniformity of the device. For this reason, neutron transmutation doped (NTD) germanium devices are very popular. A typical NTD Ge device will consist of a cube with sides between 0.2 and 0.6 mm and ion implanted contacts on either side [10]. Composite semiconductor bolometers have been reported operating at temperatures between 100mK and 3K with voltage responsivities on the order of $10^7 V/W$. Response times for these devices are typically on the order of milliseconds and the noise equivalent powers are on the order of 10^{-15} to 10^{-17} WHz^{-1/2} [7].

2.3.4 Micromachined Room Temperature Bolometers

Micromachined bolometers are devices that are fabricated on the surface of an Si wafer through conventional photolithography techniques. The first such device consisted of a thin Si slab that was supported by thin legs on the surface of an Si wafer forming what is referred to as a microbridge. Ion implantation was used to give the resistance of the absorbing body a strong temperature dependence to allow for temperature read-out [11]. The original device operated at cryogenic temperatures but more modern micromachined devices are capable of operating at room temperature. Common materials used for the absorbing medium of room temperature sensors are vanadium oxide, amorphous silicon, and silicon diodes. Vanadium oxide films that are used possess temperature coefficients of resistance of roughly 2%/K to 3%/K at room temperature [12].

2.3.5 Superconducting Bolometers

Superconducting bolometers utilize the very steep change in resistance that occurs when a superconducting material is heated above its superconducting transition temperature (T_c) . Below the material's T_c , the electrons at the Fermi energy condense into a coherent state consisting of Cooper pairs [6]. Superconducting bolometers are kept at a temperature which is at the midpoint between the superconducting state and the normal state. This allows small changes in temperature (≈ 1 mK) to produce very large changes in resistance. The first generation of superconducting bolometers used conventional superconducting materials (low T_c superconductors) like Al, Ta, Sn, Nb, or NbN which required these detectors to be operated around liquid helium temperatures. These detectors exhibited comparable performance to semiconductor bolometers that were also under development at the time and thus saw limited use [13]. These detectors exhibit responsivities on the order of 10⁴ to 10⁶ V/W and possess time constants in either the millisecond or microsecond range. The discovery of high temperature superconductors in the late twentieth century introduced a new generation of superconducting bolometers. These materials which are known as the oxygen-deficient perovskites can possess superconducting transition temperatures as high as 135K but typically around liquid nitrogen temperatures. The most common materials for high- T_c superconducting bolometers are compounds formed from Yttrium, Barium, Oxygen, and Copper [13]. Different critical temperatures can be achieved by tuning the fractions of the individual elements within the material. The abruptness of the transition between superconducting behaviour and normal behaviour can also be tuned by varying the composition even allowing the transition to occur over 30K [14]. High- T_c superconducting transition edge bolometers typically operate around 80 to 90K and are capable of achieving voltage responsivities on the order of 10^2 to 10^3 V/W, time constants on the order of microseconds, and noise-equivalent powers on the order of $10^{-12}W/\sqrt{Hz}$ [6].

2.3.6 Hot Electron Bolometers

Another type of bolometer is the hot electron bolometer. In this device, the incident radiation is absorbed directly by the electrons within a material and the coupling of the electrons to the environment constitutes the thermal link.

These devices operate at cryogenic temperatures and exploit the fact that at low temperatures electrons are typically very poorly coupled to the environment resulting in a very large thermal impedance. Incident optical energy will be absorbed by the electrons which will cause their temperature to increase above that of the heat sink. The electrons will interact with other electrons with sufficient frequency such that they will thermalize in this excited state and acquire a well-defined temperature. Steady-state will be established once the rate at which energy is absorbed and the rate at which energy is dissipated are equal. Hot electron bolometers can be classified depending on which dominant mechanism allows the electrons to dissipate energy with the two primary mechanisms being electron-phonon coupling or electron diffusion into the contacts [6]. In a diffusion-cooled device, electrons become thermally excited and eventually diffuse to the electrical contacts. For diffusion cooling to be the dominant relaxation mechanism, the microbridge must be very short with the upper limit on length set by:

$$L_{max} = 2\sqrt{D_e \tau_{ee}},\tag{2.10}$$

where D_e is the electron diffusivity and τ_{ee} is electron-electron interaction time. In a phonon-cooled device, the electrons become thermally excited and eventually release their energy as phonons into the substrate. The electronelectron interaction time τ_{ee} and the time required for a phonon to escape into the substrate-the phonon escape time- τ_{esc} must both be much shorter than the electron-phonon interaction time τ_{e-ph} . This allows both the electrons and the substrate to have well-defined temperatures [6].

Hot electron bolometers were originally conceived as a variation on superconducting transition-edge bolometers [15] [16]. The first such devices were designed to serve as heterodyne mixers since their fast response times as well as their low mixer noise temperatures allowed for their use in the intermediate infrared range (1 GHz to 10 GHz) [17].

