

# High magnetic field effects in low-dimensional carbon nanostructures

Jack A Alexander-Webber

Christ Church, Oxford



Thesis submitted in fulfilment of the requirements for the degree of  
Doctor of Philosophy at the University of Oxford

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## Abstract

This thesis describes studies of graphene, single walled carbon nanotubes (SWNTs) and InSb. Optical and electronic measurements probe the effects of high magnetic fields on these low-dimensional systems.

Chapter 1 introduces a theoretical description and background behind the materials and physical phenomena studied in this work. The structure and unique properties of carbon nanomaterials are described. The experimental methods used in this thesis are described in Chapter 2.

Chapter 3 describes magnetotransport measurements on InSb/AlInSb heterostructures revealing that the large energy gaps, and extremely high mobility, associated with this system leads to exceptionally well defined quantum Hall plateaux for both even (Landau level) and odd (spin-split) filling factors. Even higher cyclotron energy gaps are expected in graphene. Chapter 4 reveals that due to a combination of large cyclotron energy gaps and fast electron-phonon energy loss rates, the quantum Hall effect (QHE) in graphene can be observed to unprecedented current densities (43 A/m) and temperatures ( $> 45$  K). The behaviour of epitaxial graphene grown on silicon carbide in the quantum Hall regime is shown to be characterised by a strongly magnetic field dependent carrier density due to charge transfer from surface donor states in the substrate.

Chapter 5 shows that polymer wrapping of SWNTs can achieve high quality purified samples. Individual SWNTs were probed using micro-photoluminescence measurements in magnetic fields up to 30 T. The combination of high magnetic fields and high spectral and spatial resolution allowed a detailed study of exciton fine structure. High intensity laser irradiation is shown to induce bound excitons in pristine tubes. The optical properties of a number of tubes are dominated by defect sites which may be imaged along the tube using the magnetic brightening of dark excitons associated with such defects.

To Mum, Dad, Mir and Doug for all your help and encouragement.

# Acknowledgements

Firstly I wish to thank my supervisor Prof. Robin Nicholas for his unwavering guidance and assistance, and for going beyond the call of duty during research and in times of need. In addition I thank all members and visitors of the Nicholas research group past and present. In particular I thank Anton Baker for his insight and companionship in the lab, for the GBK trips, and for the always entertaining facts, figures, statistics and reviews. Thanks to Sam Stranks for the finest carbon nanotube samples and sharing your deep understanding. The lithography skills I learned under the patient tuition of Thomas Altebaeumer have already proven invaluable. Thanks to the rest of the RJN group I have had the pleasure to work with; Richard Tuley, Beate Dirks, Severin Habisreutinger, Jacob Wang, Nate Jian Huang and Joseph Sharkey.

I have been lucky enough to receive support from a great number of collaborators and co-workers in Oxford and far beyond. The people in Grenoble high magnetic field laboratory made my stays there both pleasurable and productive. Particular thanks go to Clement Faugeras for his expertise, and for the coffee and company required to keep me working till dawn, as well as Benjamin Piot, Piotr Kossacki, and Marek Potemski. Back in Oxford, Robert Storey and Tony Hickman expertly kept the magnet running and retrieved the occasional lost sample. JT Janssen and Sasha Tzalenchuk at the National Physical Laboratory allowed me to build a fruitful collaboration out of my summer studentship there prior to starting in Oxford. I hope for and look forward to a continued collaboration as successful as the one I have enjoyed so far, a collaboration made possible from the “wonder-samples” fabricated by Rozitza Yakimova (Linköping), Samuel Lara-Avila and Sergey Kubatkin (Chalmers). The exceptional quality InSb/AlInSb samples provided the perfect introduction to magnetotransport experiments and the quantum Hall effect in my early research, for these I thank Phil Buckle, Lisa Buckle, Tim Ashley



and Martin Emeny.

Within Condensed Matter Physics at Oxford lies the community of Semiconductor Materials, Devices and Nanostructures. Without this community my time at Oxford would be less productive and a whole lot less fun. For all the lunches, tea breaks and pub trips I thank all the members of the Nicholas, Herz, Johnston, Lloyd-Hughes, Snaith and Taylor groups. Thanks to Dash for all the free sandwiches on Fridays. Thanks to Agnese Abrusci, Mike Lee and James Ball for all the Orange Wednesdays. Thanks to Ed Crossland, Nakita Noel, Varun Sivaram, Thomas Leijtens and Henry Snaith for turning a ski trip into a Nature paper. I am indebted to the Taylor group “wolfpack”, Tim Wang, Mark Holmes, Hee Dae Kim, Chris Chan and Ben Reid for the single nanotube photoluminescence in Oxford.

Christ Church has provided me with a home away from home for which I am extremely grateful. I thank my college advisor Alan Merchant for his support and numerous High Table invitations.

My work was made possible by funding from the European Commission, the EPSRC and NPL Strategic Research Programme. This funding, as well as that from Christ Church, the Condensed Matter Physics sub-department, and the Institute of Physics gave me the opportunity to present my work at international conferences where I met wonderful people, made great friends, and formed lasting collaborations, as well as seeing parts of the world I would never have otherwise seen.

Most of all I appreciate all of my friends and family who have helped me overcome my challenges and celebrate my successes. Thank you Hannah Joyce for all your encouragement and extensive proof reading, you never fail to make me smile, you are truly unique. Thank you Miranda for being a little sister I could look up to(!) and Douglas for your laid-back (almost horizontal) outlook on life. To my Mum and Dad, you have given me limitless care and support and never cease to be a source of inspiration, I couldn't have done it without you.

*“Well, it took an hour to write. I thought it would take an hour to read.”*

*Philip J. Fry*

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## Manuscripts in preparation/submitted

**JA Alexander-Webber**, C FAUGERAS, P KOSSACKI, M POTEMSKI, X WANG, SD STRANKS, RA TAYLOR, AND RJ NICHOLAS. Hyperspectral imaging of exciton dynamics in individual carbon nanotubes controlled by high magnetic fields. *Submitted to Nature Photonics* (2013).

# Chapter 1

## Introduction and Theoretical Background

---

This chapter introduces the structure and properties of two nanostructured carbon allotropes, graphene and carbon nanotubes. The dimensionality of the system is key to understanding its properties. We shall see that the two-dimensional physics of graphene converts to one-dimensional behaviour when graphene sheets are rolled into carbon nanotubes. For each of these systems the application of a magnetic field has dramatic effects on its optical and electronic properties.



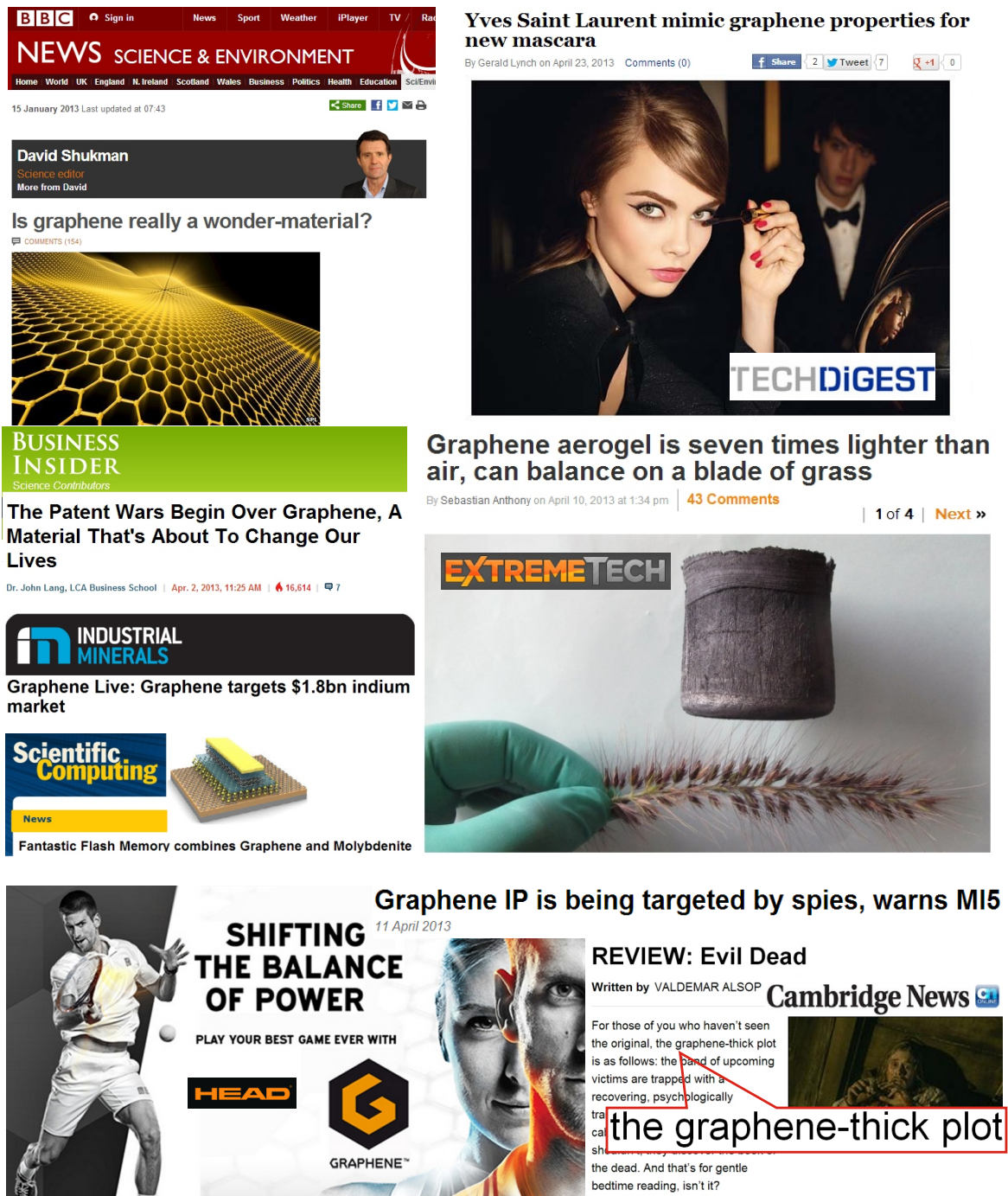


Figure 1.1: A small selection of graphene in the media from early 2013

## 1.1 Graphene

Since it was first isolated in 2004 graphene has taken on the title of a “*wonder material*”, in both the scientific community and increasingly among the public (Fig. 1.1). With unparalleled mechanical strength and stiffness, the highest intrinsic carrier mobility and thermal conductivity of any material, and a number of other potentially lucrative properties such as elasticity and gas impermeability, it is no wonder that so much interest has grown in research and development into applying graphene to solve real world problems.

### 1.1.1 The Graphene Lattice

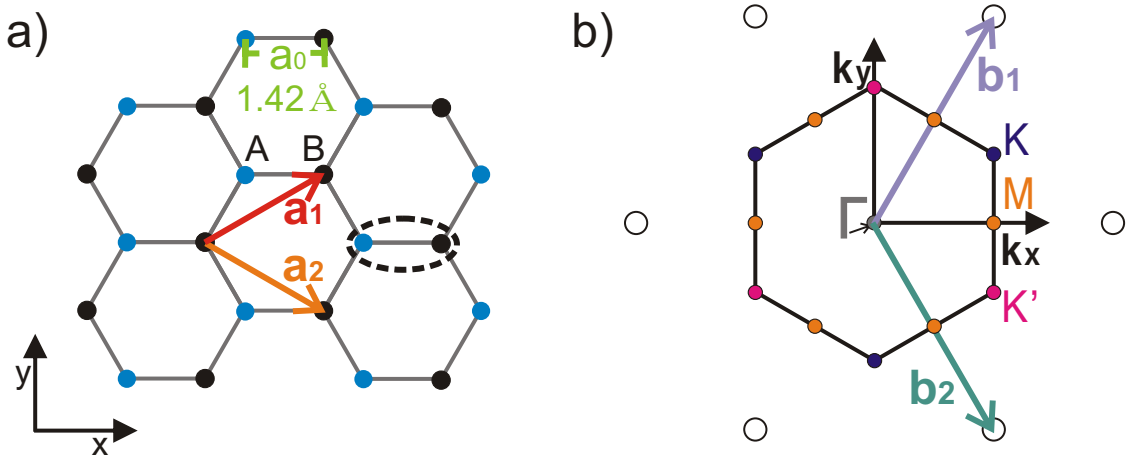


Figure 1.2: a) The honeycomb structure of graphene, a triangular lattice with two atoms, A and B, per unit cell. b) The reciprocal lattice of graphene and the first Brillouin zone. Also shown are the high symmetry points,  $\Gamma$ , M, K and  $K'$ .

Graphene is a single layer of carbon atoms arranged in a honeycomb structure which may be modeled as a triangular lattice with two atoms per unit cell, A and B. The two lattice vectors in cartesian coordinates are defined as

$$\mathbf{a}_1 = \frac{a_0}{2}(3\hat{x} + \sqrt{3}\hat{y}), \quad \mathbf{a}_2 = \frac{a_0}{2}(3\hat{x} - \sqrt{3}\hat{y}), \quad (1.1)$$

where  $a_0 = 0.142 \text{ nm}$  [1], the average length of a carbon-carbon bond in graphene, as described in figure 1.2a. The reciprocal space lattice, and the first Brillouin zone (FBZ), may be calculated through the Fourier transform of the real space lattice. Given a real space lattice of points  $\mathbf{R}$ , a point  $\mathbf{L}$  is in the reciprocal lattice if  $e^{\mathbf{L} \cdot \mathbf{R}} = 1$ , i.e.  $\mathbf{L} \cdot \mathbf{R} = 0, n i \pi$ , for integer  $n$ . The reciprocal lattice vectors of graphene are

$$\mathbf{b}_1 = \frac{2\pi}{3a_0} \hat{k}_x + \frac{2\pi}{\sqrt{3}a_0} \hat{k}_y, \quad \mathbf{b}_2 = \frac{2\pi}{3a_0} \hat{k}_x - \frac{2\pi}{\sqrt{3}a_0} \hat{k}_y, \quad (1.2)$$

as described in figure 1.2b. The first Brillouin zone is also hexagonal but rotated from the real space lattice with four high symmetry points,  $\Gamma$ ,  $M$ ,  $K$  and  $K'$  (Fig.1.2b). Of these,  $K$  and  $K'$  at the corners of the hexagon, known as the Dirac points, as we shall see are the most important in determining the electronic properties of graphene at low energy ( $< 2 \text{ eV}$ ) and for typically observed ( $\lesssim 10^{13} \text{ cm}^2$ ) carrier densities.

### 1.1.2 Tight-binding model

Graphene is a covalent solid which owes its structure to three  $\text{sp}^2$  hybridised carbon orbitals per atom forming localised  $\sigma$  bonds. Sigma bonds are responsible for the strength of carbon in all its allotropes, and do not contribute to the conduction. This leaves one electron per carbon atom to form out of plane  $\pi$  (bonding) and  $\pi^*$  (antibonding) orbitals perpendicular to the lattice. A good description can be obtained from a tight binding model of the electronic band structure, where electrons are assumed to be tightly bound to their respective atom with weak interaction between neighbouring atoms [1, 2]. The  $\pi$  and  $\pi^*$  bands are effectively decoupled from the  $\sigma$  bonds and may therefore be treated independently. It was Wallace in 1947 [1], who first used the tight binding approximation calculating for three nearest neighbours using a Bloch function to represent the wavefunction of each orbital in the unit cell. This was later compared to ab initio calculations and next nearest neighbour models by Reich *et al.* [2] and found to be in good

qualitative agreement, especially in the region of the Dirac points.

The conduction,  $E^+$  ( $\pi^*$ ), and valence,  $E^-$  ( $\pi$ ), bands are described by [2]

$$E^\pm(\mathbf{k}) = \frac{\epsilon_{2p} \pm \gamma_0 \sqrt{f(\mathbf{k})}}{1 \mp s_0 \sqrt{f(\mathbf{k})}} \quad (1.3)$$

where

$$f(\mathbf{k}) = 3 + 2 \cos(\mathbf{k} \cdot \mathbf{a}_1) + 2 \cos(\mathbf{k} \cdot \mathbf{a}_2) + s_0 \cos(\mathbf{k} \cdot (\mathbf{a}_1 - \mathbf{a}_2)), \quad (1.4)$$

and  $\epsilon_{2p}$  is the energy of the 2p orbital,  $\gamma_0$  is the carbon-carbon interaction energy and  $s_0$  is the integral of the overlap between a carbon atom and its nearest neighbours. The three free parameters are generally fitted around the Dirac points to experimental data, such as cyclotron resonance studies by Deacon *et al.* [3], or *ab initio* calculations [2]. Typically  $\epsilon_{2p}$  is set to zero, so that the bands meet at the  $K$  and  $K'$  points. The Fermi velocity,  $v_F$ , is determined by  $\gamma_0$ . Experimentally  $\gamma_0$  is found to be 3.38 eV, resulting in a measured  $v_F = 1.093 \times 10^6 \text{ ms}^{-1}$  [3]. There is an electron-hole asymmetry in graphene, this is accounted for by  $s_0$  and is typically 0.129 [2, 3]. The resulting bandstructure is shown in Figure 1.3.

The tight-binding model is based in the assumption that electrons do not interact with one another. When many-body interactions are included the previously linear low-energy dispersion relation can change [4]. The Dirac cone is squeezed such that at low carrier densities ( $|n| \lesssim 3 \times 10^{12} \text{ cm}^{-2}$ ) the Fermi velocity is increased and has been measured up to  $v_F > 1.3 \times 10^6 \text{ ms}^{-1}$  at the lowest carrier densities [4].

### 1.1.3 Low-Energy Spectrum

By fixing values of  $k_x$  or  $k_y$ , we can take slices of this three dimensional plot to clarify the different regions in  $k$ -space (Fig. 1.4). Expanding around the  $K$  (or  $K'$ ) points,

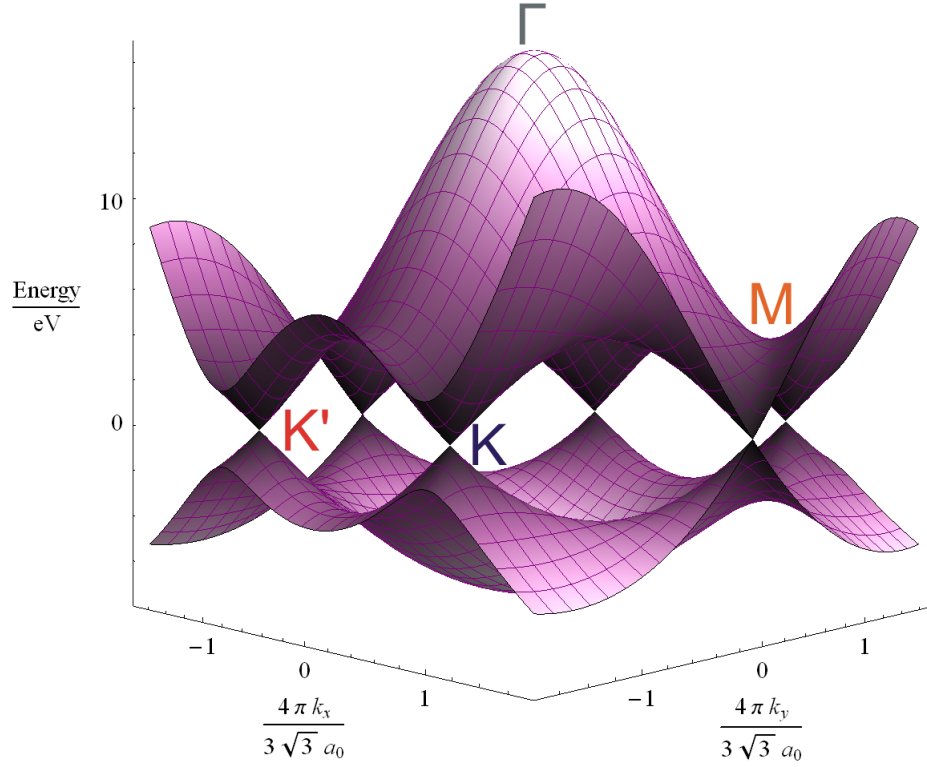


Figure 1.3: The bandstructure of graphene using equation 1.3 with  $\gamma_0 = 3.38$  eV,  $\epsilon_{2p} = 0$  and  $s_0 = 0.129$ .

such that  $\mathbf{k} = \mathbf{K} + \mathbf{q}$  ( $|\mathbf{k}| \ll |\mathbf{K}|$ ), gives us a linear dispersion relation

$$E^\pm(q) \approx \pm \hbar v_F |\mathbf{q}|, \quad (1.5)$$

where  $v_F$  is defined as

$$v_F = \frac{3\gamma_0 a_0}{2\hbar}. \quad (1.6)$$

This linear dispersion relation is in contrast to conventional semiconductors where  $E \propto k^2$ , and is similar to that of ultra-relativistic particles with zero rest mass  $m_0$ , where

$$E(\mathbf{q}) = \sqrt{m_0^2 c^4 + c^2 \hbar^2 q^2} = c \hbar q. \quad (1.7)$$

Under these conditions Schrödinger's equation for Bloch electrons reduces to the 2D Dirac equation [5, 6], which thus should be used to model carriers in graphene close to the  $K$  and  $K'$  (Dirac) points with the speed of light,  $c$ , replaced with,  $v_F$ , where  $v_F \sim c/300$ , such that [6]

$$\hat{H} = \hbar v_F \begin{pmatrix} 0 & q_x - iq_y \\ q_x + iq_y & 0 \end{pmatrix} = \hbar v_F (\boldsymbol{\sigma} \cdot \mathbf{q}), \quad (1.8)$$

where  $\sigma$  is the Pauli spinor matrix in 2D, where, in the case of graphene, the “spin” is actually a pseudo-spin ( $\theta_q$ ) which is not a real spin but determined by a linear combination of excitations arising from the  $A$  and  $B$  sublattices, determined by the angle in momentum space

$$\theta_q = \arctan \left( \frac{q_x}{q_y} \right). \quad (1.9)$$

It is this ability to probe relativistic Dirac physics in a solid-state system which has been the driving force in the rapid progression of graphene research.