Class	Material	T(K)	Area (mm^2)	$R_v~({ m V/W})$	au (ms)	NEP ($WHz^{-1/2}$)	Comments
Thermistor	Mixture of oxides	297	14.1	41	4.56	1×10^{-8}	[18]
	of Mn, Ni, and Co						
Semiconductor	doped Si	1.6	40	I	40	4.5×10^{-15}	Composite [7]
Semiconductor	doped Ge	0.97	16	$1.3 imes 10^7$	20	$1.6 imes 10^{-15}$	Composite [7]
Semiconductor	NTD Ge	0.3	4	$8.7 imes 10^7$	11	$1 imes 10^{-16}$	Composite [7]
Micromachined	Si	0.35	0.01×0.075	$3.2 imes 10^7$	17	$< 6.1 \times 10^{-16}$	[11]
Superconducting	Sn	3.05	3×2	850	10	$7 imes 10^{-13}$	[9]
Superconducting	Al	1.27	4×4	3.5×10^4	80	$7 imes 10^{-13}$	[9]
HTSB	YBaCuO	20	1×1	0.1	4×10^{-4}	4×10^{-13}	[9]
HTSB	YBaCuO	86	1×1	40	13	$1.5 imes 10^{-9}$	[9]
Hot Electron	Bilayer graphene	5.16	1×10^{-4}	$2 imes 10^5$	$2.5 imes 10^{-7}$	3.3×10^{-14}	[2]
Hot Electron	Disordered graphene	1.5	1.25×10^{-5}	$1.6 imes 10^5$	I	1.2×10^{-15}	[3]

In this chapter, an overview of the basic operating principles of bolometers has been presented. In addition, the various types of bolometers have been discussed. In this work, a hot electron bolometer with hydrogenated graphene as the active medium will be presented.

Chapter 3

Hot Electrons in 2D Materials

In this chapter, the physics of hot electrons in two-dimensional materials will be reviewed. The first section will discuss the conditions required for electrons to become "hot". The second section will discuss the various thermal channels through which hot electrons can dissipate heat.

3.1 Hot Electron Theory

Hot electrons are electrons that possess a well-defined temperature above that of the lattice. Electrons can become "hot" through either Joule heating or optical heating. For the electrons to establish a well-defined temperature, electron-electron interactions must be sufficiently frequent and electronphonon and electron-photon interactions must be sufficiently weak-this ensures that the electrons have time to attain a proper thermal distribution in between relaxation events [19]. It has been shown theoretically that the electrons do in fact adopt a thermal distribution when excited and that this temperature can be probed directly through the Nyquist voltage noise [20]. Hot electron effects in semiconductors have been known about for quite some with the first device relying on such effects being made in 1960 [21]. Hot electron effects in metals took more time to be fully understood as these effects are very weak at room temperature due in part to their high carrier density. Carrier relaxation in graphene was initially studied using optical techniques such as ultrafast pump-probe spectroscopy and ultrafast optical differential transmission spectroscopy [22] [23]. Optically excited electrons thermalize in 150 fs due to the rapid electron-electron interactions. This thermal distribution will then cool back towards the lattice temperature through the initial emission of two high energy optical phonons (194 and 330 meV) and then through coupling to acoustic phonons. The cooling of the electrons through coupling to acoustic phonons has been shown to occur on a timescale of 1 ps for highly doped layers and between 4-11 ps for undoped layers [23].

3.2 Heat Dissipation Mechanisms

3.2.1 Electron-Phonon Coupling

Thermally excited electrons can dissipate energy by coupling to phonons within the material. For a material with two atoms in the unit cell like graphene, both acoustic and optical phonons are available for coupling. Whether the electron couples to an acoustic or an optical phonon depends on both the electronic temperature and the carrier density. Initial theoretical works on graphene have shown that electrons couple predominantly to optical phonons at temperatures above 200K for carrier densities in the range of 10^{11} - 10^{13} cm⁻² and that coupling to acoustic phonons is the dominant mechanism at low temperatures [24]. Electronic energy loss to acoustic phonons is typically described by the power law:

$$P = \Sigma (T_e^\beta - T_s^\beta), \tag{3.1}$$

where P is the power per unit area, Σ represents the coupling strength, T_e is the electronic temperature, T_s is the lattice temperature, and β is the exponent associated with the coupling. This general relation has been shown to apply to a wide range of materials. In bulk materials, the value of β has been shown to be equal to 6 in neutron transmutation doped germanium and 5 in NbSi films [25] [26]. In graphene, theoretical and experimental works have shown that the value of β is 4 [27] [28]. The coupling coefficient Σ depends on carrier concentration and values of 2 and $0.42 \text{ mW/m}^2\text{K}^4$ have been measured [28]. Electron-phonon coupling has been shown to be significantly enhanced in the presence of disorder. Defects in the graphene allow for a new interaction to contribute to electronic cooling called supercollisions. Supercollisions are three-body interactions involving an electron, a phonon, and a defect. The addition of defects allows for arbitrarily large phonon recoil momentum values which allows for significantly more energy transfer per collision. The presence of this additional electron-phonon coupling mechanism results in a shift of the β value from the value of 4 associated with pristing graphene to a value of 3 [29]. This β value of 3 has been confirmed through multiple theoretical and experimental works [30][31][32]. The coupling coefficient Σ was measured to be on the order of $1 \text{ W/m}^2\text{K}^3$ with a linear dependence on carrier density [32]. This heat dissipation mechanism is depicted in figure 3.1 a).

3.2.2 Electronic Heat Diffusion

Hot electrons can also dissipate energy through thermal diffusion into the electrical contacts. The contribution to the cooling of hot carriers through electronic heat diffusion can be estimated through the Wiedemann-Franz law. The Wiedemann-Franz law relates the electrical conductivity to the electronic contribution to thermal conductivity. This relation takes the form:

$$\frac{\kappa}{\sigma} = \mathcal{L}T,\tag{3.2}$$

where κ is the thermal conductivity, σ is the electrical conductivity, \mathcal{L} is the Lorenz number, and T is the temperature in kelvin. The Lorenz number is equal to $(\pi^2/3)(k_b/e)^2$ where e is the electron charge and k_b is the Boltzmann constant.

When subjected to electrical or optical heating in the case where other cooling channels are negligible, the situation reduces to a one-dimensional heat transfer problem. Power is assumed to be uniformly deposited throughout the sample and the temperature is assumed to be uniform in the direction orthogonal to the channel. The contacts are typically assumed to be at the same temperature as the heat bath due to the frequent electron-phonon interactions in metals at most temperatures.

The temperature distribution is pseudoparabolic at low bias and tends towards a uniform electron temperature at high bias [33][28]. Under low bias conditions, the electron temperature is distributed as follows:

$$T_e = 4\Delta T_{mid}x(1-x) \tag{3.3}$$

and the electron temperature in the middle of the sample is given by:

$$\Delta T_{mid} = \sqrt{\frac{RP}{2L} + T_s^2} - T_s, \qquad (3.4)$$

where x is the normalized distance from one end of the device to the other, R is the sample resistance, P is the input power, and T_s is the substrate temperature [34].

The heat balance equation when only electronic heat diffusion need be considered is:

$$P\frac{x}{L} = w\kappa t \frac{dT_e}{dx},\tag{3.5}$$

where P is the input power, L is the sample length, w is the sample width, t is the sample thickness, and κ is the thermal conductivity. The solution of this differential equation is as follows [34]:

$$P = 4\mathcal{L}\frac{\Delta T_{mid} + 2T_s}{R}\Delta T_{mid}.$$
(3.6)

This heat dissipation mechanism is depicted in figure 3.1 b).

This thermal channel can be suppressed through the use of superconducting contacts [34]. When a metal is in a superconducting state, electrons are paired together to form Cooper pairs. A Cooper pair is a low energy state consisting of two electrons that carries zero entropy and, as a result, is incapable of transporting heat. For electrons to disassociate from this pair, sufficient energy is required to excite the electrons above the superconducting energy gap ΔE . The electronic contribution to thermal conductivity κ_e in a superconducting metal is proportional to:

$$\kappa_e \propto T e^{-\Delta E/k_b T} \tag{3.7}$$

where $\Delta E = 1.76k_bT_c$ for most elemental superconductors. This contribution decreases rapidly with temperature. This allows for superconducting contacts to be used to suppress the electronic heat diffusion cooling channel [35].

3.2.3 Blackbody Photon Emission

Thermally excited electrons will also release energy in the form of blackbody radiation. Blackbody radiation is described through the Stefan-Botlzmann law which is typically written as:

$$J_{\nu} = \sigma T^4 = \left(\frac{\pi^2 k_b^4}{60\hbar^3 c^2}\right) T^4,$$
(3.8)

where J_{ν} is the radiative flux density, σ is the Stefan-Boltzmann constant, and T is the temperature. For total power radiated, the area A and the emissivity ϵ must be taken into account. The total power radiated is given by:

$$P = A\epsilon\sigma T^4 = A\epsilon \left(\frac{\pi^2 k_b^4}{60\hbar^3 c^2}\right) T^4.$$
(3.9)

In a system where the thermal relaxation of hot electrons was dominated

by electron-photon coupling, electrons would initially warm when subjected to an external radiation source. As the electrons would warm, they would emit increasingly large amounts of blackbody radiation. The amount of emitted energy would increase until the incident energy and the emitted energy would be equal at which point steady-state would be attained. This heat dissipation mechanism is depicted in figure 3.1 c).

3.2.4 Blackbody Phonon Emission

Electrons in a 2D system can also couple to 3D phonons in the substrate or surrounding medium. This particular cooling mechanism has been studied in two-dimensional electron gases (2DEGs) formed at heterojunctions. In low disorder samples where the electrons are in plane wave states, it has been shown that the power dissipation will take the form:

$$P \propto T_e^{d+2},\tag{3.10}$$

where P is the incident power, T_e is the electron temperature, and d is the dimensionality of space seen by the phonons. This power scaling can be justified using phase space arguments. The T_e^{d-1} factor stems from the energy scaling of the phonon density of states. The remaining factors of T_e can be attributed to the statically screened phonon matrix element, the average energy k_bT carried away by an emitted phonon, and the number of excited electrons that are available to emit a phonon [36].

The power dissipated by a 2DEG into a 3D material through phonon emission will scale proportionally to T^5 . It has been shown that, in the presence of
strong disorder or high magnetic field, the power law in this case changes and the power dissipated through phonon emission will now scale proportionally to T_e^4 with a dramatic enhancement to the overall emission rate. The relation between emitted power and electron temperature in the presence of disorder or high magnetic field has been shown theoretically to be equal to [36]:

$$P = \frac{e^2}{h\sigma_{xx}} 6.75 \times 10^{-2} \left(\frac{T_e}{1\text{K}}\right)^4 \frac{\text{W}}{\text{m}^2}$$
(3.11)

in a GaAs/AlGaAs heterostructure. This expression was derived using the standard Fermi's Golden Rule expression for the rate of phonon emission. This expression was found to be in good agreement with experimental results [36]. This heat dissipation mechanism is depicted in figure 3.1 d).