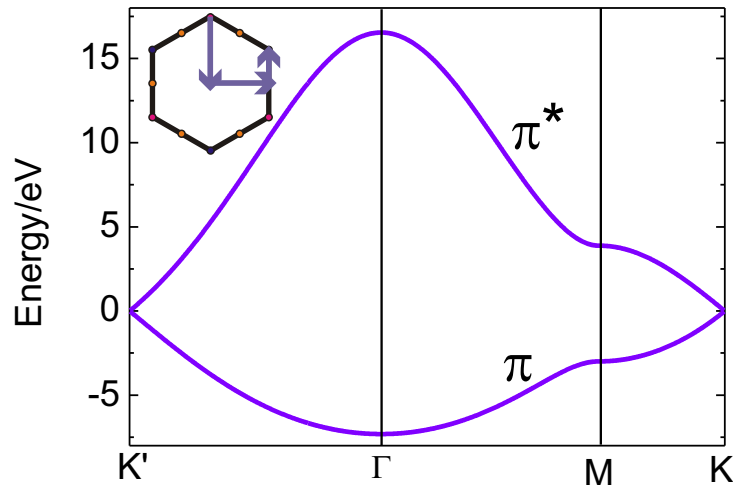


Figure 1.4: Sections of the  $\pi$  and  $\pi^*$  bands of the graphene band structure. (Inset) The path of the plot around the FBZ in  $k$ -space.

## 1.2 Indium Antimonide

Indium antimonide is a III-V semiconductor and a close analogue to graphene in terms of its electronic properties having the lowest effective mass ( $0.014 m_e$ ), narrowest bandgap and highest intrinsic mobility ( $78,000 \text{ cm}^2/\text{Vs}$  at 300 K) [7]. In addition InSb has an exceptionally large effective Landé g-factor ( $g^* \sim -50$ ) [8]. Indium antimonide has a zinc blende structure i.e. two interpenetrating face-centred cubic lattices (Fig. 1.5a). The band structure has a direct gap of 170 meV between the conduction band and the light and heavy hole bands at the  $\Gamma$  point [9] as shown schematically in Figure 1.5b.

A large lattice mismatch between InSb and any potential alloys [10]. This lattice mismatch means that at a junction between InSb and an alloy in a crystal there will be considerable strain which may result in defects which perturb local potential and can cause additional electron scattering thus reducing the mobility. Recent advances have allowed the growth of high quality InSb quantum well structures where thin ( $< 50 \text{ nm}$ ) layers of InSb are sandwiched between layers of  $\text{Al}_x\text{In}_{1-x}\text{Sb}$  [8, 10, 11]. Initial measurements of the resulting heterostructures have shown mobilities exceeding  $200,000 \text{ cm}^2/\text{Vs}$  below 40 K [10]. Chapter 3 describes the study of these heterostructures where the high mobility and confinement to two dimensions leads to the observation of quantum Hall effect at low temperatures, described below.

## 1.3 The Quantum Hall Effect

### 1.3.1 Classical Hall Effect

By measuring an increase in the electric potential of thin gold leaf perpendicular to an applied current when applying a magnetic field normal to the surface of the leaf Edwin Hall, in 1879 [12], discovered what was to be known as the Hall effect. When a carrier

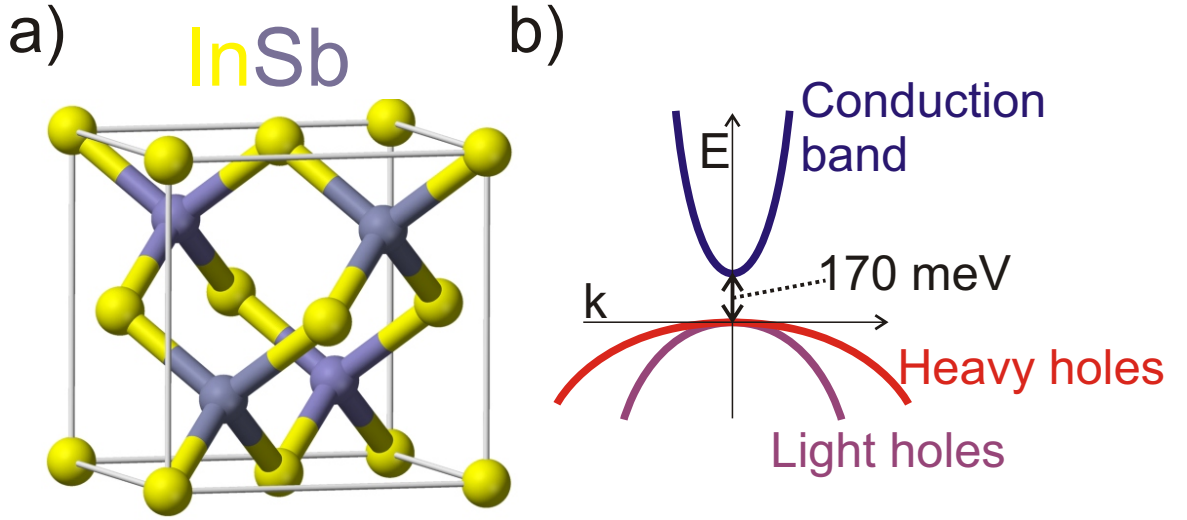


Figure 1.5: a) Zinc blende structure of indium antimonide. b) Schematic dispersion relation of InSb at low energies.

with charge  $q$  moves through a conductor with a velocity  $\mathbf{v}$  under a simultaneous electric ( $\mathbf{E}$ ) and magnetic ( $\mathbf{B}$ ) field it experiences a Lorentz force given by

$$\mathbf{F} = q(\mathbf{E} + \mathbf{v} \times \mathbf{B}) \quad (1.10)$$

In testing such phenomena in modern experiments, a “Hall bar” geometry is often used as described in figure 1.6. A current  $I_{xx}$  is applied in the  $x$  direction and two simultaneous voltage measurements are taken; the longitudinal voltage  $V_{xx}$  and the perpendicular voltage  $V_{xy}$ , also known as the Hall voltage. A magnetic field  $B_z$  is applied in the  $z$  direction with flux threading normal to the plane of the device. The applied magnetic field causes an accumulation of charge perpendicular to the current direction and thus, a non-zero  $V_{xy}$ . The resistivity of a 2D system,  $\rho_{2D}$ , with an infinitesimal thickness,  $d$ , can be related to the 3D resistivity by  $\rho_{2D} = \rho_{3D}/d$ , and in 2D has the same units as resistance. The resistivity,  $\rho$ , is defined as a tensor of differing conductivities  $\sigma$ , in the directions parallel ( $\sigma_{xx}$ ) and perpendicular ( $\sigma_{xy}$ ) to the applied current and



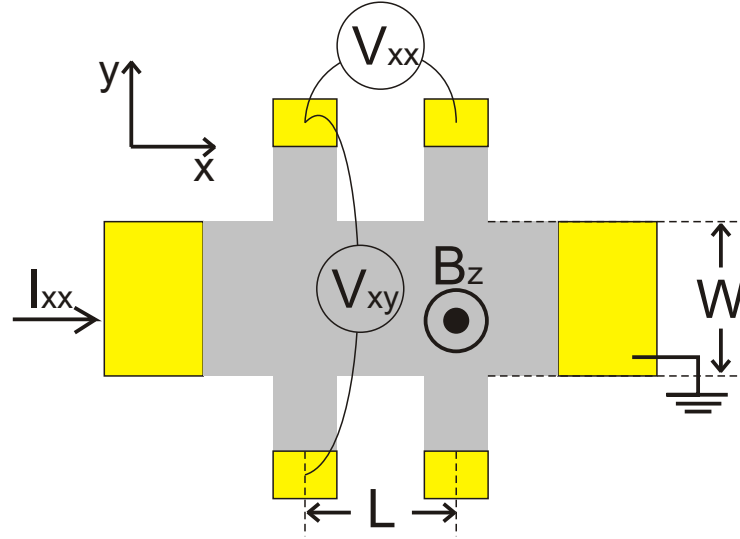


Figure 1.6: A Hall bar geometry showing typical voltage probes  $V_{xx}$  and  $V_{xy}$ . The longitudinal resistivity is determined by  $\rho_{xx} = \frac{W}{L} \frac{V_{xx}}{I_{xx}}$ .

relates the current density  $\mathbf{j}$  to the electric field  $\mathbf{E}$  given by

$$\rho_{xx} = \frac{\sigma_{xx}}{\sigma_{xx}^2 + \sigma_{xy}^2}, \quad \rho_{xy} = \frac{\sigma_{xy}}{\sigma_{xx}^2 + \sigma_{xy}^2} \quad (1.11)$$

$$\begin{pmatrix} E_x \\ E_y \end{pmatrix} = \begin{pmatrix} \rho_{xx} & \rho_{xy} \\ -\rho_{xy} & \rho_{xx} \end{pmatrix} \times \begin{pmatrix} j_x \\ j_y \end{pmatrix}. \quad (1.12)$$

The Hall resistivity is determined by the magnetic field and the 2D carrier density per unit area,  $n$ ,

$$\rho_{xy} = \frac{V_{xy}}{I_{xx}} = \frac{B_z}{ne}. \quad (1.13)$$

The longitudinal resistivity is defined by the geometry of the sample with a length  $L$  (between the voltage probes), and width  $W$  (Fig.1.6),

$$\rho_{xx} = \frac{W}{L} \frac{V_{xx}}{I_{xx}}. \quad (1.14)$$

Low field Hall effect measurements are a useful tool in characterising the type of majority carrier (electrons or holes), the carrier density, and the carrier mobility  $\mu = 1/en\rho_{xx}$ . The carrier mobility may also be expressed in terms of a characteristic scattering time,  $\tau$ , and the effective mass  $m^*$ , where  $\mu = e\tau/m^*$ .

### 1.3.2 Integer Quantum Hall Effect

At high magnetic fields using high mobility two-dimensional samples, the classical Hall effect breaks down, and the quantum Hall regime [13] dominates where quantised steps appear in the Hall resistance in units of  $\rho_{xy} = h/\nu e^2$ , with a simultaneously vanishing  $\rho_{xx}$ . The quantisation of the Hall resistance is so precise, and being defined purely by fundamental constants, that it currently used as a quantum electrical resistance unit standard used in metrology to define the Ohm [14] (Section 1.3.4). An example of such behaviour is shown in Figure 1.7.

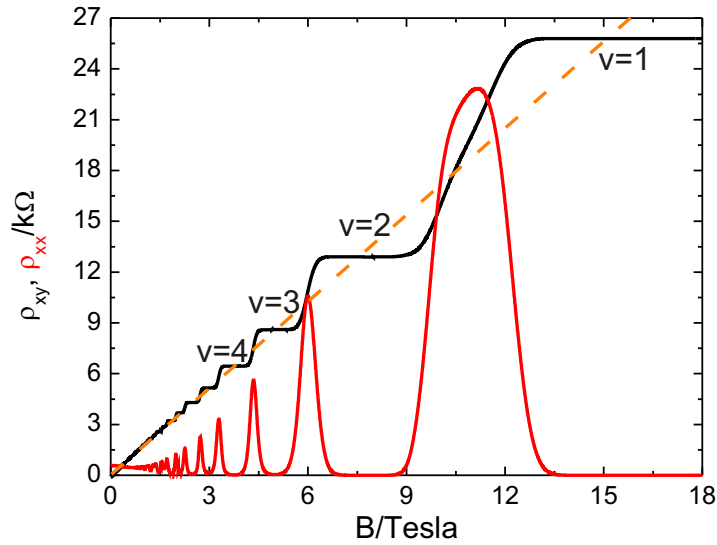


Figure 1.7: Quantum Hall effect in InSb showing a mobility of  $160,000 \text{ cm}^2/\text{Vs}$  and carrier density of  $3.5 \times 10^{11} \text{ cm}^{-2}$ . Extrapolation of the classical Hall effect is shown in orange. Adapted from Chapter 3.

The energy spectrum of a two dimensional system in high magnetic fields becomes

discrete due to Landau quantisation [15]. Electrons in a high magnetic field undergo cyclotron motion with a frequency given by  $\omega_c = eB/m^*$ . When the mobility of a sample and magnetic field is high enough such that the carriers may complete several cyclotron orbits before scattering ( $\tau\omega_c \gg 1$ , or  $B \gg \mu^{-1}$ ), the size of the cyclotron orbit may only take certain quantised values at integer ( $N$ ) values of the electron wavelength. Thus the energy spectrum of the system, found through solving the Schrödinger equation for free 2D electrons under magnetic and electric fields, simplifies to the Hamiltonian of a harmonic oscillator for localised electrons confined within the magnetic length,  $l_B = \sqrt{h/eB}$ , [16] given by

$$E_N = \hbar\omega_c(N + \frac{1}{2}). \quad (1.15)$$

The Landau level separation in GaAs as a function of magnetic field are shown in Figure 1.8a. In addition, the Landau levels are split when the spin degeneracy is lifted at high magnetic fields due to the Zeeman effect with an energy  $E_{SS} = g^*\mu_B sB$ , where  $g^*$  is the effective Landé g-factor ( $\sim 2$  for GaAs and graphene),  $s = \pm 1/2$  is the spin of the electron and  $\mu_B = \frac{e\hbar}{2m_e}$  is the Bohr magneton. Calculating the classical Hall resistance using the condition that  $\nu$  Landau levels are fully occupied with  $n_{LL}$  carriers [17], we arrive at the equation for quantised Hall resistance,

$$\rho_{xy} = \frac{B_z}{e\nu n_{LL}} = \frac{h}{\nu e^2}. \quad (1.16)$$

The theoretical density of states for each Landau level is a highly degenerate delta function, but in reality each level is broadened by disorder where the localised states scatter inelastically with impurities. Between Landau levels are localised states and delocalised (“extended”) states lie at the centre [17, 18] (Fig. 1.8b). The most common interpretation of the integer QHE is that of current-carrying edge states, i.e. those at the centre of the Landau level, extending around the perimeter of the Hall bar and localised states undergoing cyclotron motion in the middle of the sample [19]. Due

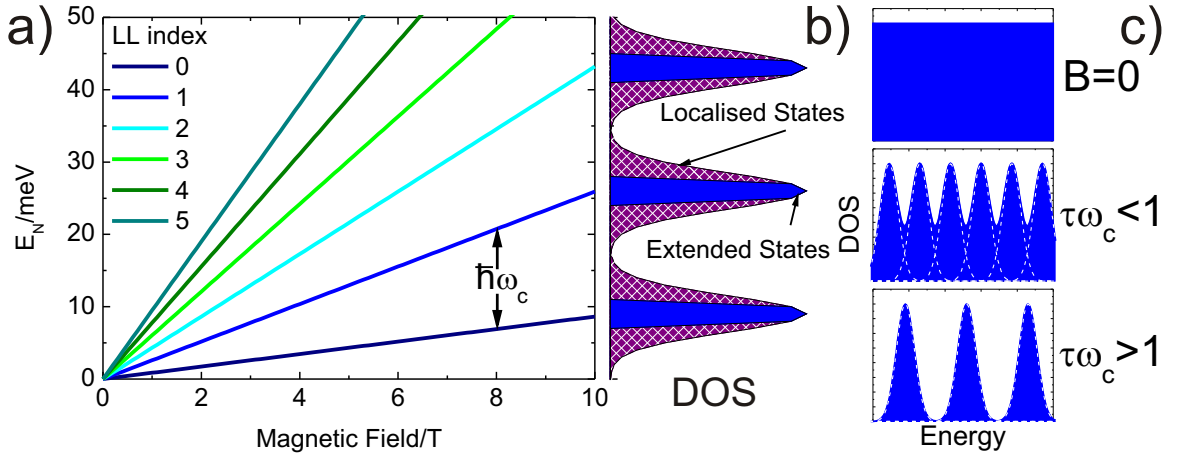


Figure 1.8: a) Landau level energy,  $E_N$ , for GaAs as a function of magnetic field for  $n = 0 - 5$ . b) Density of states of the three lowest Landau levels at  $B_z = 10$  T. Localised states (purple) occupy the states between Landau levels whereas extended states lie in the centre. c) Three regimes for the density of states for massive carriers confined to two-dimensions with varying perpendicular magnetic field.

to the physical separation of the edge states backscattering is suppressed leading to dissipationless transport along the perimeter at low temperatures and low measurement currents. When the voltage measurement is along the same edge state a zero resistivity is measured, whereas probing between the two edges will measure the quantised Hall resistance.

Since the total resistance of the sample remains finite, the dissipation has to be located somewhere in the sample. In an elegant experiment [20], a GaAs/InGaAs Hall bar was immersed in superfluid Helium-4 and imaged in the quantum Hall regime with a high applied current. The temperature gradient induced by the thermal dissipation caused a fountain effect [21] in the superfluid, visually changing the thickness of the helium film. This showed that dissipation only occurred at the two opposite corners of the current injection contacts. This was later confirmed by Ikushima *et al.* through imaging of cyclotron emission using a scanning terahertz microscope [22]. Above a critical current Ikushima *et al.* observe an exponential increase in cyclotron emission. This behaviour is indicative of the current induced breakdown of the quantum Hall effect

which has been the subject of much study since the first observation of the quantum Hall effect (Chapters 3 and 4).

### 1.3.3 Quantum Hall Effect in Graphene

As described in equation 1.7 carriers in graphene can be modelled as having no mass. This dramatically changes the magnetic field effects on the electronic properties when compared to conventional semiconductors. The cyclotron frequency for Dirac fermions is given by [23]

$$\omega_c = \sqrt{2} \frac{v_F}{l_B} = v_F \sqrt{\frac{2eB}{h}} \quad (1.17)$$

In finding the Landau level spectrum we must no longer solve the Schrödinger equation but the 2D Dirac equation for free electrons in magnetic and electric fields, which yields [23]

$$E_{LL} = \text{sgn}(N) \hbar \omega_c \sqrt{|N|} = \text{sgn}(N) v_F \sqrt{2 \hbar e B |N|} \quad (1.18)$$

where  $N$  is an integer including zero representing electrons ( $N > 0$ ) or holes ( $N < 0$ ). The first consequence of this is the presence of a Landau level at the Dirac points ( $E_F = 0$ ) which when filled contains an equal contribution from electrons and holes, and that the energy spacing between Landau levels is related to  $\Delta_{LL} \propto B^{1/2}$  as opposed to  $\propto B$  for carriers in conventional semiconductors. It is worth noting at this point that whilst the dispersion relation of the carriers is modelled using a zero mass, the cyclotron mass remains finite given by [23]

$$m_c = \frac{E}{v_F^2} = \left( \frac{\hbar^2 n}{4\pi v_F^2} \right)^{1/2}. \quad (1.19)$$

Whilst the cyclotron mass is not zero, it is significantly smaller than in semiconductor systems. This results in the cyclotron energy gap between the  $N = 0$  and  $N = 1$  Landau levels in graphene being a factor of 5 larger at 10 Tesla than in GaAs, implying that the

QHE should be observable at lower magnetic fields and higher temperatures (Chapter 4).

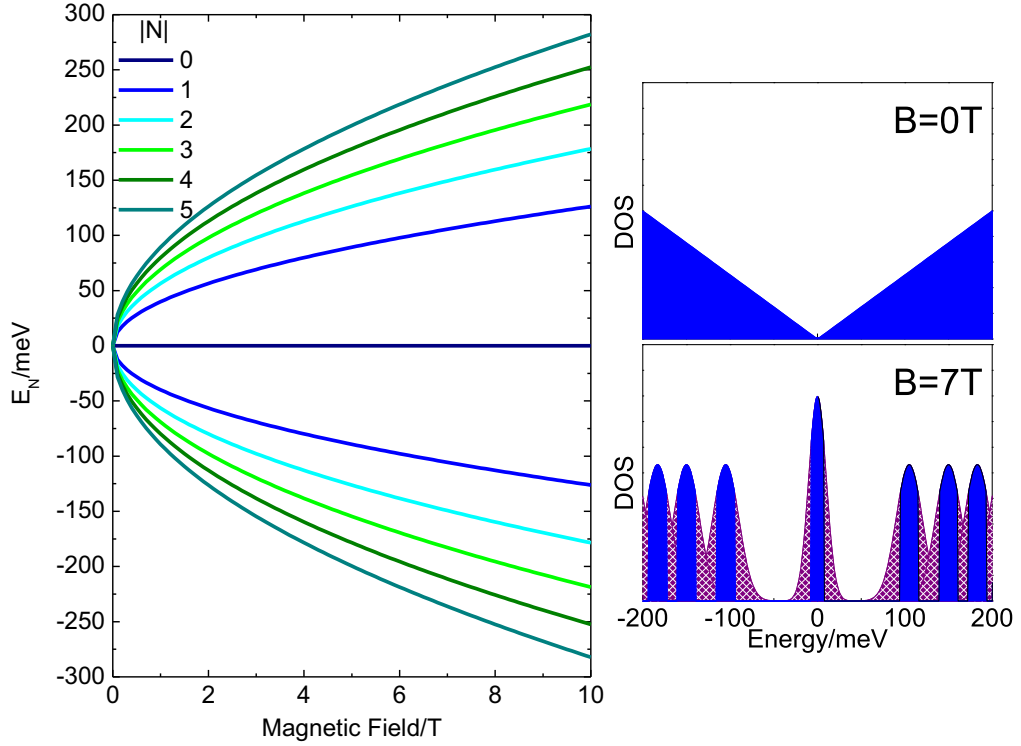


Figure 1.9: Landau level energy,  $E_N$ , for graphene as a function of magnetic field for  $N = -5 - 5$ . Also shown is the schematic density of states at 0 T and 7 T for graphene near the Dirac point with and without magnetic field.

A property of spin-1/2 pseudo-spinors, such as  $\sigma$  in Equation 1.8, is that they can be thought of as having a rotational symmetry of order 1/2, that is to say a rotation of  $360^\circ$  will add a phase of  $\pi$  to the wavefunction, reversing its sign[5]. This additional phase is commonly known as the Berry's phase [24], and has a direct connection to the quantisation condition. The addition of a Berry's phase of  $\pi$  shifts the quantisation condition by a half integer when compared to semiconductor systems (Eq. 1.16) [25] such that

$$\nu = \eta \left( N + \frac{1}{2} \right) \quad (1.20)$$

and therefore,

$$\rho_{xy} = \frac{h}{e^2} (\eta(N + 1/2))^{-1}, \quad (1.21)$$

where the degeneracy  $\eta = 4$  accounts for spin ( $\uparrow$  and  $\downarrow$ ), and valley ( $K$  and  $K'$ ) degeneracies. This leads to a characteristic  $\nu = 2, 6, 10, \dots$  sequence of plateaux unique to monolayer graphene.

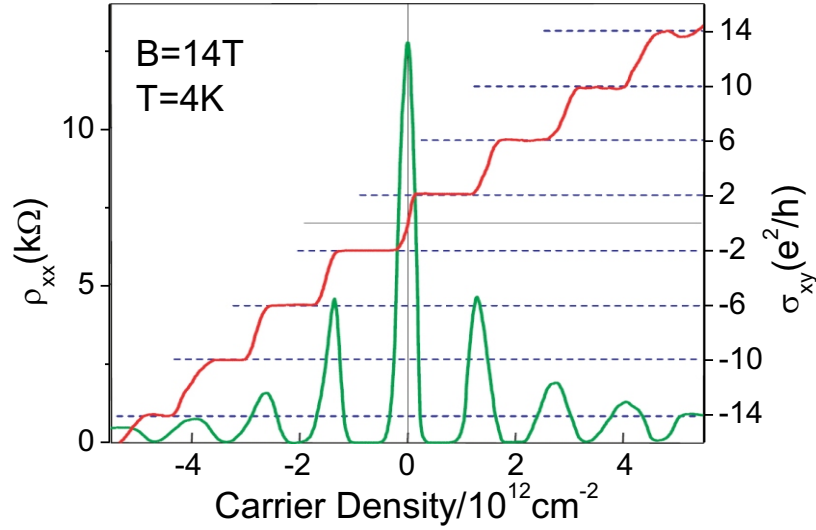


Figure 1.10: Quantum Hall effect in exfoliated graphene at a fixed magnetic field of 14 T. A back gate is used to sweep the carrier density through the Dirac point. Adapted from Ref [23].

### 1.3.4 Quantum Resistance Metrology

One Ohm is defined as the resistance between two points in a conductor such that an applied potential difference of one Volt will produce a current of one Ampere [26]. Before 1990 the way the Ohm was defined experimentally was through a set of wire resistors maintained at several labs throughout the world kept in oil baths at a constant temperature and pressure. The length of the wire would determine the resistance for which the preparation would often require adding or removing tiny amounts of metal so as to reach the desired resistance. These resistors were difficult to maintain at constant

resistances. Indeed, when a set of resistors in one lab were compared to those in other standards laboratories they could only be measured to a relative uncertainty of about one part in  $10^6$  [27]. The title of the seminal von Klitzing *et al.* paper; “New Method for High-Accuracy Determination of the Fine-Structure Constant Based on Quantized Hall Resistance”, makes clear the authors’ views on the significance to metrology of having a resistance defined purely by fundamental constants. Since 1990 the QHE has been the standard used to define the Ohm for which the precision is set by the amount of current one can pass through the Hall bar whilst still maintaining quantisation. Figure 1.11 shows recent work comparing the resistance quantisation of the  $\nu = 2$  plateau in graphene and GaAs. The measurements showed universality with a relative uncertainty dropping to  $8.6 \times 10^{-11}$  as the measurement current is increased to  $100 \mu\text{A}$ . This is limited by the quantum Hall breakdown current of the GaAs tested. To further improve upon these measurements we must study how the breakdown current behaves in systems with well defined quantum Hall states due to large cyclotron gaps (graphene and InSb) and large spin splitting (InSb). Chapters 4 and 5 study the high current limits of the QHE in InSb and graphene respectively and show how these limits vary with magnetic field, temperature and carrier density, as well as sample geometry and the electron-phonon coupling in the material.

### 1.3.5 Bootstrap Electron Heating Model

The breakdown of the quantum Hall effect is the subject of great theoretical and experimental interest. At present the theoretical model which seems to best describe the breakdown is that of bootstrap-type electron heating (BSEH) by Komiyama and Kawaguchi [29]. This model predicts a critical breakdown electric field,  $E_c$ , determined by the rate at which excited (“hot”) carriers can lose energy back to the lattice. Above  $E_c$  an infinitesimal fluctuation in the electron energy distribution grows rapidly and the



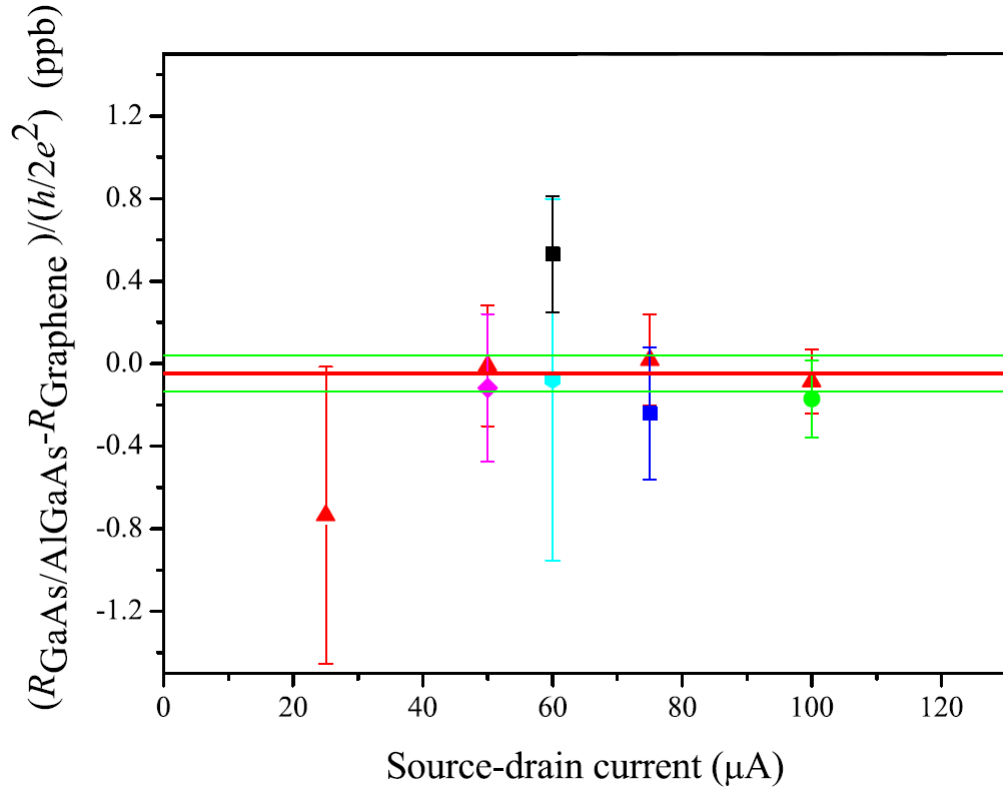


Figure 1.11: Universality test of the quantum Hall effect by measuring  $h/2e^2$  in the  $\nu = 2$  plateaux of graphene and GaAs. The relative difference between  $\rho_{xy}$  in the two systems is plotted as a function of measurement current. As the measurement current is increased the relative uncertainty reduces to  $8.6 \times 10^{-11}$ . Adapted from Ref. [28]

QHE breaks down in a transition to a dissipative state. The rate of energy loss  $P(T_e)$ , typically through electron-phonon interaction, is governed by the electron energy distribution which is characterised by an effective electron temperature  $T_e$ . When the rate of energy gain induced by and applied electric field is greater than the energy loss rate then the system is unstable, runaway heating occurs and the QHE breaks down. Chapters 3 and 4 apply this theory to the quantum Hall breakdown as observed in both InSb and graphene.

## 1.4 Carbon Nanotubes

Hollow cylinders of rolled up graphene, carbon nanotubes (CNTs) are mechanically stable and very strong [30]. Their electronic properties show extreme sensitivity to atomic configuration, leading to either metallic or semiconducting behaviour with band-gaps varying from zero to  $\gtrsim 1$  eV, and have been demonstrated to show near ballistic transport at room temperature. For over two decades CNTs have proved a fertile landscape for studying a rich variety of 1D physics. The following section is an overview of the basic structure and properties of CNTs, leading to the physics which give rise to excitonic fine structure and the Aharonov-Bohm effect which is predicted to dramatically modify the optical properties of CNTs [31, 32].

### 1.4.1 Origins of Carbon Nanotubes

The first evidence of the tubular nature of some nano-scale carbon allotropes is believed to have been published in the often cited but rarely read paper of Radushkevich and Lukyanovich [33]. The paper was not widely cited until recently due to the restriction of access of Russian journals to the west during the cold war and the fact that it was written in Russian, already a barrier to most. The transmission electron micrographs (TEM) which they describe appear to show tubes of carbon  $\sim 50$  nm wide made up of approximately 15-20 concentric sheets of graphene [34]. It was not until 1991 that CNTs became more widely acknowledged when they were observed by Iijima [35] (Fig.1.12) as a by-product of the electric discharge growth of fullerenes, another nano-carbon allotrope consisting of graphene sheets rolled into hollow spheres in pentagon-hexagon formations [36]. These were multi-walled carbon nanotubes (MWNTs) in that they were formed of multiple carbon shells. It was not until 1993 that two reports of single walled carbon nanotubes (SWNTs) were published back-to-back in *Nature* by Iijima and Ichihashi of NEC Japan [37] and Bethune *et al.* of IBM, California [38] (Fig. 1.12).

These SWNTs have a small diameter of typically 1 nm. The growth of CNTs however may date back over 400 years, as TEM imaging of the steel in Damascus blades, known for their exceptional mechanical properties and sharp cutting edge, revealed MWNTs incorporated into the structure [39].

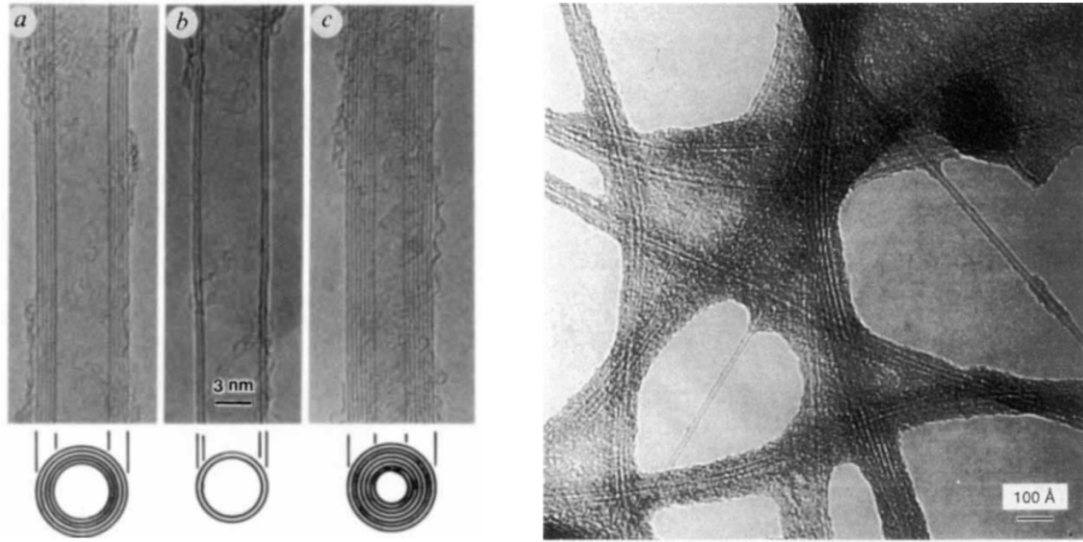


Figure 1.12: Transmission electron microscope imaging which resulted in the discovery of MWNTs (left [35]) and SWNTs (right [38]).

### 1.4.2 Carbon Nanotubes Structure

Since graphene is the basis of the microscopic structure of carbon nanotubes, they are often labelled in terms of the graphene lattice vectors. A SWNT is made by rolling up a single ribbon of graphene [40]. The direction it is rolled in relative to the lattice vectors ( $\mathbf{a}_1$  and  $\mathbf{a}_2$ ) and the width of the ribbon (circumference of the SWNT) are determined by the circumferential vector,  $\mathbf{C}$ , which connects two crystallographically equivalent sites on the graphene lattice which when rolled onto each other will join to make the tube, as described in figure 1.13. The structure of all SWNTs in this way may be completely specified simply by a pair of integers  $(n, m)$  which are contained in the circumferential

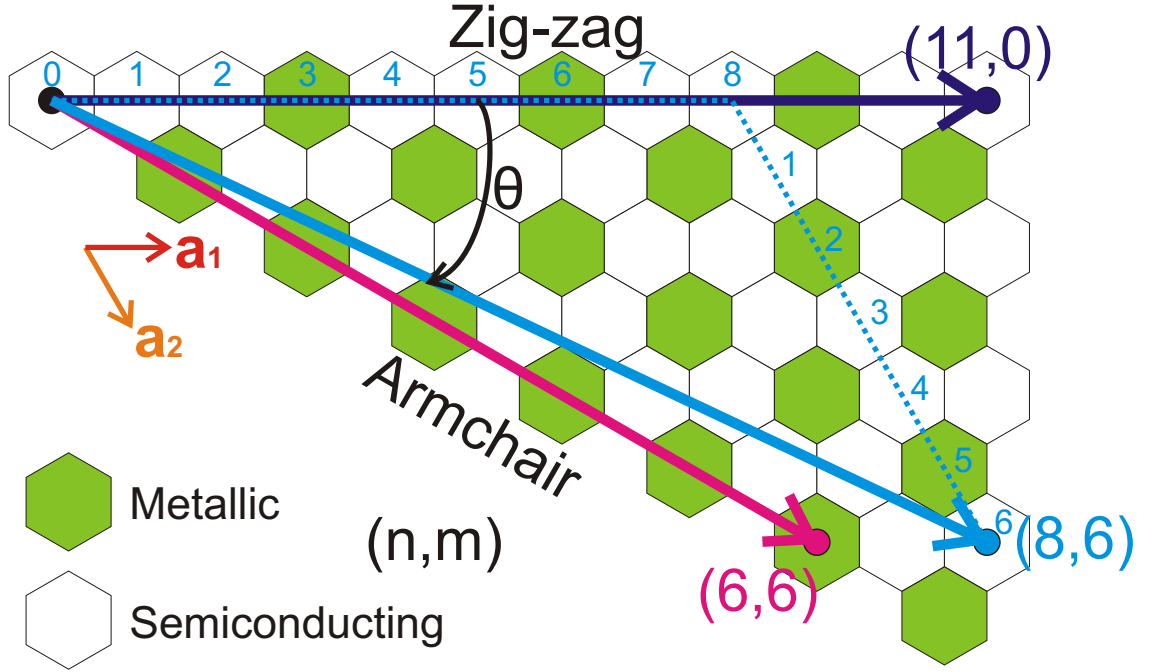


Figure 1.13: Chirality assignment and  $(n,m)$  notation of SWNTs. The chiral vector,  $\vec{C}$  (arrows), follows the circumference of the tube which for an  $(n,m)$  chirality tube is found by  $\vec{C} = n\vec{a}_1 + m\vec{a}_2$  (blue dots). The axis along the tube direction is perpendicular to  $\vec{C}$ . One third of CNT chiralities are metallic (green) with the condition  $n - m = 3l$ , with  $l$  integer.

vector,

$$\vec{C} = n\vec{a}_1 + m\vec{a}_2. \quad (1.22)$$

The diameter of the tube can be estimated trivially using

$$d = |\vec{C}|/\pi = \frac{\sqrt{3}a_0}{\pi} \sqrt{n^2 + nm + m^2}. \quad (1.23)$$

There is also an associated chiral angle,  $\theta$ , between  $\vec{C}$  and  $\vec{a}_1$  (the “zig-zag” direction), calculated using

$$\cos \theta = \frac{\vec{C} \cdot \vec{a}_1}{|\vec{C}| \cdot |\vec{a}_1|} = \frac{2n + m}{2\sqrt{n^2 + nm + m^2}} \quad (1.24)$$

where  $0 \leq |\theta| \leq 30^\circ$  due to the six-fold symmetry of the lattice. Two special cases arise from this notation:  $(n, 0)$  ( $\theta = 0^\circ$ ), known as zig-zag tubes, exhibiting a zig-zag pattern along the circumference, and  $(n, n)$  ( $\theta = 30^\circ$ ), known as armchair tubes which look like armchairs along the circumference (Fig. 3.1). These special cases are achiral, all other  $(n, m \neq n \neq 0)$  SWNTs are chiral (Fig. 3.1). The structure of a tube also determines the unit cell and the number of atoms within it. For this we can define the smallest lattice vector  $\mathbf{T} = t_1 \mathbf{a}_1 + t_2 \mathbf{a}_2$  which is perpendicular to  $\mathbf{C}$  and defines the translational period  $|\mathbf{T}| = t$  given by

$$t_1 = \frac{2m+n}{N_R}, \quad t_2 = -\frac{2n+m}{N_R}, \quad |\mathbf{T}| = t = 3a_0 \frac{\sqrt{n^2 + nm + m^2}}{N_R} \quad (1.25)$$

where  $N_R$  is the greatest common divisor of  $(2m+n)$  and  $(2n+m)$ . Therefore the unit cell of a SWNT is a cylinder of diameter  $d$  with a height  $t$ , (i.e.  $|\mathbf{C} \times \mathbf{T}|$ ) where the number of carbon atoms per unit cell  $N_C$ , can be defined in terms of  $n$  and  $m$  where

$$N_C = \frac{4(n^2 + nm + m^2)}{N_R}. \quad (1.26)$$

The number of hexagons per unit cell is  $Q = N_C/2$ .