Blackbody phonon emission has the same temperature scaling as phonon emission across an interface between two materials with differing acoustic impedances. The same temperature scaling can be attributed to the temperature scaling of the energy density of an acoustic phonon gas. The energy density scales with temperature to the fourth power and thus an acoustic phonon gas emits energy from a surface or interface with the same temperature dependence. The acoustic mismatch between the two materials gives rise to a thermal resistance which is referred to as Kapitza resistance. Kapitza resistance was originally studied in the context of heat transfer between liquid helium and a solid. Thermal power emission from helium into a solid limited by Kapitza resistance will take the form:

$$P = A\left(\frac{\rho_h v_h}{\rho_s v_s}\right) \left(\frac{\pi^2 k_b^4}{30\hbar^3 v_s^2}\right) T^4$$
(3.12)

where ρ is the density, v is the phonon velocity, and the subscripts h and s are used to denote helium and solid respectively. Such an expression is characteristic of thermal power transfer across an interface where an acoustic impedance ρv mismatch is present [35].

In this chapter, the theory of hot electrons was introduced and various electronic heat dissipation channels were presented. The thermal models associated with these heat dissipation channels will be used to identify the dominant heat dissipation channel in hydrogenated graphene and extract relevant thermal properties.



Fig. 3.1: Diagrams of the four heat dissipation channels for hot electrons in graphene: a) depicts electron-phonon coupling, b) depicts electronic heat diffusion, c) depicts blackbody photon emission, and d) depicts phonon emission into the substrate.

Chapter 4

Material Synthesis and Characterization

In this chapter, the details of the fabrication process that was used in this work will be presented. The first section will discuss the hydrogenation process that was used. The second section will begin with an introduction to Raman spectroscopy before presenting the specific results that were obtained for the devices used in this work.

The graphene used in this work was large-area graphene that had been grown by chemical vapour deposition on copper. The graphene was then transferred to an oxidized silicon substrate. The substrate was then cleaved down to the desired geometry. The samples used in this work were roughly 2mm by 4mm in dimensions. Indium contacts were deposited on the surface to allow for two-point resistance measurements. Indium was selected as it superconducts at 3.4K. This allows the diffusive cooling channel through the contacts to be suppressed.

A total of 13 devices were fabricated of which 3 were selected for electrical transport measurements and characterization by Raman spectroscopy.

4.1 Hydrogenation

The hydrogenation process took place in an ultra-high vacuum environment at room temperature. The sample was initially annealed for fifteen minutes at $\approx 473K$. This ensured that the presence of adsorbates on the surface was minimized. The sample was then exposed to an atomic hydrogen beam for durations between 3 and 10 minutes at a pressure of $\approx 1 \times 10^{-5}$ torr. The atomic hydrogen was produced by thermally cracking molecular hydrogen with a white-hot tungsten capillary. The tungsten capillary, which is heated by electron bombardment, reaches temperatures of 2000K. This has been shown to completely disassociate molecular hydrogen [37]. The incident atomic hydrogen will bond covalently to the surface. Exposure to the hydrogen beam has been shown to increase the two-point resistance of the sample exponentially over time. This increase in the sample resistance is due to the increased levels of point defects that strongly scatter electrons. Increasing the level of disorder increases the frequency with which collisions occur and the extent to which electrons are localized. The defect spacing is such that the electrons are spatially localized and conduction has been shown qualitatively to occur through a conduction mechanism known as variable-range hopping. In this conduction regime, electrons hop from localized state to localized state. This hydrogenation process has been previously demonstrated by our group with the same

experimental setup [38] [39].

4.2 Raman Spectroscopy

The degree of hydrogenation was independently verified using Raman spectroscopy. Raman spectroscopy is a particularly useful means of measuring the degree to which the translational symmetry associated with the graphene crystal lattice is broken. This breaking of the translational symmetry can occur through the addition of point defects—such as hydrogen that has been covalently bonded to the surface—or line defects—such as crystal grain boundaries.

Raman scattering is an inelastic scattering process where an incident photon creates or absorbs a phonon before being reemitted from the material as a photon with a greater or lesser energy than the original photon. The particular phonon modes that are probed through this technique are the optical phonon modes. This allows for Raman scattering to serve as a probe of the crystal's unit cell structure. The in-plane stretching of the carbon-carbon bond gives rise to both the in-plane transverse optical (iTO) and the longitudinal optical (LO) phonon branches. These phonon modes result in a specific Raman absorption band known as the G-band which is present at around 1580 cm^{-1} . The G-band is a characteristic of all sp^2 carbon structures and can be seen in graphene, carbon nanotubes, fullerenes, and even graphite. The process which gives rise to the G-band in the raman spectra is shown pictorially in k-space in figure 4.1.

The carbon-carbon sp^2 bond also gives rise to higher-order Raman processes where multiple phonons may be emitted. An important higher-order process is the second-order two-phonon process. This process is responsible for the higher-frequency feature in the Raman spectrum known as the G'-band. The G'-band appears in the frequency range 2500-2800 cm⁻¹ and is notable for having a strong frequency dependence on the laser excitation energy. The G'-band is a useful probe for graphene–easily allowing for the differentiation of single-layer and multi-layer graphene. The Raman spectra for graphene and graphite are shown in figure 4.2.



Fig. 4.1: K-space diagrams for common Raman processes in graphene [40].

In the presence of broken translational symmetry new features become visible in the Raman spectra. The presence of such defects results in two new sharp peaks in the Raman spectra. These two new peaks are dispersive (similar to the G'-band) and are thus dependent on the excitation energy. When an excitation energy of 2.41 eV is used, these peaks appear at 1345 cm⁻¹ and 1626 cm⁻¹. These peaks are referred to as the D and the D'-bands respectively. The evolution of these peaks under increasing levels of disorder can be seen in figure 4.3. The Raman processes that result in the various peaks are shown in figure 4.1.



Fig. 4.2: The Raman spectra for graphene and graphite. [41].

The relative intensity of these disorder-induced features is important for quantifying the level of disorder in the system. The quantity of interest is the ratio of the peak intensity of the D-band (1345 cm⁻¹) to the peak intensity of the G-band (1585 cm⁻¹). This is referred to as the I_D/I_G ratio. When used to quantity the level of disorder in the presence of point defects, this ratio can be used to determine the mean defect spacing (L_D) . This is based on the assumption that point defects are the dominant source of Raman scattering at the D-peak. The I_D/I_G ratio has a nonmonotonic dependence on L_D . The I_D/I_G ratio will increase as L_D decreases until about ≈ 3.5 nm at which point I_D/I_G will decrease sharply as L_D is decreased further. The initial increase in



Fig. 4.3: Left) The evolution of the Raman spectra for graphene under increasing levels of disorder. The disorder is induced here through argon ion bombardment and consists of vacancy sites in the graphene lattice. Right) The dependence of the I_D/I_G ratio on mean defect spacing for point defects [1].

the I_D/I_G ratio with decreasing defect spacing is due to an increase in the area that can contribute to scattering-this will strengthen the D-peak. As the defect spacing is further decreased, the D-peak will reach a maximum. This is due to the fact that the activated regions start to overlap and eventually saturate. A further decrease in the mean defect spacing will result in a decrease in the intensity of the D-peak as the structurally disordered areas begin to dominate the material's surface. An empirical model has been proposed that allows for the mean defect spacing to be calculated from the I_D/I_G ratio [1]. The dependence of the I_D/I_G ratio on L_D is shown in figure 4.3.

In this work, the I_D/I_G ratio was used to quantify the level of electronic disorder in each of the measured samples.

Raman spectroscopy was performed on all three devices whose transport properties were investigated. Raman spectroscopy was performed using a Bruker Senterra Raman Microscope. The pump laser operated at a wavelength of 532nm with an incident power of 20mW. A 40x objective was used for the pump laser. A comparison of the spectra obtained for devices D1 and D3 is shown in figure 4.4. The spectrum of D1 is representative of the spectra typically obtained for hydrogenated graphene and the spectrum of D3 is representative of the spectra typically obtained for pristine graphene grown by CVD. The strong enhancement of the D peak upon hydrogenation suggests a partial breakdown of the translational symmetry in the lattice. Raman was performed at five different points for each sample. The average I_D/I_G ratios and the standard deviation associated with these ratios for all three devices are displayed in table 4.1.

Table 4.1: Raman parameters for the three measured devices. The twopoint resistance of each device at 300mK and the mean defect spacing are also included.

Device	$R_{2pt} (k\Omega) (300 \text{mK})$	I_D/I_G	I_D/I_G st dev	$L_d (\mathrm{nm})$
D1	53	2.4	0.15	6
D3	8.9	0.40	0.11	17
D5	721	2.1	0.65	2

This chapter briefly introduced the science associated with both hydrogenation and Raman spectroscopy and discussed the specifics of how samples in this work were prepared. The I_D/I_G values obtained from Raman spectroscopy for the different devices will serve as an independent measure of electronic disorder and will allow for defect density to be correlated with electronic properties. The thermal properties of the different devices is expected to vary solely with electronic disorder.



Fig. 4.4: A comparison of the Raman spectra obtained for D1 and D3. The pumping was done with a 532nm laser.

Chapter 5

Electrical and Thermal Characterization

This chapter will discuss the electrical transport measurements that were performed in this work and the procedure through which thermal transport properties were extracted. The first section will introduce two electrical transport models that could potentially give rise to a nonlinear IV curve. The exact details of the electrical transport measurements that were performed in this work are then covered. The second section will detail the method through which the thermal properties were extracted from the electrical transport measurements and report all values for the devices measured in this work. The third section will provide estimates for bolometric figures of merit should hydrogenated graphene be used as the absorbing medium in such a device.

5.1 Electron Transport

The electron transport experiments will characterize the dependence of the 2-point resistance on input power and temperature over a given range of gate voltage. Three devices were measured each with a different level of hydrogenation. The level of hydrogenation was quantified through Raman spectroscopy as was discussed in the previous chapter.

The temperature dependence of the resistance in such a disordered material at low temperatures is expected to be driven by the mechanism referred to as variable-range hopping. In this scheme, localized electrons "hop" from localized state to localized state. The temperature of the electrons determines the ease with which these transitions occur. There are two conventional models for variable-range hopping: Mott and Efros-Shklovskii. Mott's model which was proposed in 1968 stated that the resistivity should take the following form:

$$R(T) = R_0 exp\left(\frac{T_0}{T}\right)^p,\tag{5.1}$$

where R_0 is the prefactor, T_0 is the characteristic temperature, and the exponent p is a function of the dimensionality of the system (D) and is equal to 1/(D + 1). Hopping conduction occurs between states that are close to the chemical potential and is thus very dependent on the density of states around the chemical potential. In the Mott formulation, the density of states is assumed to be constant in this area. A formulation later developed by Efros and Shklovskii took into account the effect of a Coulomb gap in the density of states. This resulted in an equation of the same form as equation 5.1 but with an exponent of 1/2 which is independent of the system's dimensionality. This variable-range hopping model is referred to as Efros-Shklovskii variable-range hopping (ES-VRH) [42].