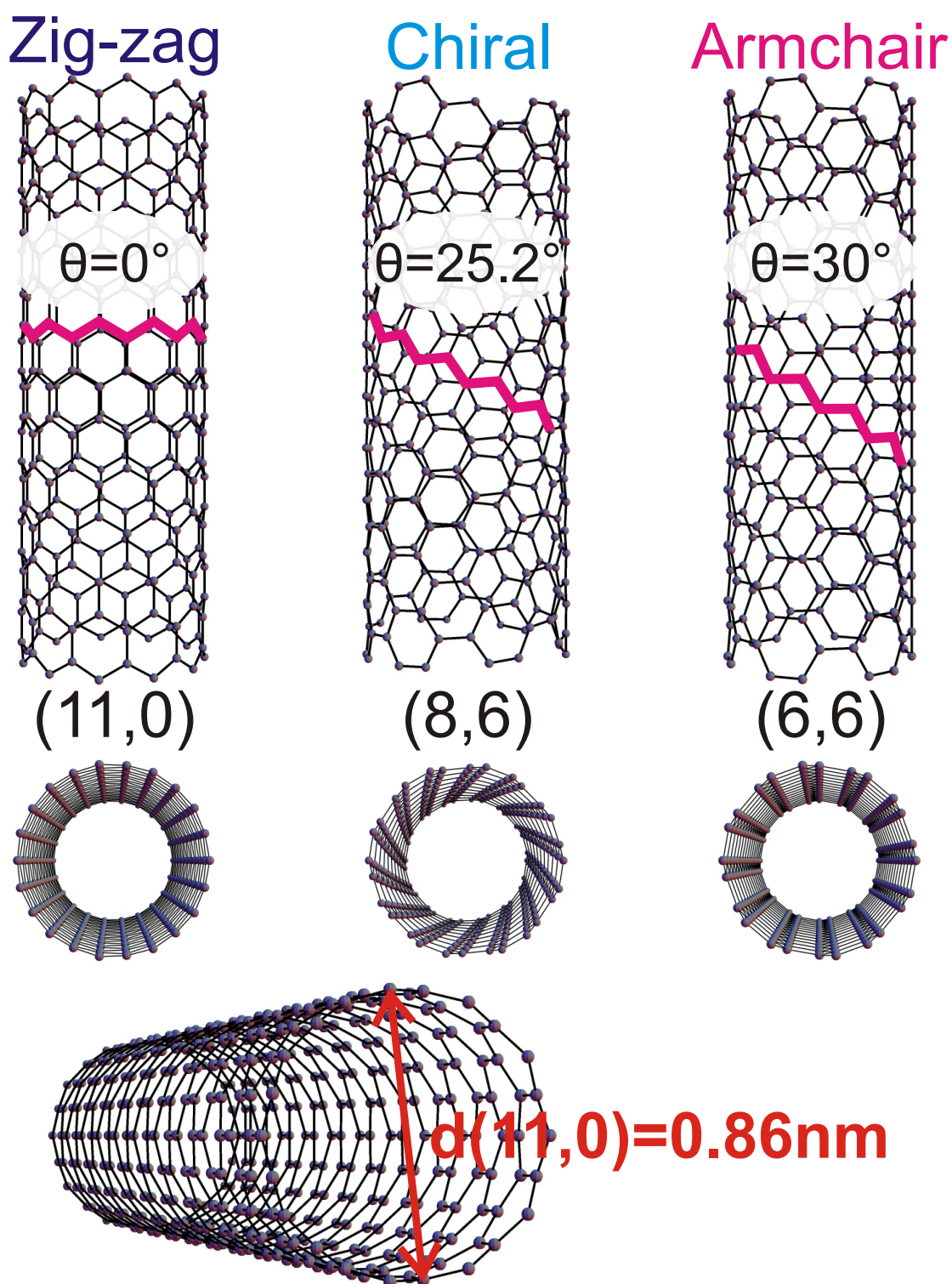


Figure 1.14: Top: The honeycomb structure of graphene folded with three different chiralities, representative of zig-zag, chiral, or armchair type CNTs. For clarity, the direction of the folding is shown by following a consecutive line of A-B-A-B... atoms (magenta). Bottom: The calculated diameter of an (11,0) chirality CNT.

### 1.4.3 Carbon Nanotube Bandstructure

#### Zone Folding Approximation

The reciprocal lattice vectors are obtained through the Fourier transform of the vectors  $\mathbf{C}$  and  $\mathbf{T}$ , yielding the circumferential ( $\mathbf{k}_\perp$ ) and axial ( $\mathbf{k}_\parallel$ ) wave vectors respectively given the definition [41],  $\mathbf{C} \cdot \mathbf{k}_\perp = \mathbf{T} \cdot \mathbf{k}_\parallel = 2\pi$  and  $\mathbf{C} \cdot \mathbf{k}_\parallel = \mathbf{T} \cdot \mathbf{k}_\perp = 0$ . These are defined in terms of the graphene reciprocal lattice vectors [42]

$$\mathbf{k}_\perp = \frac{2n+m}{QN_R} \mathbf{b}_1 + \frac{2m+n}{QN_R} \mathbf{b}_2 \quad (1.27)$$

$$\mathbf{k}_\parallel = \frac{-m}{Q} \mathbf{b}_1 + \frac{n}{Q} \mathbf{b}_2 \quad (1.28)$$

Periodic boundary conditions of electrons in a SWNT are imposed due their tubular nature resulting in the allowed wave vectors in the circumferential direction ( $\mathbf{k}_\perp$ ) to be quantised such that [40]

$$\Psi_{\mathbf{k}_\perp}(\mathbf{r} + \mathbf{C}) = e^{i\mathbf{k}_\perp \cdot \mathbf{C}} \Psi_{\mathbf{k}_\perp}(\mathbf{r}) = \Psi_{\mathbf{k}_\perp}(\mathbf{r}), \quad (1.29)$$

with the vector  $\mathbf{r}$  taken on the tube surface, i.e.

$$\mathbf{k}_\perp = \frac{2\pi}{|\mathbf{C}|} \cdot i = \frac{2}{d} \cdot i \quad (1.30)$$

where integer  $i$  takes values from  $(1 - Q/2)$  to  $Q/2$ . Along the nanotube axis the wave vectors  $\mathbf{k}_\parallel$  remain continuous (for an infinite tube). The allowed wave vectors (Fig. 1.15) of a SWNT can be viewed as a series of  $Q$  parallel (to  $\mathbf{k}_\parallel$ ) lines of length  $2\pi/t$  spaced every  $2/d$  in  $\mathbf{k}_\perp$  crossing the first Brillouin zone of graphene. The electronic band structure of a SWNT is calculated using a *zone-folding approximation*, by finding a superposition of the electronic bands of graphene from Equation 1.3 with the allowed

$\mathbf{k}$  vectors, and folding in  $k$ -space such that the bands form continuous lines, to give

$$E_{SWNT}^{\pm}(i, \mathbf{k}_{\parallel}) = E^{\pm}(i\mathbf{k}_{\perp} + \mathbf{k}_{\parallel}) \quad (1.31)$$

The resulting bandstructure of two chiralities are shown in Figure 1.15, showing that the chirality of a SWNT can determine whether it is semiconducting or metallic.

### Semiconducting and Metallic Bandstructures

When the bandstructure of a material has a bandgap between the valence band and the conduction band, it is a semiconductor, whereas if a finite density of states remains throughout the bandstructure the material will show metallic behaviour. Figure 1.15 shows two examples of SWNT bandstructure calculated using the zone-folding approximation. The bandstructure calculated for the (11,0) tube has a bandgap centred at  $\mathbf{k}_{\parallel} = 0$ , and the bandstructure of the (6,6) chirality tube shows two points of intersection and is metallic. The points of intersection occur when the lines of the allowed  $k$ -vectors cross the  $K$  point in the FBZ of graphene, where  $\mathbf{K} = (\mathbf{b}_1 - \mathbf{b}_2)/3$ . The condition for this crossing and thus for metallic behaviour is given by [40]

$$e^{i\mathbf{K} \cdot \mathbf{C}} = 1 \quad (1.32)$$

therefore,

$$(n - m) = 3l \quad (1.33)$$

where  $l$  is an integer. In general we have the following rule:

$$(n - m) = 3l + q, \quad q = \begin{cases} 0 & \text{metallic} \\ \pm 1 & \text{semiconducting.} \end{cases} \quad (1.34)$$



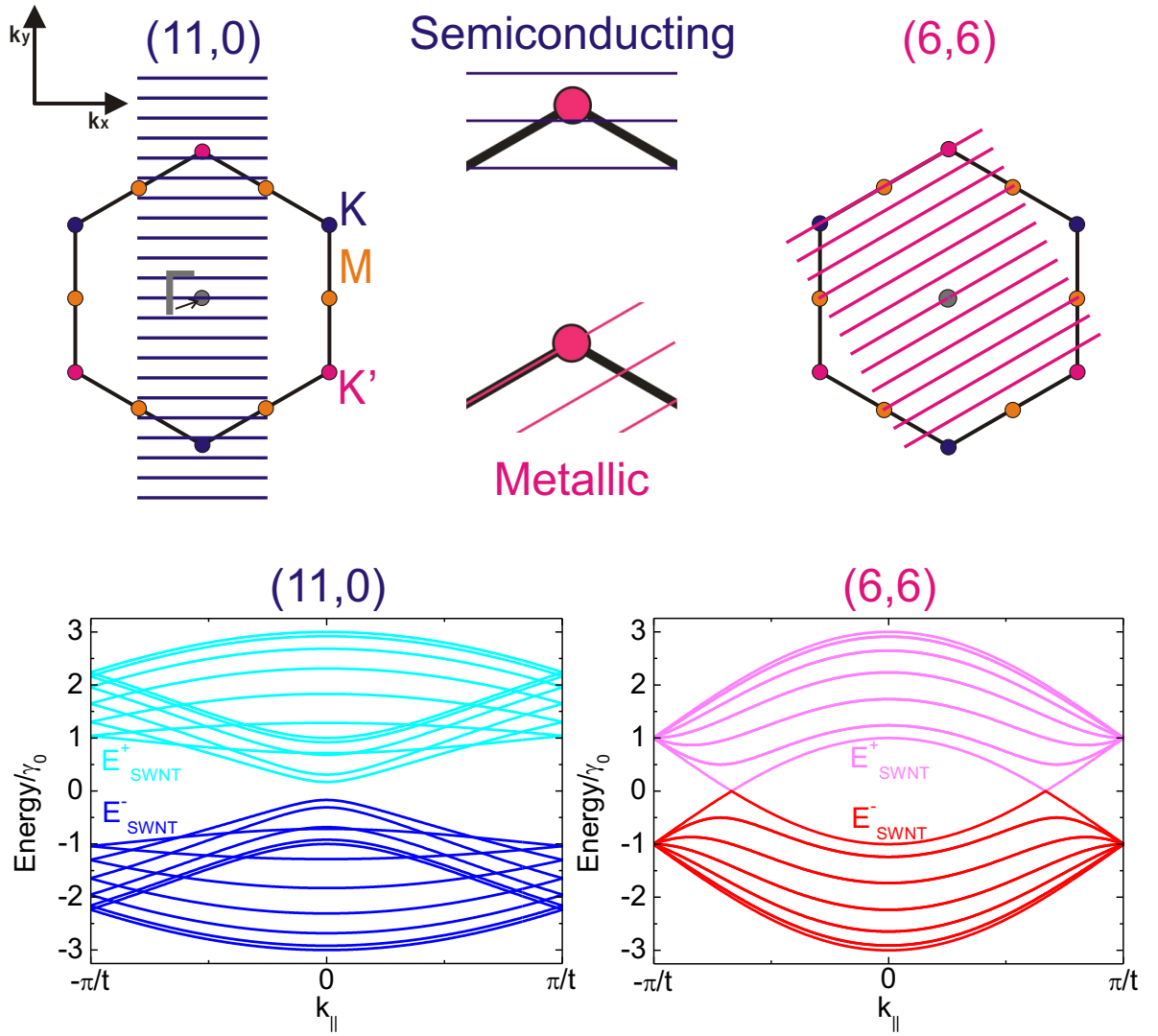


Figure 1.15: top) The first Brillouin zone of (11,0) and (6,6) chirality SWNTs representing metallic and semiconducting properties respectively. If the allowed  $k$ -vectors of the tube (do not) cross the  $K$  point of the graphene FBZ then (semiconducting) metallic behaviour is observed. bottom) Band structure calculations for (11,0) and (6,6) chirality SWNTs using a zone-folding approximation with  $\epsilon_{2p} = 0$  and  $s_0 = 0$ .

One in three chiralities is metallic. The condition  $(n - m) = 3l$  is always true for armchair nanotubes and for  $(n, 0)$  zig-zag tubes where  $n$  is a multiple of 3. When the Fermi energy lies in the vicinity of the  $K$  point for metallic tubes the energy dispersion follows that which is described in Equation 1.5, where  $v_F = \frac{3}{2}\gamma_0 a_0 / \hbar \approx 8 \times 10^5 \text{ ms}^{-1}$  typically using  $\gamma_0 = 2.9 \text{ eV}$  [40]. For semiconducting nanotubes the dispersion relation

close to  $E_F$  becomes

$$E_i^\pm(k_\parallel) \approx \pm \frac{3a_0}{2} \gamma_0 \sqrt{\left(\frac{2\pi}{|\mathbf{C}|}\right)^2 + \left(i \pm \frac{1}{3}\right)^2 + k_\parallel}. \quad (1.35)$$

Which leads to an energy gap,  $E_g$ , opening at the Fermi level (Fig. 1.15) since

$$E_{i=0}^+(k_\parallel = 0) - E_{i=0}^-(k_\parallel = 0) = \frac{2\pi a_0 \gamma_0}{|\mathbf{C}|} = E_g. \quad (1.36)$$

The bandgap decreases for increasing tube diameter since  $E_g \propto \frac{1}{|\mathbf{C}|} = \frac{1}{\pi d}$ , which in the limit of a very large diameter tube reduces to zero as we recover the graphene bandstructure. A typical value for an (8,6) tube with  $d = 0.96$  nm, is calculated to be 0.86 eV.

### Density of States

The density of states (DOS) is the number of electron states available per unit energy and is a key quantity in determining the electronic and optical properties of a system. The DOS varies dramatically as a function of the dimensionality of the system (Fig. 1.16). In three dimensions the DOS increases as the square root of the energy. When electrons are spatially confined to two dimensions in a semiconductor quantum well (with massive bands), the dependence becomes step-like. One dimensional systems, such as semiconductor nanowires [43], are characterised by a set of peaks in the DOS as a function of energy, with high-energy tails proportional to  $E^{-1/2}$ . Finally, the DOS for zero-dimensional systems such as quantum dots, where there is confinement in all three spatial dimensions, becomes a series of delta functions where the energy separation is dependent on the size of the dot.

Owing to the one dimensional nature the DOS of a carbon nanotube is a series of van Hove singularities, spikes close to the band edges (Fig. 1.17), as found both theoretically

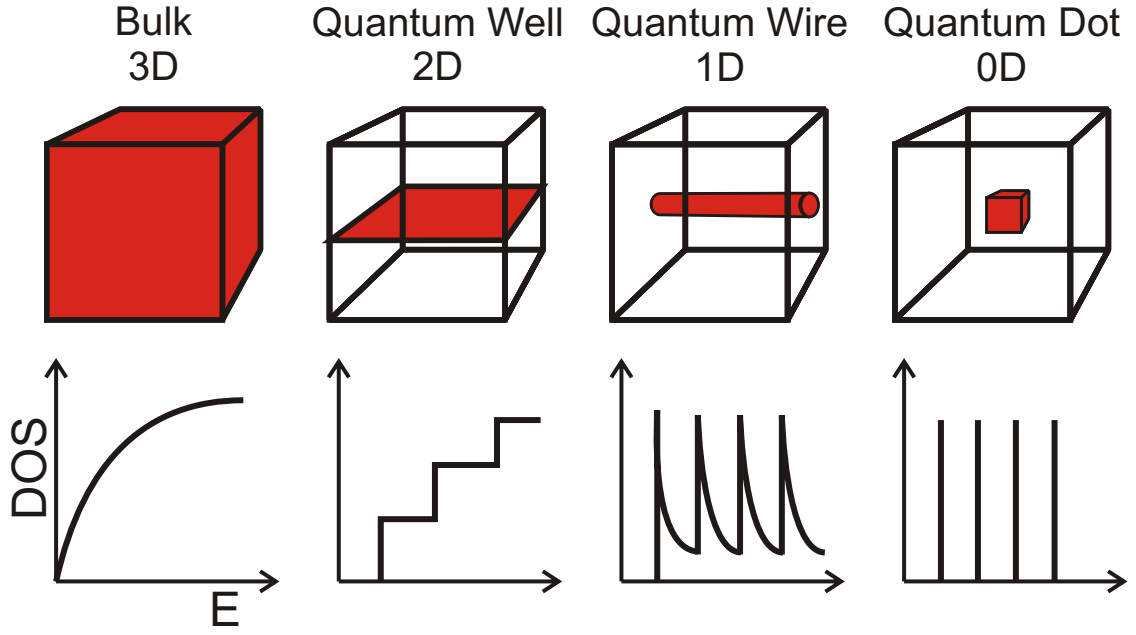


Figure 1.16: Density of states as a function of dimensionality.

[44] and through scanning tunnelling spectroscopy experiments [45]. Figure 1.17 shows the calculated DOS for semiconducting armchair and metallic zig-zag SWNTs using the theoretical description in Ref. [44] which assumes a linear dispersion relation around the  $K$  point, as described in Equation 1.5, and therefore is only an approximation. Higher order corrections to the bandstructure include next nearest neighbour calculations and trigonal warping [46]. Their approximation calculates the DOS,  $n(E)$  based on the diameter where the final result is given by [44]

$$n(E) = \frac{4\sqrt{3}a_0}{\pi^2 d \gamma_0} \sum_{i=-\infty}^{\infty} g(E, E_i), \quad (1.37)$$

where  $E_i = |3i - q| \frac{a_0 \gamma_0}{d}$ , for integer  $i$ , and

$$g(E, E_i) = \begin{cases} \frac{|E|}{\sqrt{E^2 - E_i^2}} & |E| > |E_i| \\ 0 & |E| < |E_i| \end{cases} \quad (1.38)$$

The van Hove singularities lie at values of  $E_i$ . For clarity the singularities in semi-conducting SWNTs are labelled  $E_i^\pm$  and for metallic tubes,  $M_i^\pm$  for  $i > 0$  as described in Figure 1.17. Electronic transitions can occur between singularities which are labelled  $E_{ij}$  for transitions between  $E_i$  and  $E_j$ . This has a very dramatic effect on the optical properties which are described below.

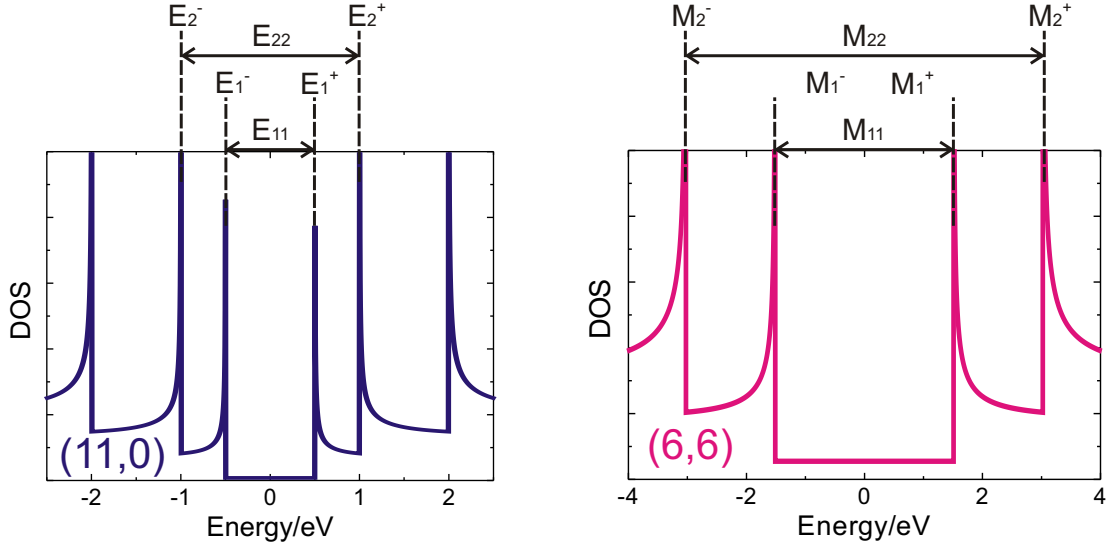


Figure 1.17: Density of states for (11,0) and (6,6) chirality CNT. Also shown are the relevant energy levels and energy gaps described in the text. It is worth noting the difference in scales here and that the magnitude of the  $M_{11}$  transition is over twice that of the  $E_{11}$ .