The nonlinear behaviour of the 2-point resistance can be driven by at least two different effects: electron heating or electric field dependence. In the case of electron heating, the change of resistance is due to the heating of electrons within the material. The resulting energetic electrons will be able to hop from localized state to localized state more readily. This will result in a drop in resistance.

If the change in resistance is largely driven by electric field depdendence, then the electrons and the phonons are at the same temperature and the resistance will depend on both the temperature and the electric field across the device. The electric field model predicts for ES-VRH a resistance of the form:

$$R(E,T) = R_0 exp(\sqrt{\Delta/T})exp\left(-\frac{eE\ell}{k_bT}\right)$$
(5.2)

where e is the electron charge, E is the electric field across the channel of the device, Δ is a constant, and ℓ is the characteristic hopping length [43] [25].

It is also possible for the effect of junctions to contribute to the nonlinearity. Larger voltages will improve the ability of electrons to move across electrical junctions increasing the current. This source of nonlinearity is due to the junction between the metal contacts and the material. Contacts can either be ohmic or rectifying. Ohmic contacts contribute resistance to the channel without degrading the channel's linearity. Rectifying contacts introduce a nonlinear rectifying effect into the system's IV curve. This nonlinearity is due to the Schottky effect. In addition, it is increasing difficult to establish ohmic contacts as the density of states is reduced.

The text that preceded served to briefly introduce physics associated with electrical transport. These models will be employed to determine the underlying electrical transport mechanisms in the devices that were measured in this work. The text that proceeds describes original work that was conducted in this thesis.

The electrical measurements were conducted in an Oxford helium-3 cryostat between the temperatures of 0.3K and 4K in high vacuum conditions. An AC signal was sourced using a Stanford Research Systems SR830 lock-in amplifier as a means of probing the material's two-point resistance. A Stanford Research Systems SIM928 isolated voltage source was used to supply DC electrical input power into the device. An additional DC voltage source, a Keithley 2400 Sourcemeter, was used to establish the gate-source voltage. The measurement setup is shown in figure 5.1. The applied power is taken to be the sum of both the AC and the DC power contributions and is given by $P_{applied} = V_{ac,rms}I_{ac,rms} + V_{dc}I_{dc}$. The frequency of the AC signal was set to 11.438 Hz. This frequency was used as it is not a subharmonic of 60 Hz and because it is sufficiently low such that the capacitance of the back gate does not introduce extraneous phase. The phase was typically less than 2 degrees indicating a resistive load.

The measured resistance at various input powers at zero gate voltage and the measured resistance at various temperatures for device 5 is shown in figure



Fig. 5.1: The measurement setup used to perform the electron transport experiments.

5.2. The temperature dependence of the two-point resistance at low bias could not be fit convincingly to either the Mott or ES variable-range hopping models.

The nonlinear dependence of the two-point resistance on input power can be explained quite readily using the electron heating model. This is discussed in the next section.

The presence of other effects that would introduce nonlinearity was deemed unlikely. The devices that were measured in this work possessed channels that were too long for the nonlinearity to be due to an electric field effect. The voltage across a device never exceeded 200mV and the channels were typically around 2mm in length. This would place the upper bound on the electric field at 100mV/mm. Rectification was also deemed unlikely to play a role as attempts to fit the data to a diode model or a Schottky model proved unsuccessful.



Fig. 5.2: Top: The measured dependence of the resistance on the input electrical power for D5. Bottom: The measured dependence of the resistance on temperature for D5.

5.2 Thermal Transport

To determine the strength of the thermal channels it is necessary to possess a means of measuring the electron temperature. Under the assumption that the resistance is purely a function of electron temperature, the resistance vs temperature curve at low bias can be used as a calibration curve–allowing for the resistance to be mapped directly to electron temperature. Curve fitting was done to determine an empirical expression for the resistance as a function of temperature. The fitting was done with an expression of the form $R = AT^B + C$ where A, B, and C are fitting parameters, R is the two-point resistance of the device, and T is the temperature. This function was used to map the measured resistance to an electron temperature. This procedure was repeated for all three devices. The quality of the curve fits was determined using the Rsquared method. For all three devices at all three gate voltages the R-squared value was higher than 0.99 indicating high quality curve fits. The electron temperature as a function of applied electrical power for D5 is shown in figure 5.3.

The coupling coefficients and the exponents associated with the power law were found by curve fitting the electron temperature vs applied power curves. Electron temperature and applied power are expected to take the form P = $\Sigma(Te^{\beta} - Ts^{\beta})$ where P is the applied electrical power, Te is the electron temperature, Ts is the substrate temperature, and Σ and β are the parameters to be determined. This expression was used as the fitting function. To assess the quality of the curve fit, it was necessary to use a metric that considered data at different orders of magnitude with equal weight. This was accomplished by taking the natural logarithm of the values of cooling power and using the R-squared goodness of fit method. The electron temperature vs applied power curves for each device were curve fitted for each of the temperatures at which measurements were performed. The fitting function was best able to fit the data at temperatures 900mK and below. The values of β and Σ as well as the R-squared fit parameter are summarized in table 5.1 along with the standard deviation associated with each value for temperatures 300mK, 600mK, and 900mK.

 Table 5.1: Power law parameters and fit quality for the three measured de

 vices

Device	β	β st dev	Σ	Σ st dev	log(P)	log(P)
			(mW/K^4m^2)	(mW/K^4m^2)	R-squared	R-squared st dev
D1 (hydro)	3.66	0.048	1.3	0.097	0.982	0.018
D3 (clean)	3.87	0.14	0.80	0.0073	0.791	0.23
D5 (hydro)	3.82	0.16	0.11	0.029	0.970	0.021

Across the three devices that were measured, the exponent was found to always be equal to approximately 4 (3.78 + - 0.14) regardless of the applied gate voltage. Figure 5.4 shows that the three devices all follow a power law with an exponent of 4 but with differing coupling strengths.

The characteristics of the three devices are summarized in table 5.2. The extracted coupling coefficients were 1.3, 0.80, and 0.11 mW/K⁴m² for D1, D3, and D5 respectively. These values are of the same order as those previously reported for graphene (~ 0.42 mW/K⁴m²) [28]. The extracted coupling coefficients were found to be independent of gate voltage. The coupling coefficient varied across the devices although it is not clear if this is due to degree of hydrogenation. The moderately hydrogenated device (D1) had the largest



Fig. 5.3: The dependence of the electron temperature on the electrical input power for D5.

coupling coefficient and the heavily hydrogenated device (D5) had the smallest coupling coefficient. This suggests that the coupling coefficient has some dependency on the level of hydrogenation.

Once the relation between electron temperature and power is known, the nature of the dominant electron cooling channel can be explored. The most notable signature of different cooling channels is the exponent associated with the power law. An exponent of 4 is associated with multiple cooling channels. In particular, electron-phonon coupling in clean graphene, blackbody radiative emission, and blackbody phonon emission. Electronic heat diffusion is not expected to contribute because superconducting contacts have been used.



Fig. 5.4: The cooling dynamics of all three measured devices fits a power law with an exponent of 4. The three devices differ in the strength of their coupling coefficients. Figures A), B), and C) are for D1, D3, and D5 respectively. Figure D) is a comparison of the 350mK data for all three devices with a gate voltage of 0V.

Blackbody photon emission is also not expected to be the thermal bottleneck as the power emitted through this process ($\approx 10 \text{nW}/\text{K}^4\text{m}^2$) is simply far too low to be the dominant electron cooling mechanism.

The cooling dynamics are inconsistent with in-plane electron-phonon coupling as the exponent has been shown to be equal to 3 in disordered graphene and the coupling coefficient has been shown to exhibit strong gate dependence--neither of which were observed [31] [32]. The coupling coefficient was found to not vary even as the gate voltage was varied between -10V and +10V. This gate voltage change resulted in an order of magnitude resistance change and an approximate carrier density decrease from $1.8 \times 10^{12} \text{ cm}^{-2}$ to $3.6 \times 10^{11} \text{ cm}^{-2}$. It's important to note however that the level of disorder present in this work is significantly higher than that of the previous works and that the nature of the graphene used is rather different. In this work the level of disorder is such that the Ioffe-Regel limit has been surpassed. Previous works focused on micrometer scale exfoliated graphene whereas in this work large-scale CVD polycrystalline graphene was used. It is most likely that blackbody phonon emission is the main thermal relaxation mechanism. The exponent associated with this mechanism is 4 as was seen in the data. This mechanism however has only ever been studied in 2DEG systems and there is no theory as to how this would occur in graphene mounted on oxidized silicon.

Table 5.2: Power law parameters for the three measured devices. The listed two-point resistance is that of the device at 300mK.

Device	$R_{2pt} (k\Omega)$	I_D/I_G	I_D/I_G st dev	β	$\Sigma (mW/K^4m^2)$	$n_d \mathrm{cm}^{-2}$
D1 (hydro)	53	2.4	0.15	3.66	1.3	8.8×10^{11}
D3 (clean)	8.9	0.40	0.11	3.87	0.80	1.1×10^{11}
D5 (hydro)	721	2.1	0.65	3.82	0.11	$8.0 imes 10^{12}$

5.3 Bolometric Response

Some preliminary bolometric figures of merit were determined from the data taken in the electrical measurements. The quantities that were extracted were the temperature coefficient of resistance (α), the thermal resistance (R_{th}), the response time (τ), as well as an estimate of the voltage responsivity.

The temperature coefficient of resistance is a measure of how useful a given material is as a thermometer. This quantity is given using equation 2.4 which was presented in chapter 2. The value of α for D5 (the most resistive device) is shown in figure 5.5.



Fig. 5.5: The temperature coefficient of resistance of D5.

The value of α can be tuned by varying the gate voltage. The highest observed value of α was $2.4K^{-1}$. This occurred when the gate voltage was set to +10V and the device was at 335mK. A gate voltage of +10V corresponds approximately to a carrier density of 3.6×10^{11} cm⁻². The thermal resistance can be estimated using the following expression:

$$R_{th} = \frac{dT_e}{dP} = \frac{dR/dP}{dR/dT}$$
(5.3)

This was used to extract the thermal resistance for the hydrogenated devices. The thermal resistance of the three devices as a function of applied power at the lowest measured temperature and 0V gate voltage is shown in figure 5.6. The thermal resistance was inferred using the generic expression for a power law (equation 3.1) with fitting parameters determined from curve fitting as described in the previous section. The expression was rearranged such that electron temperature T_e was given in terms of applied electrical power. This expression was then differentiated with respect to applied power to obtain an analytical expression for thermal resistance.