#### 1.4.4 Optical Properties of SWNTs

##### Optical Transitions

Van Hove singularities in the DOS mean carbon nanotubes exhibit strong optical absorption at well defined energies corresponding to  $E_{ij}$  transitions. Due to the chirality dependence of the DOS, probing these optical transitions is an accurate method for determining the structure of any given nanotube.

Due to intertube energy transfer, in particular from semiconducting SWNTs to metallics, the bandgap photoluminescence (PL) expected from SWNTs is quenched in nanotube bundles [47]. It is only when SWNTs are spatially isolated through low density growth [48], or through surfactant coating in solution [49] that the predicted bandgap PL is observed. In a typical PL experiment a semiconducting SWNT is optically excited across the  $E_{22}$  transition, the excited carriers then decay through phonon relaxation and PL occurs across the  $E_{11}$  transition. Each chirality has unique optical resonances, and as such by varying the excitation energy and measuring the PL emission through photoluminescence excitation (PLE) spectroscopy, the chirality of an individual tube or ensembles of tubes can be determined [50]. The chirality, in particular the diameter, dependence of the optical transitions is shown in what is known as a Kataura plot [50] (Fig. 1.18).

In all optical transitions linear momentum is conserved ( $\Delta\mathbf{k} = 0$ ). The selection rules [51] governing the conservation of angular momentum require that for light polarised along the nanotube axis only  $E_{11}$ ,  $E_{22}$ ,  $E_{33}$  and higher order  $E_{ij}(i = j)$  transitions are allowed. For light polarised perpendicular to the tube axis only  $E_{ij}(i \neq j)$  transitions such as  $E_{21}$  are allowed. A strong depolarisation, or antenna, effect to the geometry of the SWNT causes the optical absorption perpendicular to the axis to be strongly suppressed [31]. Optical transitions across van Hove singularities are a single particle approximation however. Confinement of carriers to 1D requires many-body effects to be taken into account, as will be described below.

### Excitons in SWNTs

Many-body effects play an important role in one-dimensional systems which impact strongly on their optical properties. The large Coulomb interaction for carriers confined to a dimension of  $\sim 1$  nm means that excitons, a bound pair of a photoexcited electron

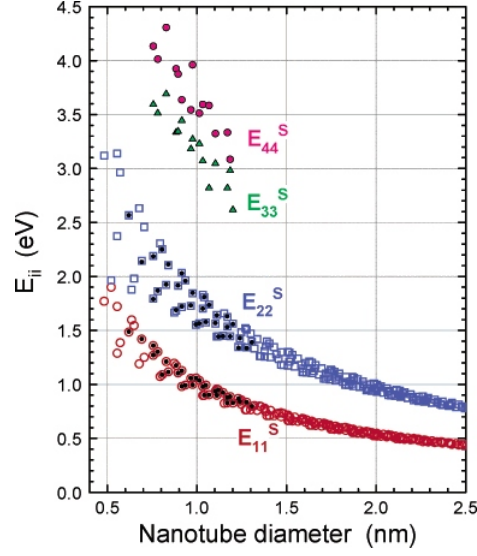


Figure 1.18: The theoretical (open) and experimentally observed (filled) optical transitions of semiconducting SWNTs as a function of diameter, as measured in Ref. [50]. Each chirality has well defined set of transitions.

and a hole, are exceptionally strongly bound in SWNTs. Semiconductors such as Si and III–V compounds have exciton binding energies of order  $\sim 10\text{meV}$ , and as such excitonic effects are only observed at low temperatures. In a SWNT the electron-hole binding energy can be as large as  $1\text{eV}$  [52], and as such, excitonic effects must be included in any explanation of the optical properties of SWNTs [53].

The wave vector of the electron and hole are defined as  $\mathbf{k}_e$  and  $\mathbf{k}_h$  respectively, where the wave vector at the centre of mass of the exciton is  $\mathbf{k}_{ex} = (\mathbf{k}_e - \mathbf{k}_h)/2$ . Conservation of linear momentum dictates that only excitons with  $\mathbf{k}_{ex} = 0$  are optically active (bright) i.e. they can recombine through the emission of a photon, all others with  $k_{ex} \neq 0$  are optically inactive (dark) as shown in Figure 1.19.

Each individual electron or hole may have spin  $\uparrow$  or  $\downarrow$ . An exciton has net spin,  $S$ , where spins aligned parallel ( $S = 1$ ) or antiparallel ( $S = 0$ ) form triplet and singlet states respectively. The triplet exciton is optically inactive due to the non-zero net spin. Therefore accounting for spin degeneracy results in four possible excitons, one bright

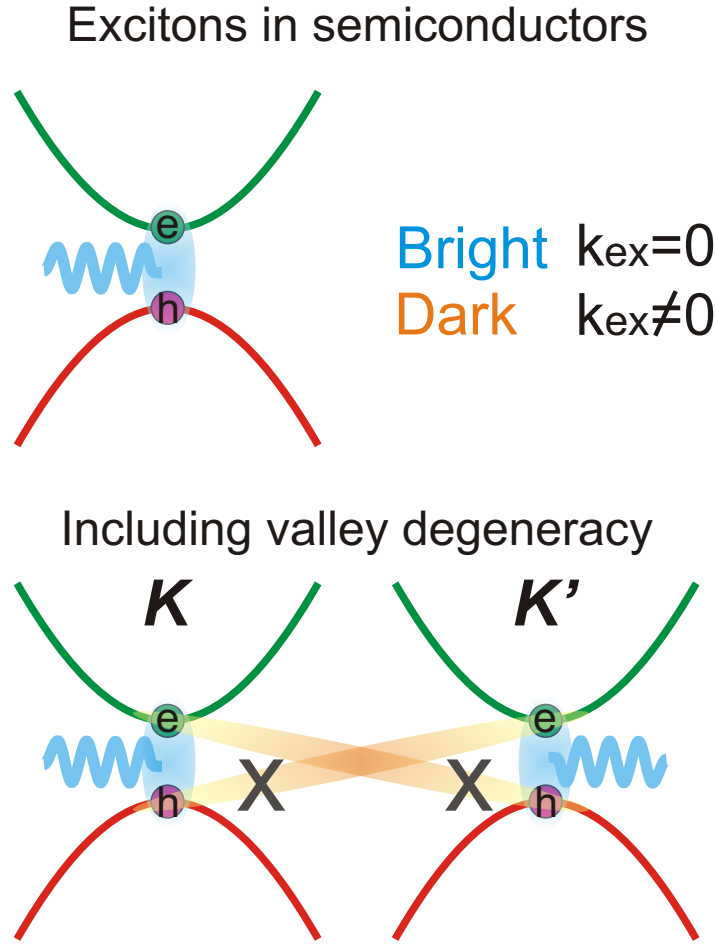
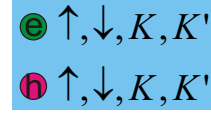


Figure 1.19: Overview of the selection rules for excitons. Top: A singlet exciton with  $k = 0$ . When  $k_c \neq k_v$ ,  $k_{ex} \neq 0$ , the resulting exciton is optically inactive, or dark. Bottom: Four different electron-hole configurations where intervalley excitons are optically inactive and only the direct ( $KK$  and  $K'K'$ ) transitions are bright.

and three dark.

The presence of two valleys  $K$  and  $K'$  as well as spin in SWNTs results in 16 possible exciton states [54]. The complete set of exciton wavefunctions are detailed in Figure 1.20. The nomenclature  $|KK'\rangle$  represents an electron in the conduction band at the  $K$  point and the hole in the valence band at the  $K'$  point. The states are classified as triplet or singlet states depending on the spin, as described above. Singlet states where the

## Spin Degeneracy



$$\text{Spin Triplet} \quad \frac{1}{\sqrt{2}} \begin{cases} |\uparrow\uparrow\rangle \\ |(\uparrow\downarrow) + (\downarrow\uparrow)\rangle \\ |\downarrow\downarrow\rangle \end{cases}$$

$$\text{Spin Singlet} \quad \frac{1}{\sqrt{2}} |(\uparrow\downarrow) - (\downarrow\uparrow)\rangle$$

## Valley Coupling

$$\text{Doublet} \quad |K, K'\rangle, \quad |K', K\rangle$$

$$\text{Coupled Singlets} \quad \begin{aligned} &\frac{1}{\sqrt{2}} |(K, K) - (K', K')\rangle \\ &\frac{1}{\sqrt{2}} |(K, K) + (K', K')\rangle \end{aligned}$$

Figure 1.20: The spin and valley wavefunctions which make up the sixteen possible exciton states in a carbon nanotube.

electron and hole are in different valleys,  $|KK'\rangle$  and  $|K'K\rangle$ , can form an exciton but decay non-radiatively [52]. Singlet states containing an electron-hole pair in different valleys are uncoupled, whereas the other states,  $|KK\rangle$  and  $|K'K'\rangle$ , are coupled into even-parity (dark) and odd-parity (bright) combinations where a coulomb-induced splitting is expected [55] between the bright state and the lower energy dark state. The spin triplet states are similarly split with the inclusion of valley degeneracy, and remain dark due to the net spin. Of all 16 possible exciton states only the odd-parity valley bonding state is bright and the other 15 are dark. However, symmetry breaking effects, such as the application of a magnetic field, are able to brighten some previously dark states. The



presence of a number of low lying dark states is important for potential applications of nanotubes in optical devices as such states dramatically reduces the PL efficiency of an isolated tube [40].

### 1.4.5 Magnetic Field Effects in SWNTs

#### Single Particle Picture

When a magnetic field is applied parallel to the tube axis the bandstructure is predicted to change dramatically. This change is due to the addition of a phase factor to the circumferential component of the wavefunction,  $\Psi_{k_\perp}$ , which is varied periodically with applied magnetic flux threading the nanotube cross section. This phenomenon was first described theoretically by Aharonov and Bohm in 1959 [56] and predicted in carbon nanotubes by Ajiki and Ando in 1993 [57]. The bandgap is expected to oscillate with applied magnetic flux where the period of oscillation is  $\phi_0 = e/h$ . In semiconducting nanotubes the bandgap will close and reopen in a complete oscillation, whereas the addition of an Aharonov-Bohm phase will open a bandgap in metallic tubes [31]. The magnetic flux dependence of the bandgap of a semiconducting nanotube is given by

$$E_g(\phi) = \begin{cases} E_0 \left| 1 - 3\frac{\phi}{\phi_0} \right| & (0 \leq \phi \leq \frac{\phi_0}{2}) \\ E_0 \left| 2 - 3\frac{\phi}{\phi_0} \right| & (\frac{\phi_0}{2} \leq \phi \leq \phi_0) \end{cases} \quad (1.39)$$

where  $E_0 = E_g(\phi = 0)$  as defined in equation 1.36. The initial bandgap continuously decreases with increasing magnetic flux and completely closes at  $\phi/\phi_0 = 1/3$ . In a metallic tube, a bandgap will open defined by

$$E_g(\phi) = \begin{cases} 3E_0 \frac{\phi}{\phi_0} & (0 \leq \phi \leq \frac{\phi_0}{2}) \\ 3E_0 \left| 1 - 3\frac{\phi}{\phi_0} \right| & (\frac{\phi_0}{2} \leq \phi \leq \phi_0) \end{cases} \quad (1.40)$$

the threading of  $\phi_0$  through tubes of 1nm, 10nm, 20nm and 40nm corresponds to 5325T, 53T, 13T and 3T respectively.

### Aharonov-Bohm Effects on Exciton Fine Structure

Moving on from the single particle model of the bandstructure, an applied magnetic flux threading a nanotube will also have a dramatic effect on the exciton fine structure. Figure 1.21 describes the energy levels of the  $KK$  and  $K'K'$  spin-singlet exciton energy levels with and without an applied magnetic field. At zero magnetic field the  $K$  and  $K'$  valleys are degenerate and  $K$  and  $K'$  exciton states are mixed in even-parity and odd-parity linear combinations. The odd-parity state,  $X^b$ , is optically active and has a higher energy than the dark state,  $X^d$ . The amount of splitting at zero field,  $\Delta_x$  is governed by the electron-hole interaction strength [55] and is typically a few meV.

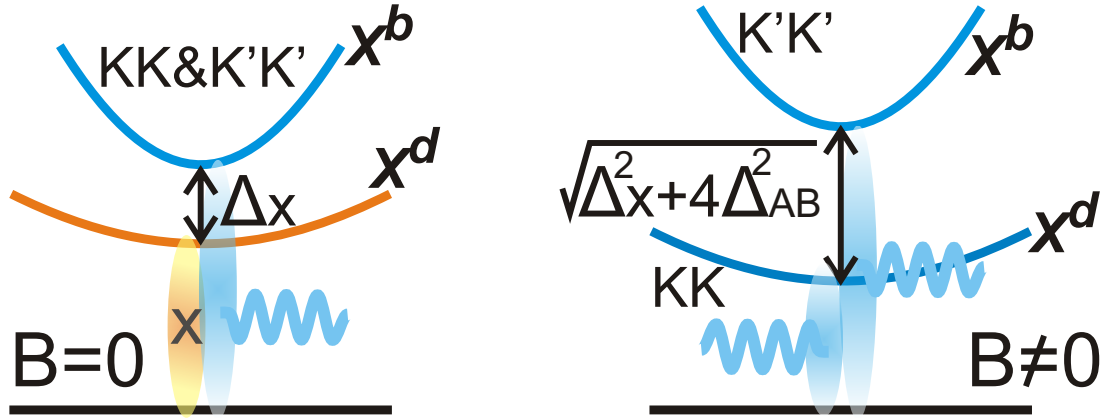


Figure 1.21: Schematic for the energy levels of the bonding ( $X^b$ ) and antibonding ( $X^d$ ) superpositions of the  $KK$  and  $K'K'$  exciton states. Orange transitions represent dark states and blue represents bright states. The black line is the ground state.  $\Delta_x$  is the zero-field Coulomb-induced splitting and  $\Delta_{AB}$  is the Aharonov-Bohm-induced shift. In an applied magnetic field both states become optically active.

When a magnetic field is applied the degeneracy between the  $K$  and  $K'$  valleys is lifted [32] and the two states split (Fig. 1.22). With increasing magnetic field the energy of the  $K'K'$  ( $KK$ ) state increases (decreases) by an amount,  $\Delta_{AB}$ , determined

by the Aharonov-Bohm phase which can be related to the single particle picture by  $\Delta_{AB} = E_g(\phi) - E_0$ . At high enough applied magnetic field when  $\Delta_{AB} \gg \Delta_x$ , the lower energy  $X^d$  becomes optically active and two peaks with equal oscillator strength are expected [32]. Accurate experimentally determined values of  $\Delta_x$  and  $\Delta_{AB}$  are essential for determining the exciton fine structure. Chapter 4 describes experimental work studying the magnetic field dependence of exciton fine structure through individual carbon nanotubes photoluminescence at magnetic fields up to 30T where the model above, whilst being a good description of pristine nanotubes, must be extended to include defect states and impurities.

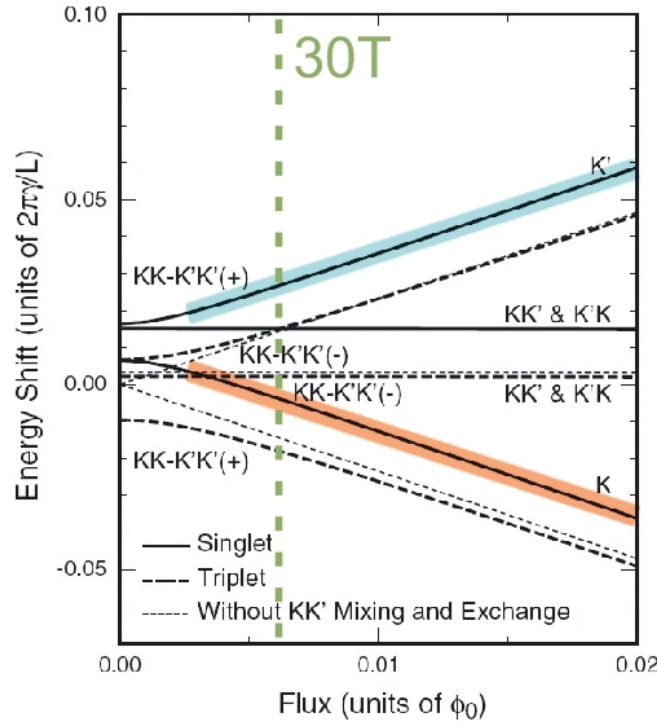


Figure 1.22: Magnetic field dependence of the exciton energy levels for singlet and triplet states as predicted by Ando [32]. Highlighted is the predicted magnetic field dependence of the intra-valley spin-singlet excitons  $X_b$  (blue) and  $X_d$  (orange). Adapted from Ref. [32].

## Chapter 2

# Experimental Methods

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This chapter introduces some of the growth, processing and characterisation techniques used for low-dimensional nanomaterials. A typical fabrication and electrical characterisation procedure for a two-dimensional crystal is described. Finally, the solution processing and optical characterisation of carbon nanotube samples will be outlined.

## 2.1 Graphene Synthesis

A large part of the rapid progression of graphene research is due to the relative ease and low cost of fabrication of high-quality samples. Early devices [58, 59] were fabricated using a top-down approach from peeling layers from bulk graphite, typically Highly Oriented Pyrolytic Graphite (HOPG). Future synthesis of graphene will depend on the individual requirements of the particular application with respect to factors such as mobility, size and substrate, which are strongly dependent on the production method. Below, the most common top-down and bottom-up fabrication techniques are described.

### Mechanical Exfoliation

To date the highest quality graphene devices have been derived from flakes mechanically exfoliated from graphite. Micromechanical exfoliation refers to the ability of graphite, and other layered materials, to be cleaved into layers by gently rubbing against a surface, such as when writing with a pencil. The process commonly referred to as the “Scotch tape” method, begins with an adhesive tape pressed onto a clean graphite surface and being peeled off. This leaves large graphite flakes containing tens or hundreds of atomic layers. A second piece of tape is pressed onto the peeled graphite, effectively thinning all the flakes. This is repeated several times, by which time some of the flakes will contain a single atomic layer.

The flakes are transferred to a Si/SiO<sub>2</sub> substrate by simply pressing on the surface and removing the tape. Flakes which are sufficiently thin add to the optical path of light reflected from the underlying silicon, creating an interference effect which gives rise to a very slight, but visible, contrast between the bare wafer and the flakes [60]. To maximise this effect the thickness of the SiO<sub>2</sub> layer is crucial, with peak contrast in visible light occurring at thicknesses of 300 nm and 100 nm. Figure 2.1a shows a large flake of graphene/graphite on Si/300nm SiO<sub>2</sub>. In this example the number of

layers of a flake can be counted by looking for the varying contrast. With thickness ranging from 1-7 atomic layers, there is a clear transition between different regions of the flake. Following initial visible characterisation the thickness can be confirmed by Raman spectroscopy [61] and magnetotransport.

The size of monolayer flakes initially were on the scale of a few microns. Using a less flexible tape and taking care to thoroughly clean the substrate including oxygen plasma etching single monolayer crystals may extend over hundreds of microns as can be seen in Figure 2.1b.

The main advantage of exfoliated graphene is the high quality, with many properties far exceeding those of any other material [62]. Of particular importance is the minimisation of substrate interaction as charge impurities and phonon scattering in SiO<sub>2</sub> [63], and substrate surface roughness [64], have been shown to dramatically reduce device performance. By placing graphene on insulating hexagonal boron nitride (hBN) substrates [65] or removing the substrate altogether and suspending the graphene [66], many of these extrinsic effects can be eliminated. Suspended devices and those on hBN are approaching the theoretical limits predicted for room-temperature electron mobility,  $1.5 \times 10^5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  [67] (theory  $\sim 2 \times 10^5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  [68]). In the case when long range disorder is removed, such as that due to charged impurities, the room temperature charge carrier mobility of graphene is limited by weak electron-phonon scattering from so-called flexural (out-of-plane) phonons [68]. A Young's modulus of 1 TPa and intrinsic strength of 130 GPa makes it the strongest material ever tested [69], and high thermal conductivity of over  $3000 \text{ W m K}^{-1}$  [70]. Exfoliated graphene will continue to be the benchmark system for driving fundamental graphene research forward, however the significant lack of scalability and control prevents large scale applications. Graphene will meet its true potential when mass produced graphene approaches these standards.

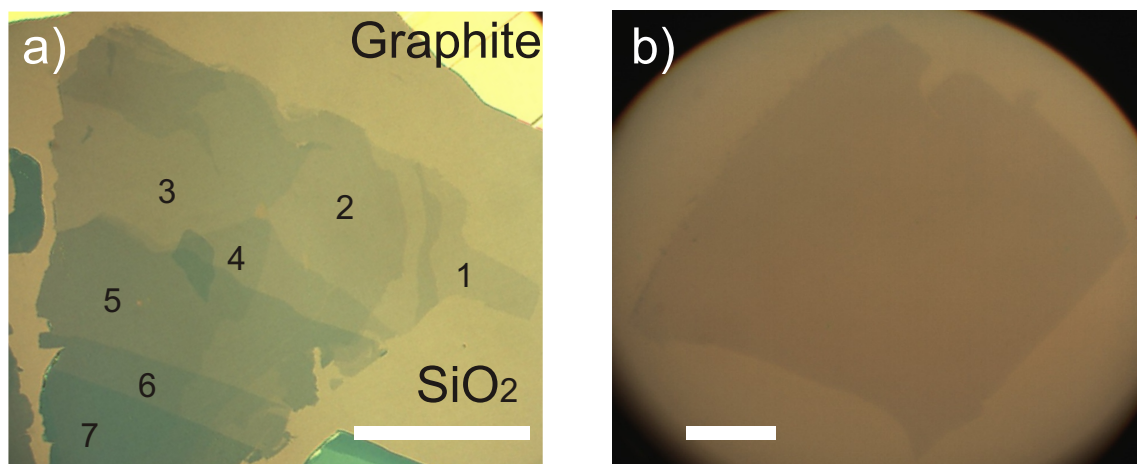


Figure 2.1: (a) Optical characterisation of an exfoliated flake on  $\text{SiO}_2$ . The numbers represent the thickness of the graphene in terms of atomic layers as estimated by the contrast ratio with from the substrate. Dark blue regions represent semi-transparent graphite flakes with the yellow areas being thicker reflective graphite. (b) A large predominantly monolayer exfoliated flake achieved by plasma etching the  $\text{SiO}_2$  before transfer. Scale bars are  $25\ \mu\text{m}$ .

### Liquid Phase Exfoliation

For some potential applications, such as composite materials, conductive paints and transparent electrodes, high mobility is often a secondary requirement. Liquid phase exfoliation (LPE) [71] is the dispersion of a layered material such as graphite [72, 73], into a solvent. This allows the subsequent deposition of flakes from solution onto a substrate or the inclusion into a composite material by blending with polymer solutions or other materials. These can be made by sonication of graphite powder in organic solvents, such as N-methylpyrrolidone (NMP), or in aqueous solutions using surfactants like sodium dodecylbenzene sulfonate (SDBS). Such solutions may be further enhanced by density gradient ultracentrifugation [74] to control the thickness of flakes. The transport properties of large areas of LPE graphene are dominated, and limited, by the percolation of charge between the small ( $\sim 1\ \mu\text{m}$ ) sized flakes, however such methods can and have been scaled to produce graphene by the tonne [75].

### Chemical Vapour Deposition

Large area synthesis of graphene is possible on transition metal crystallites by chemical vapour deposition (CVD) [76–78], with recent advances allowing growth of 30-inch graphene films on flexible copper substrates [79]. A typical growth processes [78] first involves annealing a thin Cu film in  $H_2$  at 1000 °C, then a carbon containing source (typically  $CH_4$ ) is passed through the growth chamber, and the sample is finally cooled in  $H_2$  gas. A thin layer of polymer is attached to the graphene and the Cu is subsequently dissolved in aqueous ammonium persulphate solution [79]. The graphene on polymer may then be transferred to any given substrate and the polymer removed. As well as its large area and the ability to transfer onto a variety of substrates, the end material has been shown to have properties highly amenable for transparent electrodes with sheet resistance as low as  $\sim 30 \Omega \square^{-1}$  at 90 % transmission superior to commercial indium tin oxide (ITO) transparent electrodes [79]. The strength and flexibility of graphene, areas in which ITO is lacking, means that this method could successfully be applied to bendable and wearable optoelectronic devices in the near future.

### Epitaxial Growth on SiC

Another potential method for large area growth of high quality graphene is through the high temperature annealing of silicon carbide, leading to the sublimation of silicon atoms. For more than a century graphite has been grown using silicon carbide [80], and recently controlled growth of graphite on carbon and silicon terminated faces of high quality SiC crystals [81] has gained interest with the rise graphene research. Turbostratic stacked graphite on the carbon terminated face of SiC [82] has been shown to behave as monolayer graphene as the random orientation effectively electronically decouples the layers [83]. Growth on the silicon terminated face of SiC in argon at atmospheric pressure can create high quality, predominantly monolayer graphene [84]. The graphene grows



above a buffer layer of carbon which heavily n-dopes the graphene to carrier densities  $\gtrsim 10^{13} \text{ cm}^{-2}$ , which may be reduced using polymer gating techniques [85]. Graphene on Si terminated SiC has shown promise as a quantum Hall effect electrical resistance standard [86] as well as wafer-scale high frequency transistors [87].

## 2.2 Device Fabrication

When studying new nanostructured materials, in particular their electronic and optoelectronic properties, it is commonly required to design and fabricate bespoke and novel devices. Such devices often need to be positioned and defined with sub-micron precision, and as such require the use of high resolution lithography and imaging. In this section I will describe the processes involved in identifying, designing and fabricating a typical nanostructured device from a single crystal of monolayer  $\text{MoS}_2$ .

Whilst graphene has an incredibly high intrinsic room-temperature carrier mobility ( $\mu > 100,000 \text{ cm}^2/\text{Vs}$ ) compared to silicon ( $\mu \sim 1,000 \text{ cm}^2/\text{Vs}$ ), the lack of a bandgap means that exploiting graphene in some electronic applications, in particular optoelectronics, is still difficult. For many of these applications a 2D semiconductor is vital. Two dimensional semiconductors have recently gained much interest in the nanotechnology community [88, 89]. The greatest potential is shown by atomically thin crystals of transition metal dichalcogenides (TMDCs), including  $\text{MoS}_2$ , which possess electronic bandgaps ranging from 1-2 eV. These 2D semiconductors retain many of the advantages of graphene such as high mechanical strength and high optical transparency which are desirable for flexible and transparent electronics. Properties of bulk TMDCs have been studied widely, however like graphene the material characteristics are expected to change dramatically from the bulk to 2D monolayer and bilayer crystals.

### 2.2.1 MoS<sub>2</sub> Bandstructure

In the bulk, molybdenum disulphide is a semiconductor with an indirect bandgap of 1.29 eV [90, 91] (Fig. 2.2a). It is built up from stacks of units of S-Mo-S (Fig. 2.2) bonded by van der Waals forces. One unit of S-Mo-S is stable and is known as monolayer MoS<sub>2</sub>. The properties of monolayer MoS<sub>2</sub> differ considerably from those of the bulk, where bandstructure calculations [91] show that it is a direct gap semiconductor (Fig. 2.2b). Photoluminescence experiments have shown that the band gap of monolayer MoS<sub>2</sub> is 1.9 eV with a significantly enhanced quantum yield over multi-layered crystals due to its direct gap [90].

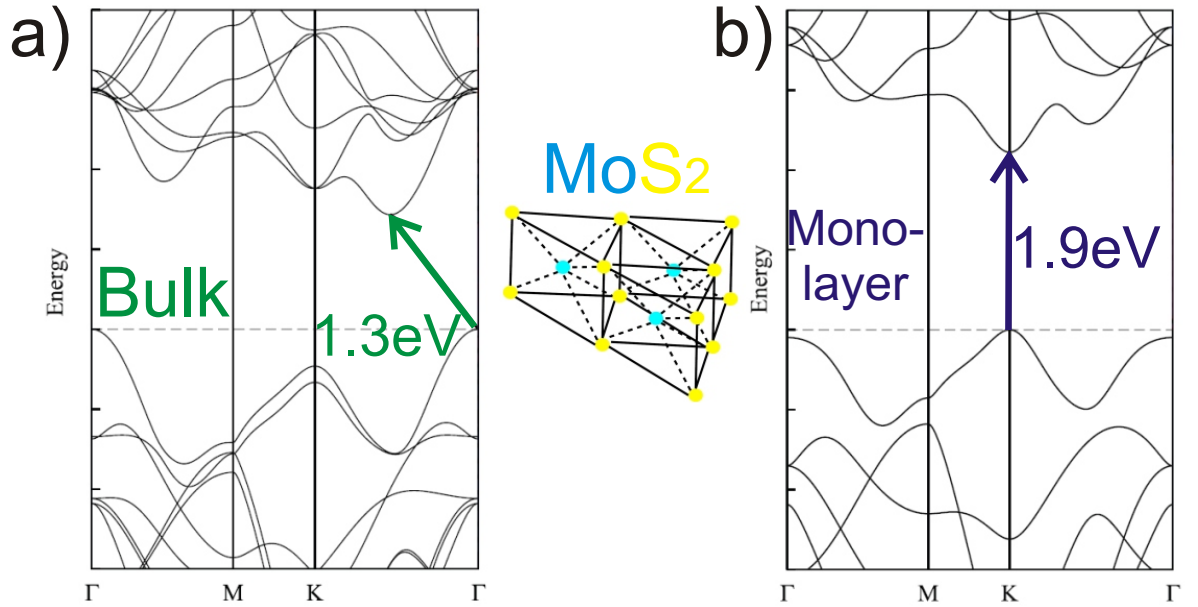


Figure 2.2: Bandstructure calculations of (a) bulk and (b) monolayer MoS<sub>2</sub> adapted from [91]. Lattice structure of monolayer MoS<sub>2</sub> [90].

### 2.2.2 Identification and Design

Like graphene, single layers of MoS<sub>2</sub> can be exfoliated from bulk crystals and transferred onto a substrate [59]. The thickness of the exfoliated flakes can be estimated as described

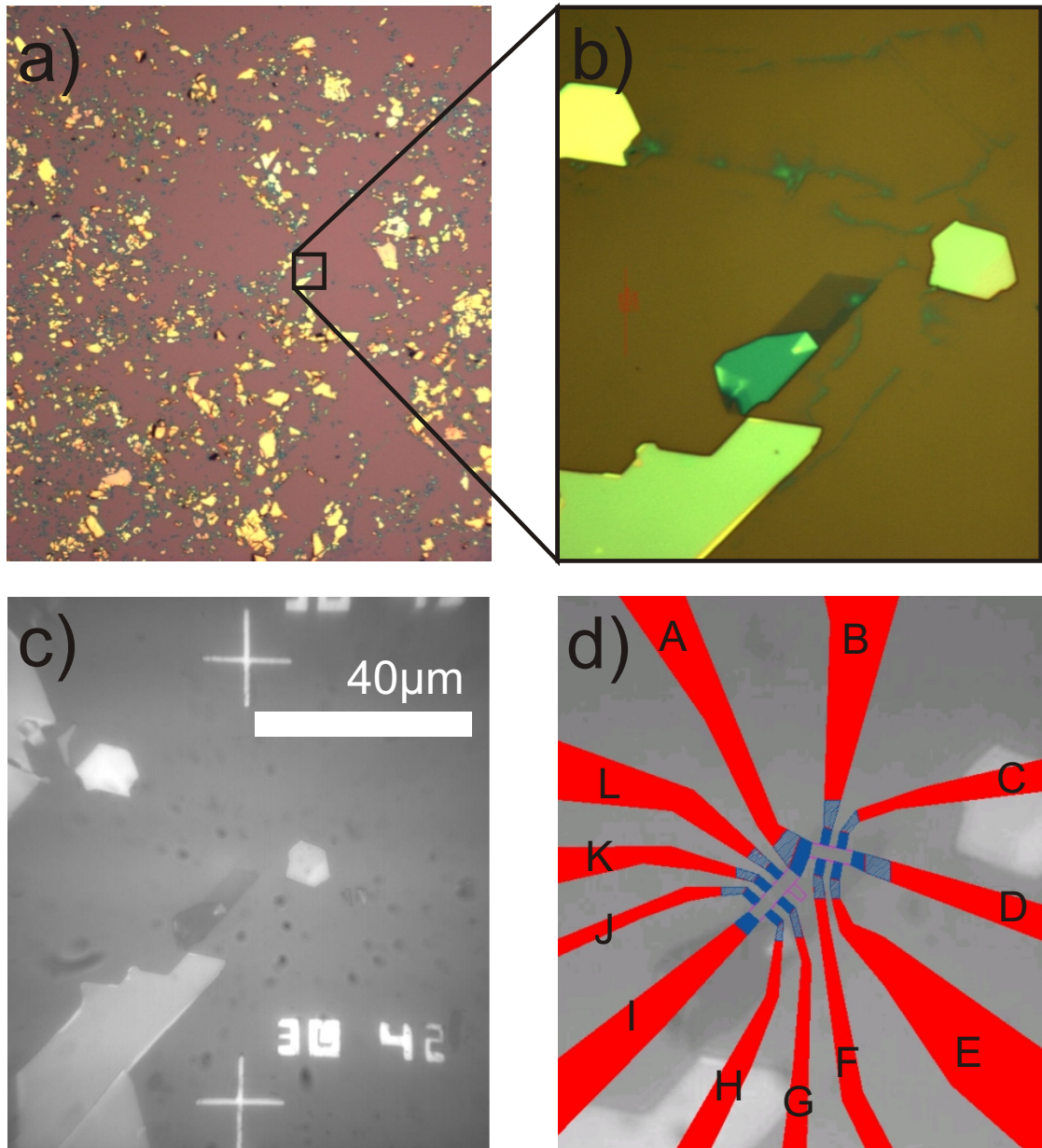


Figure 2.3: a) Optical micrograph of exfoliated flakes of MoS<sub>2</sub> transferred to Si/SiO<sub>2</sub> substrate. b) Monolayer flake. c) Optical imaging of the flake after alignment marks are deposited. d) AutoCAD design of electrodes for ebeam lithography. Red indicates the first exposure for Cr/Au tracks, dark blue indicates gold contacts to the sample with light blue representing overlap between the two exposures.

above. MoS<sub>2</sub> was exfoliated and deposited onto a Si/SiO<sub>2</sub> substrate at Pohang University, South Korea. A monolayer crystal was found through optical contrast (Fig. 2.3a,b)

and was confirmed with Raman spectroscopy, described in more detail in Ref. [92]. In the case of MoS<sub>2</sub> a “monolayer” actually refers to three atomic layers, one of molybdenum sandwiched by two layers of sulphur atoms[89]. An array of Cr/Au alignment marks were then deposited using the metal evaporation and lift-off methods described below. The alignment marks are comprised of four large ( $\sim 200\ \mu\text{m}$ ) crosses separated by a few mm for substrate alignment, and an array of smaller ( $\sim 8\ \mu\text{m}$ ) numbered crosses separated by  $80\ \mu\text{m}$ . The relevant sample may then be imaged along with the alignment marks to determine the exact position on the substrate as shown in Figure 2.3c. For graphene and MoS<sub>2</sub> optical imaging is of sufficient resolution, for smaller samples such as single carbon nanotubes and semiconductor nanowires, scanning electron microscopy may be required. Once the position is determined, the image may be imported into AutoCAD design software and electrode patterns aligned with the sample. Figure 2.3d shows the final AutoCAD electrode design. In this example two Hall bars are defined, one with six electrodes and the other with seven, one contact is common with each.

### 2.2.3 Lithography

Figure 2.4 outlines the processing steps required to achieve the final device. The chip is prepared with a bilayer electron-sensitive positive resist. Positive resists, upon exposure, dramatically change the solubility of the exposed regions in a particular developing solvent. Conversely, a negative resist becomes less soluble in developer after exposure. The change in solubility is typically due to creating or destroying of crosslinking in the polymer which will decrease or increase solubility respectively [93]. Two layers of resist are used with differing molecular weights. The lower layer is polymethylmethacrylate (PMMA) with an average molecular weight (MW) of 495,000 (PMMA 495), and the upper layer is PMMA with a MW of 950,000 (PMMA 950). The two layers are spin coated in succession from a solution of 8% PMMA in anisole (denoted A8). The purpose

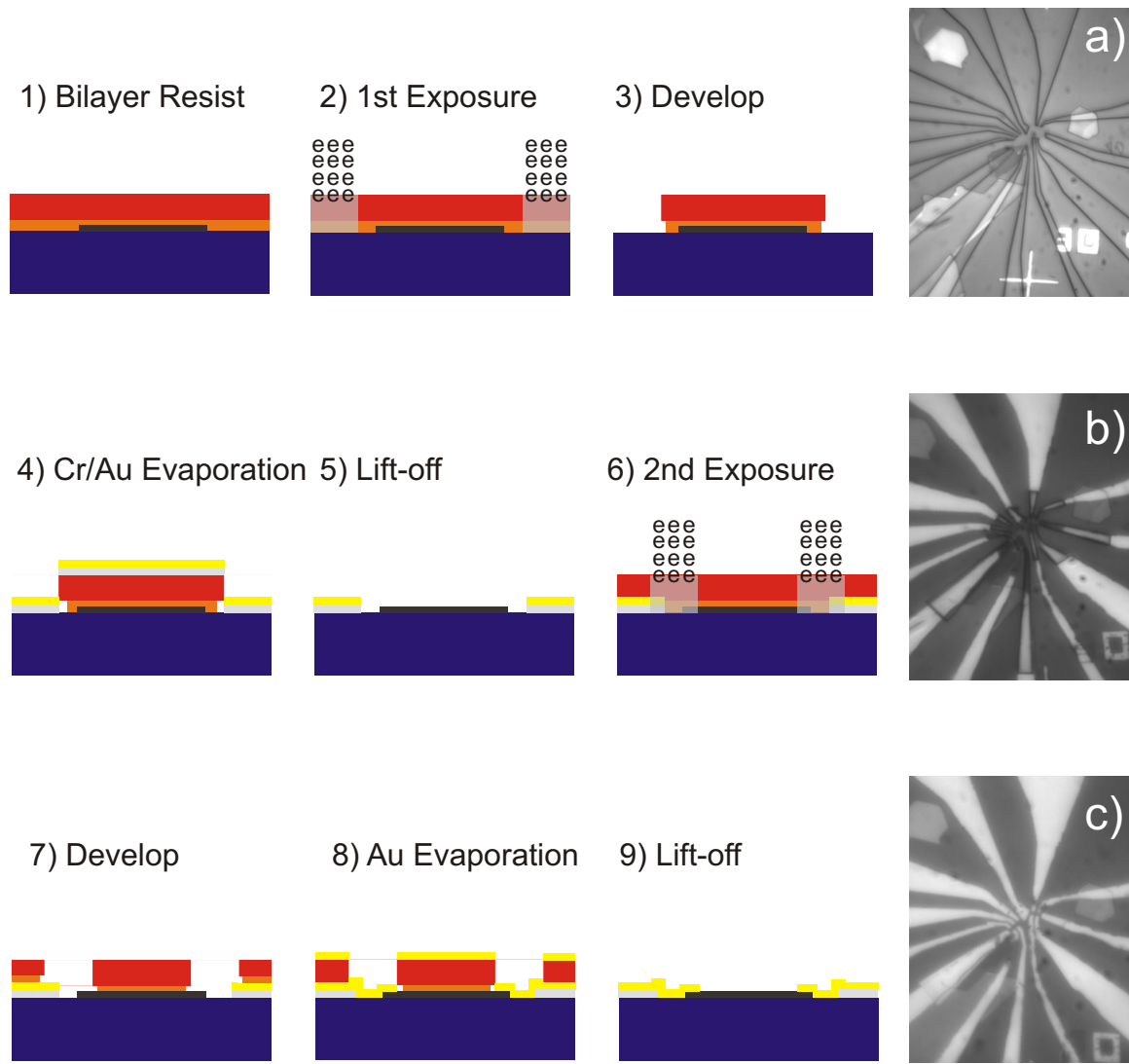


Figure 2.4: 1) The sample (grey) on Si/SiO<sub>2</sub> substrate (purple) with a bilayer resist of PMMA 495 (orange) followed by PMMA 950 (red). 2) E-beam exposure to define tracks close to the sample, followed by development (3) as shown in (a). Bilayer resist provides an undercut profile after development aiding lift-off. Cr/Au thermal evaporation (4) and lift-off in NMP (5) completes the coarse tracks towards the sample. A second e-beam exposure (6) and development (7,b) extends these tracks to the sample with a single layer of Au (to reduce contact resistance versus Cr/Au) thermally evaporated (8) followed by a final lift-off in NMP (9,c).

of the bilayer resist is to create an undercut profile after developing [94] which aids the lift-off process described below. Such a profile is created due to the enhanced solubility

of the lower layer in the developer. The first layer (PMMA 495 A8) is spin coated for 1 second at 5000 rpm to remove excess and improve uniformity at the edges, followed by 60 seconds at 1000 rpm. The sample is then baked at 180 °C for 90 seconds. The second layer (PMMA 950 A8) is spun for 60 seconds at 5000 rpm at baked again at 180 °C for 90 seconds.

The chip is mounted in a sample holder inside the evacuated chamber of a JEOL JBC-5500ZC electron beam lithography system with a minimum feature linewidth resolution of  $\sim 10$  nm. The AutoCAD design is loaded for the large tracks and bond pads. Following alignment of system to the crosses on the chip the pattern is written with a beam current of 10 nA, and a dose of  $600 \mu\text{C}/\text{cm}^{-2}$ . For smaller features, such as the extension of the contacts, a larger dose is required but with a smaller beam current.