The response time for the device could not be extracted from the resistance vs power curves described in section 5.1 as these measurements were inherently steady-state. Previous experiments have shown however that the electrical response time is under 10ms. These experiments consisted of exciting a device similar to those described in this thesis with an electrical voltage pulse. The only observable transient was the 10ms transient associated with the RC time constant. This suggests that the device has a response time faster than 10ms.

Voltage responsivity with sufficiently slow IR modulation such that $\omega \tau \ll 1$ can be estimated from the expression:

$$R_v = IR\alpha\epsilon R_{th} \tag{5.4}$$



Fig. 5.6: Inferred thermal resistance for the three measured devices.

where I is the bias current, R is the sample resistance, α is the temperature coefficient of resistance, ϵ is the emissivity, and R_{th} is the thermal resistance. The bias current must be selected with care as the sample resistance, the temperature coefficient of resistance, and the thermal resistance are all strong functions of bias current. For this estimate, it will be assumed that the input optical power and the input electrical power will both be 1nW. This corresponds to a bias current of 50nA. With this bias current, the resistance will be ~ 500k Ω , the temperature coefficient of resistance will be 0.5 K^{-1} , and the thermal resistance will be approximately $5 \times 10^8 \text{W/K}$. The absorption coefficient for unbiased pristine graphene is 2.3%-this value will be assumed for the purpose of this estimate [44]. This results in a voltage responsivity equal to $1.5 \times 10^5 \text{V/W}$.

This estimated value of voltage responsivity is competitive with that of previously reported graphene-based hot electron bolometers ($\sim 10^5 V/W$) [2] [3] and surpasses that of superconducting bolometers ($\sim 10^4 V/W$) [6].

The responsivity can potentially be improved by tuning the gate voltage, the degree of hydrogenation, and the substrate. In this work, the range of gate voltages that were employed was rather limited with the best responsivity being observed at the most positive gate voltage that was employed (+10V). This suggests that performance can be further improved by increasing the gate voltage and further depleting the channel of carriers. Increasing the degree of hydrogenation can also potentially result in improved performance. The most resistive device exhibited the largest estimated responsivity. This suggests that the responsivity could be further improved by increasing the degree of hydrogenation. The choice of substrate could also be optimized. Oxidized silicon was used as it is a standard substrate choice for graphene. Since the cooling of hot electrons involves the coupling of electrons to the substrate, this process is very likely to be sensitive to the choice of substrate potentially allowing the responsivity to be further improved.

This chapter has presented the results from the electrical transport measurements and presented the resulting thermal properties for the three devices that were measured in this work. Estimates for several bolometric figures of merit were also presented. These parameters will be used to assess hydrogenated graphene's suitability as an absorbing medium for a hot electron bolometer.

Chapter 6

Conclusion

In this work, the electronic heat dissipation channel was measured in largearea highly-disordered hydrogenated graphene. The electron temperature was found to scale with applied electrical power with an exponent of 4. This exponent was found to be independent of carrier density, temperature, and the degree of electronic disorder. The coupling strength was found to be of the order of $0.1 \text{mW/K}^4\text{m}^2$. The coupling strength was found to be independent of carrier concentration. Although the coupling strength varied across the devices, it is not clear if this is due to the degree of hydrogenation.

The electrical transport measurements were used to ascertain the dominant electron cooling channel. As superconducting contacts were employed, electronic heat diffusion through the contacts can be eliminated as a potential mechanism. Blackbody photon emission can also be eliminated as the coupling strength is far too weak. This leaves coupling to in-plane phonons and coupling to out-of-plane phonons as potential mechanisms. The fact that the coupling constant is independent of carrier density and that the exponent is 4 as oppose to 3 indicates that in-plane phonon coupling is not the dominant thermal channel in these devices. The elimination of these three thermal channels strongly suggests that out-of-plane blackbody phonon emission is the dominant channel.

Preliminary bolometric figures of merit were calculated for hydrogenated graphene should the material be used as a monolithic hot electron bolometer. The estimated optical responsivity is comparable to other hot electron devices at cryogenic temperatures. The upper bound on the response time indicates that hydrogenated graphene is faster than most bolometer types. The ability to tune characteristics such as the temperature coefficient of resistance with a back gate or the coupling coefficient through degree of hydrogenation make this material additionally interesting for bolometry.

Additional work will be done to provide further evidence towards the electron cooling channel. In particular, a more accurate method of measuring the electron temperature–Johnson noise thermometry will be used [34]. This will ensure a more direct readout of electron temperature. Resistive thermometry suffers from the fact that effects other than electron heating may also be contributing to the change in electrical resistance.

Another experiment that has been envisioned is to measure the carrier lifetimes in hydrogenated graphene using ultrafast terahertz spectroscopy. This will provide additional information concerning the thermalization process of hot electrons and their coupling strength to the phonons in the lattice.

The optical response of hydrogenated graphene must also be measured in order to fully assess the bolometric response of this material. This entails determining the absorption spectrum of the material and directly measuring the optical responsivity.

The potential of hydrogenated graphene for bolometric applications will be further examined by measuring the resistance of the device at microwave frequencies. This will allow for the noise-equivalent power and specific detectivity to be determined as flicker noise will be negligible in this frequency range.

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