The next step is to develop the exposed regions of the resist (Fig. 2.4c). This is done by immersing the sample in a 1 to 3 mixture of methyl isobutyl ketone (MIBK) to isopropanol (IPA). Nominally this should be done for 90 seconds for this specific bilayer resist recipe although variations in temperature can affect the development time required. If the sample is well adhered to the substrate a few seconds of sonication (high power ultrasound), can aid the removal of the exposed resist, however some of the more fragile samples may be adversely affected. For the first stage, that is where the device is still covered in resist, the sample is etched in an oxygen plasma for 30 seconds to remove residues and improve adhesion of the Cr/Au.

Metal evaporation is used to deposit a thin film of metal on the chip. This involves heating a small volume of metal under vacuum ( $\sim 1 \times 10^{-6}$  mbar) to the point of evaporation where, due to the vacuum metal atoms will travel ballistically to the chip which is placed  $\sim 30$  cm directly above the source. The distance and placement of the chip with respect to the source, as well as the high vacuum, ensures that the metal atoms arrive parallel to each other. This leads to straight edged metal patterns on the

substrate with no “shadowing”. The heating is most commonly achieved using either through Joule heating, by passing a high current through a “boat” or a rod with a high melting point (typically tungsten  $T_M = 3687$  K [7]) in thermal contact with the metal, or through high voltage electron beam evaporation [95]. For the process described above a chrome coated tungsten rod and gold in a tungsten boat were used as sources. Ten nanometers of chrome were deposited followed by 100 nm of gold at rates of 0.1 and 0.3 nm/second respectively.

Once the metal has been deposited the resist is removed along with the excess gold in a process known as lift-off. The sample is placed in N-Methyl-2-pyrrolidone (NMP) at 100 °C for at least 30 minutes which dissolves the resist leaving the e-beam-exposed tracks covered in metal and removing the excess. A pipette is used to agitate the sample helping to remove the metal. In some cases, careful sonication may be required to ensure complete lift-off.

The process is repeated with the second exposure for the sample contacts, at a lower current (1 nA) and higher dose ( $700 \mu\text{C cm}^{-2}$ ) followed by development (Fig.2.4b), gold evaporation (50 nm at 0.1 nm/second) and finally lift-off (Fig.2.4c). Figure 2.5 shows the current-source drain voltage ( $I - V_{DS}$ ) and current-gate voltage ( $I - V_g$ ) characteristics of the final device.

## 2.3 Electrical Characterisation

Electronic transport measurements are one of the most common methods of sample characterisation throughout condensed matter and materials science. Typical transport measurements are shown in Figure 2.5. In a two-terminal direct current (DC) measurement an electrical current is applied across two contacts and the voltage drop is also measured across the same contacts (Fig. 2.5). The disadvantage of using just two

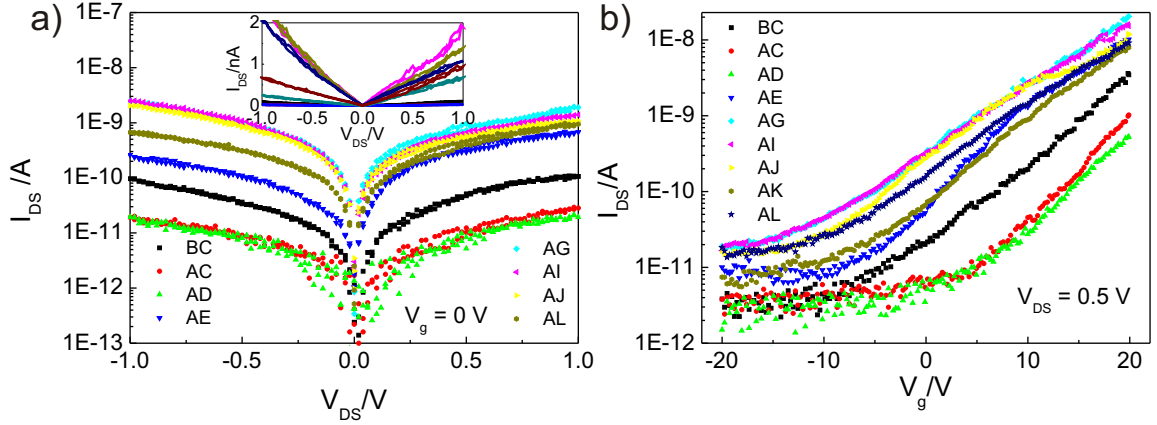


Figure 2.5: a) Two-terminal I-V characteristics of MoS<sub>2</sub> showing Ohmic contacts (inset). b) Gate voltage dependence at fixed source drain voltage  $V_{DS} = 0.5$  V. This is characteristic of a semiconductor where at negative gate voltages the chemical potential lies in the bandgap, as the gate is increased the chemical potential approaches the conduction band.

terminals is that the measured resistance includes the sample resistance and contact resistance ( $R_C$ ) which, especially in nanostructured materials [96, 97], can cause a considerable proportion of the voltage drop. To avoid this a four-terminal measurement is made where the current is applied across the sample using two contacts and the voltage drop is probed with two further contacts. In an ideal voltage measurement there is no current passed through the high resistance voltmeter and as such the resistance of the voltage probe contacts can be neglected.

A good signal-to-noise ratio often requires a large current to pass through a sample. However, high electric fields can be produced which will heat [98] (Chapters 3 and 4) and potentially damage the device. Using an alternating current (AC) lock-in technique can reduce electronic transport measurement noise. One contact of the sample is grounded, and a current is applied to another contact alternating at a set frequency and amplitude. The measured voltage drop, typically using two further contacts, uses an amplifier which is *locked-in* to the same frequency as the applied current and filters out all other frequencies. The actual frequency ( $f$ ) selected is a compromise between the



desire to reduce noise, which scales as  $1/f$  [99], and to avoid high frequency effects as it is the DC resistance which we require. As such, the frequency we select is  $10 < f < 20$  avoiding any multiples of 50 Hz or other sources of noise.

Applying a electric field in the form of a electrostatic gate can cause significant differences in transport measurements. It is used to vary the carrier density of graphene [58] and carbon nanotubes [100], is known to open a bandgap in bilayer graphene [101], and can cause confinement of carriers both in graphene [102] and carbon nanotubes [103]. Figure 2.5b shows the effect on the current flowing in MoS<sub>2</sub> with a constant applied voltage when a global backgate is varied. The backgate voltage varies the carrier density of the device, where at high gate voltages the Fermi energy moves closer to the conduction band thereby decreasing the resistance.

## 2.4 High Magnetic Fields

Two types of continuous field (as opposed to pulsed field, described elsewhere [104]) magnets were used for the experimental work in this thesis, a superconducting solenoid and a resistive Bitter coil. A superconducting solenoid (Fig. 2.6) uses the high current carrying capabilities of superconductors with zero dissipation [105] to generate a large magnetic field. To achieve this the magnet requires cooling to 4.2 Kelvin with liquid <sup>4</sup>He, although a helium flow variable temperature insert (VTI) can be used to vary the temperature of a sample under study from 1.5 K - room temperature (Chapters 3 and 4).

Superconducting magnets are limited by critical currents and critical magnetic fields of the superconductors used in the coils. Higher continuous magnetic fields can be achieved using resistive magnets at high applied currents (Fig. 2.7). Some of the measurements in Chapters 4 and 5 were carried out at the high magnetic field facilities in

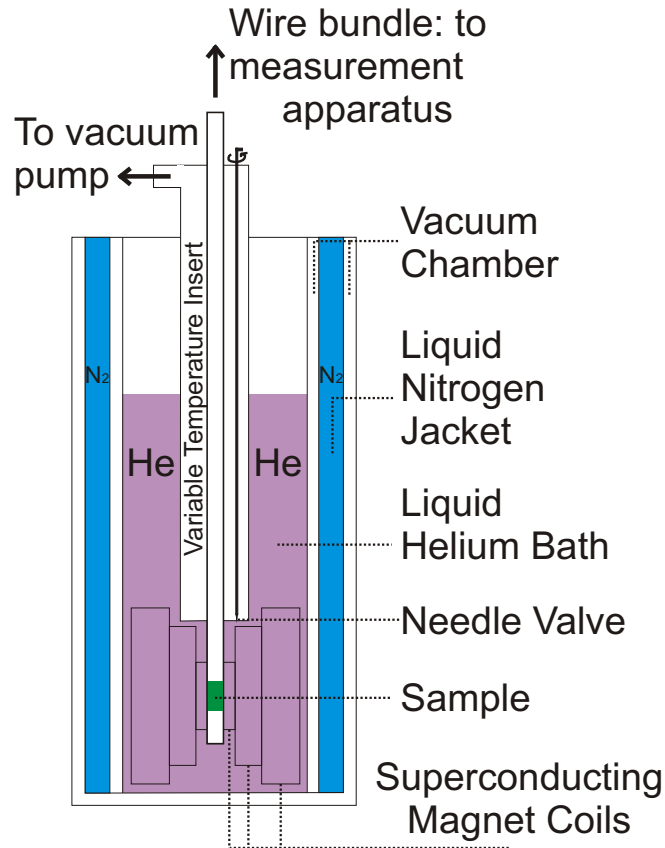


Figure 2.6: Schematic of the superconducting magnet with variable temperature insert.

Grenoble. Here a total of 14000 Amps applied with almost 10000 Volts is passed through a combination of six resistive copper coils in a Bitter configuration [106]. Passing 20 MW of electricity unsurprisingly heats the copper coils, which require cooling supplied by high pressure pumps channelling 300 litres of water per second between the coils. The water must be deionised to prevent shorting.

## 2.5 Carbon Nanotube Sample Preparation

Significant van der Waals interactions between the walls of carbon nanotubes, resulting in  $\pi - \pi$  stacking, means that bundling is very common. Figure 2.8 shows scanning



Figure 2.7: The resistive magnet (M10) at the LNCMI-Grenoble (left). At full field of 30 T the 20 MW magnet requires 300 litres of water per second for cooling the copper, comparable to the output of the 140 m high *Jet d'Eau* fountain in Geneva.

electron microscopy of as-grown carbon nanotubes. At first glance, numerous columnar structures are observed, which at higher magnification are clearly bundles of a great number of tubes. The optical properties of bundles of tubes are severely affected due to rapid energy transfer from semiconducting to metallic nanotubes, which quenches the photoluminescence emission [47]. Therefore individualising nanotubes is vital both for fundamental study and applications.

### 2.5.1 Solution Processing

Wrapping carbon nanotubes with surfactants in solution has proven an exceptional method not only in preventing bundling but also in functionalisation and purification of specific chiralities of tube. In 2002 O'Connell *et al.* used ultrasonication to break-up bundles of nanotubes and subsequently disperse them using an aqueous surfactant, sodium docetyl sulfate (SDS) [107]. The coating with SDS prevents the nanotubes from rebundling, and through ultracentrifugation the low-density individual wrapped tubes

can be separated from wrapped bundles.

Conjugated polymers have recently been used to bind to nanotubes through strong  $\pi - \pi$  interaction [108]. By wrapping with polyfluorene polymers Nish *et al.* [49], showed that they could preferentially wrap specifically semiconducting chiralities, excluding the metallic tubes which would otherwise quench photoluminescence emission. The SWNTs studied in Chapter 5 are polymer dispersed with the polymer poly(9,9-dioctylfluorenyl-2,7-diyl) (PFO), which selects predominantly (8,6) chirality semiconducting tubes.

The technique described here is based on the technique described by Nish *et al.* [49], where the toluene solvent is replaced by o-xylene which was optimised to give a greater yield of wrapped SWNTs. Single walled carbon nanotubes were grown using the HiPCO (High-Pressure Catalytic Decomposition of Carbon Monoxide) method, where metal clusters act as nucleation sites on which SWNTs grow. It is capable of producing SWNTs on a kilogram per day scale [42]. The raw HiPCO carbon nanotubes were dried in an oven for 4 hours at 120 °C. 6 mg of PFO was dissolved in 10 mL o-xylene and homogenised using a sonic bath for 60 minutes. 3 mg of raw dried nanotubes were added and the mixture was vigorously tip sonicated using an ultrasonic disintegrator for 15 minutes. The solution was then centrifuged for 8 minutes at 10,000  $\times g$  and the upper 85% of the supernatant retained, which contains the individually dispersed semiconducting nanotubes predominantly of (8,6) chirality as confirmed by PLE spectroscopy shown in Figure 2.10.

### 2.5.2 Substrate Dispersion

Many physical phenomena change dramatically when studying individual carbon nanotubes as opposed to ensembles in solution or as films. The local environment of a tube, such as local trapped charges, and defect sites and impurities, play a very important role in determining its individual characteristics. Spin coating a substrate at high spin-speeds

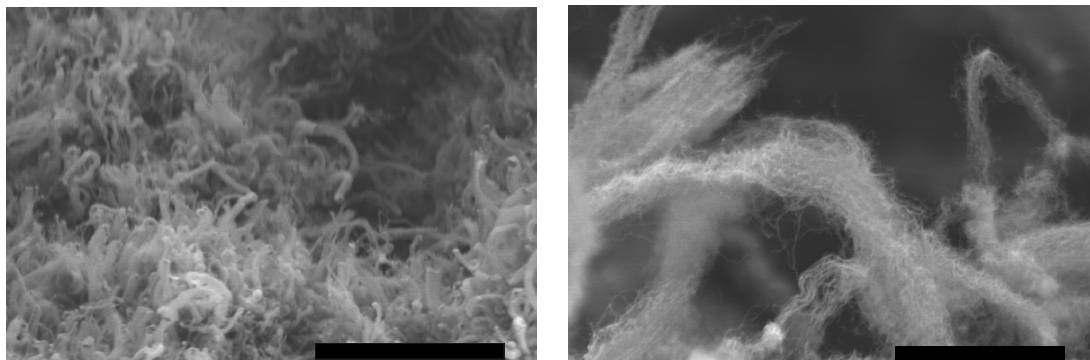


Figure 2.8: Scanning electron microscope images of a powder of unprocessed MWNTs. Large bundles of tubes are clearly observed. At high magnification each bundle is comprised of an interwoven network of MWNTs. Scale bars are 50 and 5 microns for the left and right images respectively.

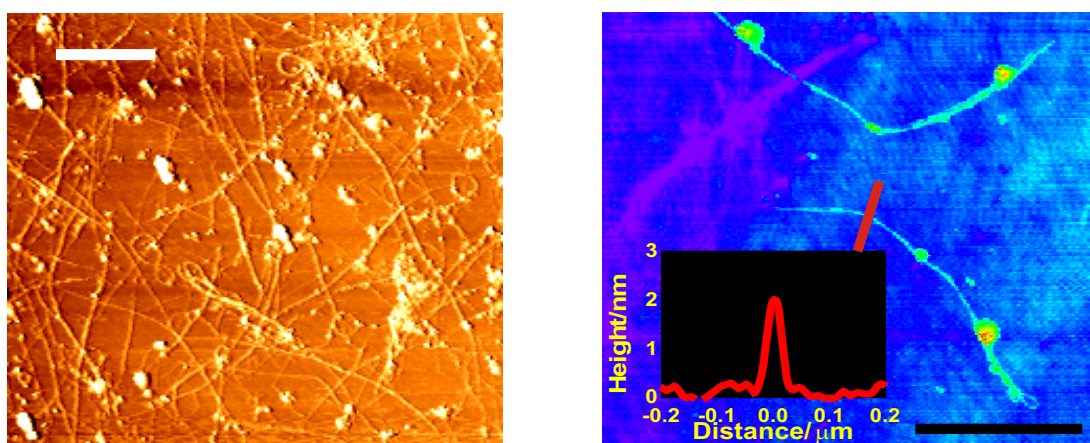


Figure 2.9: Atomic force microscopy of individualised polymer wrapped carbon nanotubes on quartz substrates. Using higher spin speeds (right) the density of tubes can be decreased. A line analysis (right, inset) reveals a height of  $\sim 2$  nm showing that these are individual polymer wrapped tubes and not bundles. Small crystals of polymer which aggregate on the SWNTs can also be seen. Scale bars are 2 microns.

from a solution of polymer wrapped SWNTs can provide spatially isolated tubes with a controllable density (Fig. 2.9). Atomic force microscopy (AFM) is a scanning probe microscopic technique where the distance between a sharp tip at the end of an oscillating

cantilever and the sample is measured through changes in the resonant frequency of the cantilever induced by van der Waals forces between the tip and the sample. It has a vertical resolution of  $\sim 0.1$  nm, and a imaging range of  $\sim 20 \times 20 \mu\text{m}^2$  and as such is a useful tool in characterising SWNT-on-substrate dispersions. To obtain individualised PFO wrapped SWNTs for the single tube photoluminescence experiments described in Chapter 5,  $10 \mu\text{l}$  of PFO wrapped SWNTs in solution, prepared using the description above, was spun at 2000 rpm for 90 seconds, and annealed in air at  $180^\circ\text{C}$  to remove excess o-xylene. The density of SWNTs was confirmed using AFM characterisation (Fig. 2.9) and scanning PL imaging (Chapter 5).

## 2.6 Optical Characterisation

### 2.6.1 Photoluminescence Excitation Spectroscopy

As described in Chapter 1, individual chiralities of SWNTs have very characteristic optical transitions. Photoluminescence excitation (PLE) spectroscopy involves photoexciting the  $E_{22}$  transition (generally in the visible regime), and measuring the subsequent  $E_{11}$  emission (near-infrared). The complete experimental setup used is described in Ref. [109] and is shown schematically in Figure 2.10. A Xenon lamp is used as a white light source which passes through a monochromator, optimised to give a full width half maximum (FWHM) below 5 nm, used as photoexcitation. The spectral output of the Xenon lamp and the spectral response of the monochromator varies as a function of wavelength. A beam splitter is used to divert a small fraction of the beam to a photodiode which is used to directly normalise the photoluminescence data. The beam is focused onto the sample and emission is collected perpendicular to the excitation using a 30 cm spectrograph attached to a liquid nitrogen cooled 512 pixel InGaAs detector. Figure 2.10 shows an example PLE map of a solution of PFO wrapped HiPCO SWNTs

in o-xylene, where the optical signatures of the four dominant chiralities present are labelled.

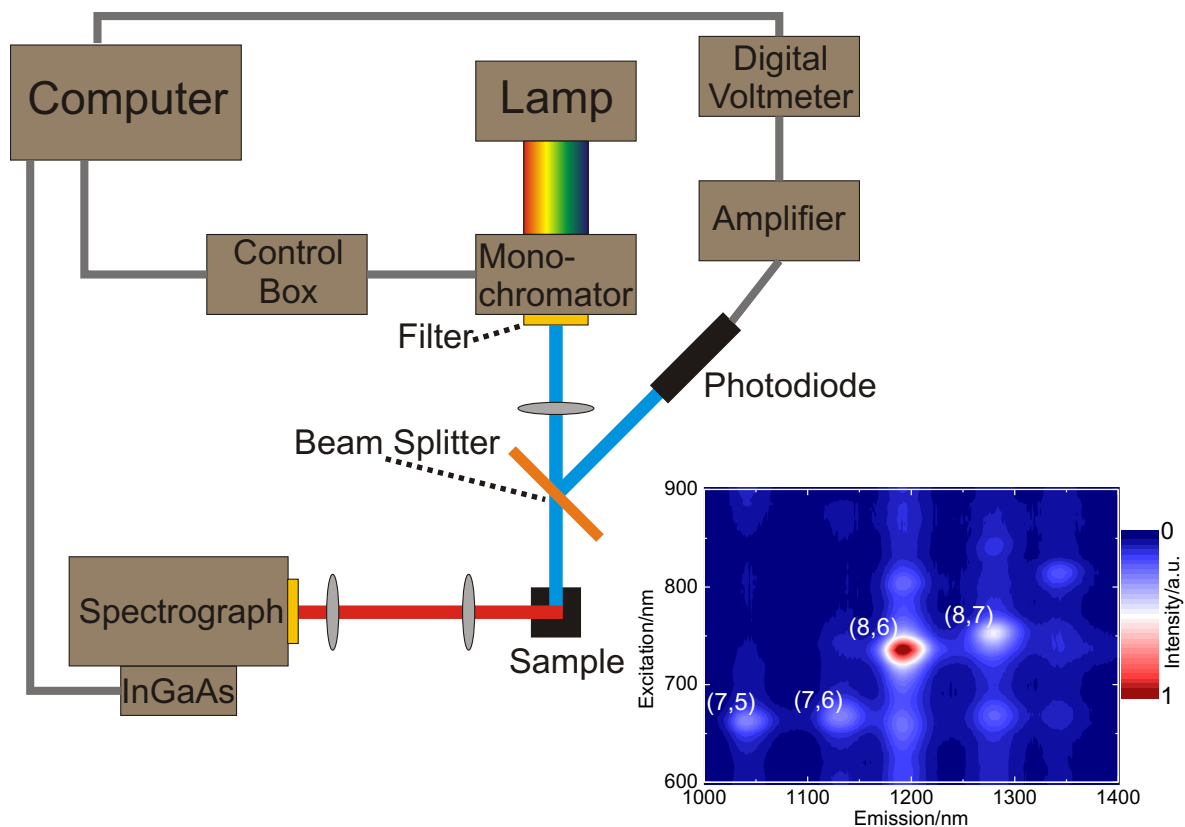


Figure 2.10: A schematic of the photoluminescence excitation spectroscopy setup, used to characterise the solutions of polymer wrapped SWNTs, which were then dispersed on substrates for use in Chapter 5 (bottom right).

### 2.6.2 Micro Photoluminescence

Low temperature micro-photoluminescence measurements are described schematically in Figure 2.11. Continuous wave resonant  $E_{22}$  optical excitation of (8,6) tubes was by a tunable Ti:Sapphire laser through a monomode fibre with  $5\text{ }\mu\text{m}$  diameter core, with wavelengths accurately controlled in the range 700-800 nm. The excitation beam passes through a polariser before reaching a dichroic beam splitter. The high energy excitation beam is reflected and focused on the sample surface with a spot size of  $\sim 1\text{ }\mu\text{m}^2$ . Lower energy emission passes through the beam splitter undeviated and is collected using a  $50\text{ }\mu\text{m}$  diameter core fibre. At the other end of the fibre the emission is detected by a nitrogen cooled InGaAs array. The position of the sample is manipulated with sub-micron precision with an Attocube *xyz*-piezostage. For the measurements described in Chapter 5, the sample was immersed in Helium gas at 4.2 K.

The sample is placed in a 30 T resistive magnet with a bore size of 50 mm. Two geometries were used to determine the magnetic field effects. Faraday geometry was used where the surface of the substrate is perpendicular to the magnetic field. Using a mirror at  $45^\circ$ , Voigt geometry, in which the light propagation vector  $\mathbf{k}$  is perpendicular to the direction of the magnetic field and the surface of the sample, was used to test the effects of flux threading the CNTs (Fig. 2.11). Polarised excitation was used to selectively excite CNTs aligned on the substrate in the direction of the magnetic field due to a large depolarisation effect[31].



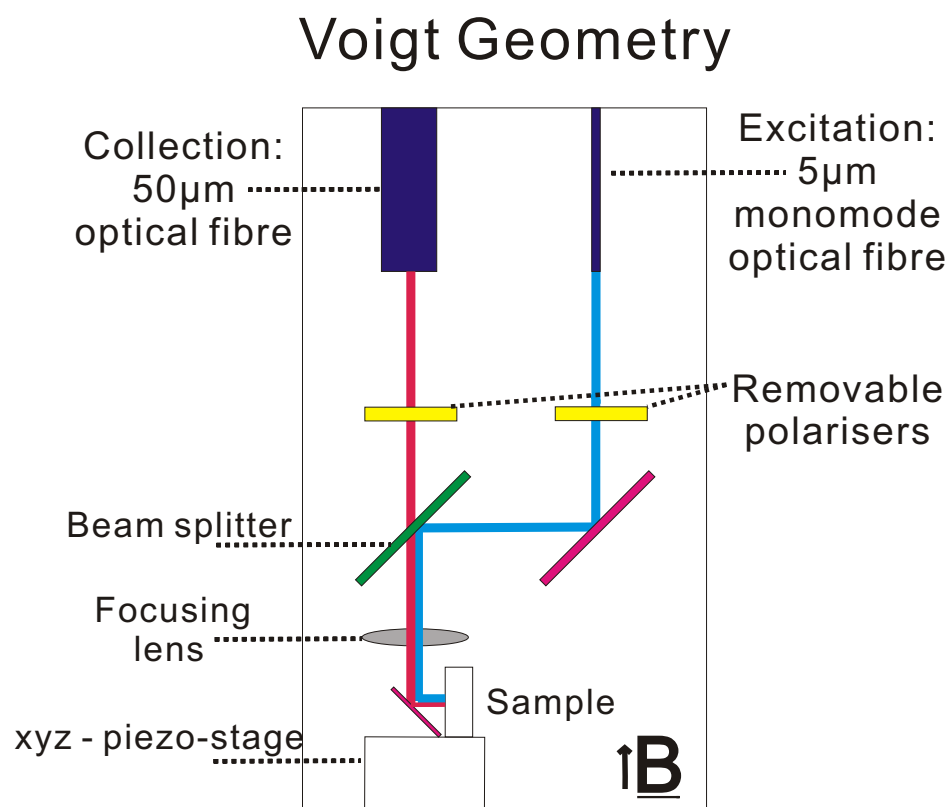


Figure 2.11: Experimental setup used for micro-photoluminescence measurements. Fibre excitation is used so that the sample may be placed in a cryostat inside the bore of a magnet. The beam then passes through a polariser to selectively excite nanotubes which are aligned with the magnetic field. A dichroic mirror is used to separate the (short wavelength) excitation beam from the (long wavelength) nanotube emission.

## Chapter 3

# High current breakdown of the quantum Hall effect and electron heating in InSb/AlInSb

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We report measurements of the temperature and electric field dependent breakdown of the quantum Hall effect in two dimensional InSb/AlInSb heterostructures. The electron temperature,  $T_e$  is studied as a function of electric field and it is shown that the energy loss rates of electrons to the lattice follow a  $(T_e^3 - T_L^3)$  dependence for  $2\text{ K} < T_e < 22\text{ K}$  at a lattice temperature,  $T_L = 1.5\text{ K}$ . The high current induced breakdown of the quantum Hall effect (QHE) is linearly proportional to sample width as deduced from the Hall resistivity and shows breakdown at lower current densities as deduced from the resistivity ( $\rho_{xx}$ ) due to non-uniformity in carrier density. Temperature dependent studies show that the quantum Hall effect persists to considerably higher temperatures than the conventional GaAs/AlGaAs system. Using the energy loss rates, we describe the QHE breakdown in terms of bootstrap-type electron heating.

### 3.1 Introduction

The quantum Hall effect (QHE) [13], observed in two dimensional electron gases (2DEGs) at low temperatures when a high magnetic field is applied perpendicular to the 2DEG plane, is characterised by a vanishing longitudinal resistivity,  $\rho_{xx}$ , and quantised Hall resistance,  $\rho_{xy} = h/\nu e^2$ , where  $h$  is Planck's constant,  $e$  the electronic charge and  $\nu$  the number of filled Landau levels. Since 1990 the QHE has been the electrical resistance unit standard, used to define the Ohm, for which the persistence of the effect at high temperatures and electrical currents is of particular importance [14] (Section 1.3.4). With increasing temperature a gradual increase of  $\rho_{xx}$  and deviation of  $\rho_{xy}$  from quantisation is observed. With increasing current however, a sudden transition occurs at critical current  $I_c$  at which point  $\rho_{xx}$  increases by several orders of magnitude. The breakdown of the QHE due to high currents has been studied extensively in semiconductor heterostructures (see Nachtwei [110] for a review) and more recently in graphene [111, 112] (Chapter 4). Breakdown phenomena are of particular interest due to their relevance in standards applications as well as their potential to elucidate the fundamental physics of the quantum Hall effect.

Indium antimonide has the narrowest bandgap of any III-V semiconductor [10], and even when confined to a 2DEG, electrons in InSb have been shown to have an effective mass of only  $m^* = 0.02m_e$  [11] and an exceptionally large effective Landé g-factor ( $g^* \sim -50$ ) [8]. Therefore like graphene (Chapters 1, 4), InSb exhibits a large cyclotron energy ( $E_c = \hbar\omega_c = \hbar eB/m^*$ ), where  $\omega_c$  is the cyclotron frequency, however the large Zeeman ( $sg^*\mu_B B$ ) energy gap, where  $B$  is the magnetic field,  $s = \pm 1/2$  is the spin of the electron and  $\mu_B = \frac{e\hbar}{2m_e}$  is the Bohr magneton, means that spin-splitting of each Landau level is comparable to that of the cyclotron gap. Using InSb heterostructures we have been able to study the effect of large energy gaps on the breakdown properties of the QHE.

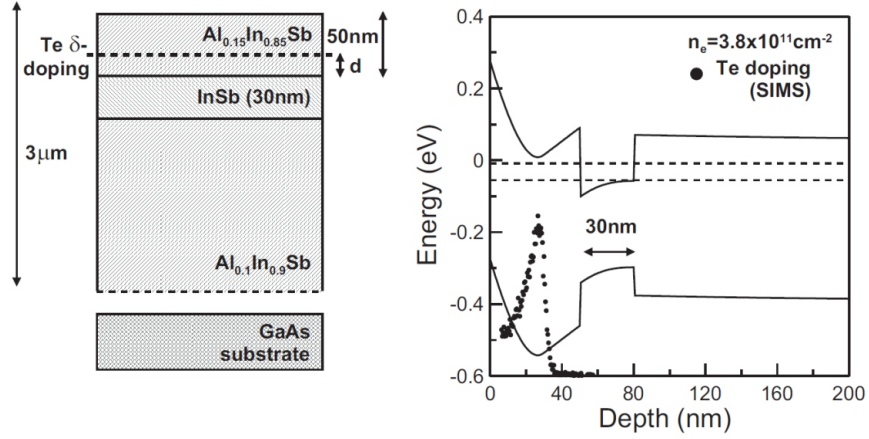


Figure 3.1: Layer structure and calculated bandstructure of the devices described in this Chapter. Adapted from Ref. [10]

## 3.2 Sample Properties

All samples studied were  $\text{InSb}/\text{Al}_x\text{In}_{1-x}\text{Sb}$  heterostructures grown on a semi-insulating  $\text{GaAs}(001)$  substrate by solid-source molecular beam epitaxy [10] by QinetiQ, Malvern, UK. The carriers are confined within a 30 nm  $\text{InSb}$  quantum well, between a  $3\text{ }\mu\text{m}$   $\text{Al}_{0.10}\text{In}_{0.90}\text{Sb}$  buffer layer and a 50 nm upper barrier layer of  $\text{Al}_{0.15}\text{In}_{0.85}\text{Sb}$  containing a  $\text{Te}$   $\delta$ -doping plane which is used to set the carrier density (Fig. 3.1). The samples were fabricated into Hall bar geometries, of widths 75, 300 and  $600\text{ }\mu\text{m}$ , with wide current injection contacts at each end and three pairs of narrow voltage probes placed along the device (Fig. 3.2 inset). Carrier densities were in the range  $2 - 3.5 \times 10^{11}\text{ cm}^{-2}$  and mobilities exceed  $160,000\text{ cm}^2/\text{Vs}$  at 1.5 K.

## 3.3 Electron Heating and Energy Loss Rates

Magnetotransport measurements were carried out using a superconducting solenoid magnet in a variable temperature insert with a base temperature of 1.5 K. A typical magnetotransport plot is shown in Figure 3.2. Several well defined quantum Hall states

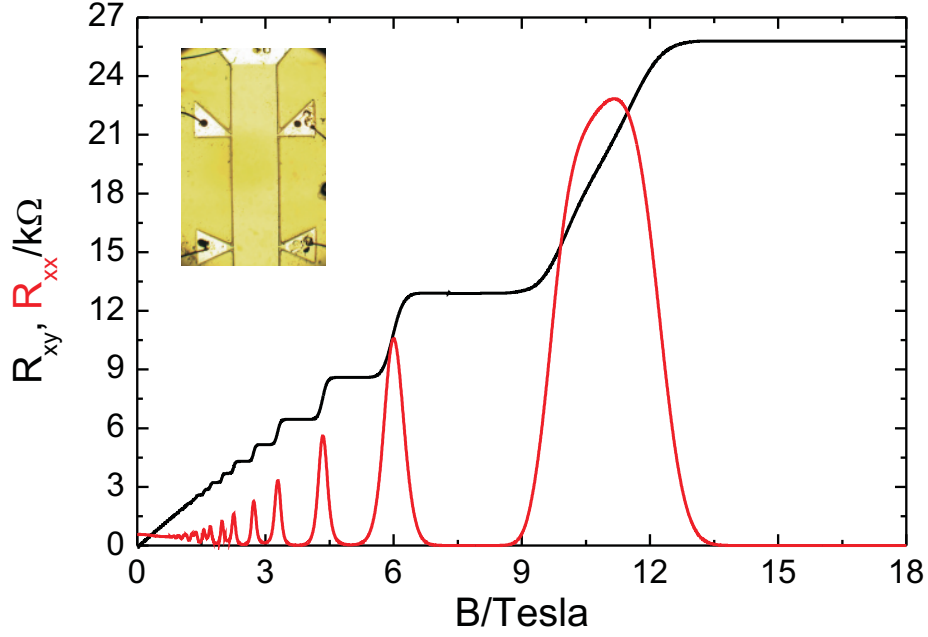


Figure 3.2: Resistivity plot showing quantum Hall effect in InSb taken at 1.5 K using a current of  $1\mu\text{A}$  with a sample carrier density of  $3.4 \times 10^{11} \text{ cm}^{-2}$ . Several well defined plateaux and minima for both even and odd integer filling factors are observed. Inset: A micrograph of part of a typical  $600\mu\text{m}$  wide eight-leg Hall bar.

are clearly observable. At lower fields the samples exhibit Shubnikov–de Haas (SdH) oscillations. At higher temperatures these oscillations are damped with the well known temperature dependence given by the Lifshitz-Kosevich formula [113]:

$$\frac{\Delta\rho}{\rho} \propto \frac{\chi}{\sinh(\chi)}, \quad (3.1)$$

with  $\chi = 2\pi^2 \frac{k_B T}{\hbar \omega_c}$ , where  $k_B$  is Boltzmann's constant,  $T$  is temperature and  $\omega_c$  is the cyclotron frequency. When measured at low electric fields ( $\lesssim 10 \text{ V/m}$ ), electrons are at thermal equilibrium with the lattice and as such the thermal damping of the SdH oscillations is governed by the lattice temperature,  $T_L$ . At high applied electric fields, however, carriers are unable to lose energy to the lattice through electron-phonon interactions at high enough rates and the two are no longer in thermal equilibrium. The electron temperature,  $T_e$ , increases relative to the lattice and the electrons collectively reach an

internal thermal equilibrium due to electron-electron scattering. Shubnikov–de Haas oscillations of hot electrons are damped in the same way as with lattice temperature. Such oscillations may therefore be used as a measure of the hot electron temperature.

Magnetotransport measurements at high lattice temperatures were taken to calibrate the height of several of the SdH oscillations as a function of  $T_L$ . This calibration was compared to the  $\rho_{xx}$  data taken at high (DC) currents for several values of the occupancy,  $\nu$ , to determine the electron temperature and to verify that Equation 3.1 holds (Fig. 3.3). As the current is increased above  $1\ \mu\text{A}$  at  $1.5\ \text{K}$ , the electron temperature increases sublinearly to over  $20\ \text{K}$  with an applied current of  $300\ \mu\text{A}$  at  $\nu = 4$  (Fig. 3.4). The total electrical power dissipated over the sample is measured for each occupancy. The experiment is taken in the steady-state and as such the power input is equal to the total energy loss rate. The energy loss rate of hot carriers through phonon emission is dependent on  $T_e$  and  $T_L$ , and is generally of the form  $P \propto (T_e^N - T_L^N)$  where integer  $N$  varies to account for different forms of electron-phonon coupling [114]. The energy loss rate per carrier,  $P$ , is thus calculated as a function of  $T_e$ . Empirically, we find

$$P = \alpha(T_e^3 - T_L^3). \quad (3.2)$$

with a value of  $\alpha = 8 \times 10^{-18}\ \text{WK}^{-3}$ . A similar power law dependence following approximately  $P \propto T^3$  has been observed in this temperature regime in GaAs [115–118], Si [119] and SiGe [120, 121] as expected for a combination of deformation potential and piezoelectric scattering [118]. In the nonequilibrium regime the carriers lose energy to the lattice with a characteristic energy relaxation time,  $\tau_e$ . This is calculated, using

$$\tau_e = \frac{\pi^2 k_b^2 T_e^2}{3E_F P} = \frac{\pi^2 k_b^2 T_e^2}{3E_F \alpha (T_e^3 - T_L^3)}, \quad (3.3)$$

where  $E_F$  is the Fermi energy and  $k_B$  is Boltzmann's constant. Energy loss times at several filling factors are shown in Figure 3.5 as a function of electron temperature. The

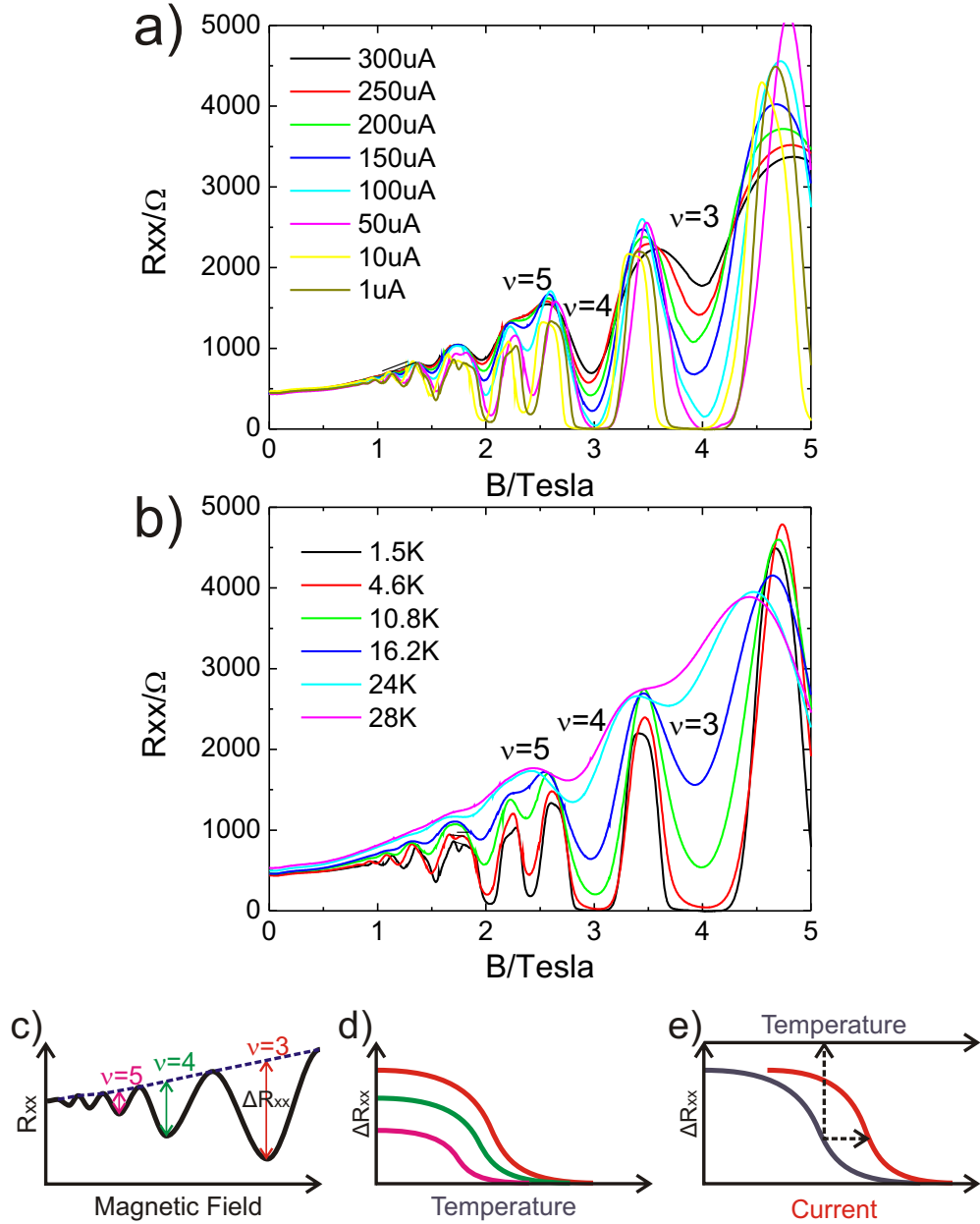


Figure 3.3: Magnetotransport for a 600  $\mu\text{m}$  wide device at (a) high currents with fixed  $T_L = 1.5\text{ K}$ , and (b) using a fixed DC measurement current ( $I = 1\text{ }\mu\text{A}$ ) with increasing  $T_L$  from 1.5 K to 28 K. Also shown is a schematic of the procedure for determining  $T_e$  from the current induced damping of the SdH oscillations. c) The height of the oscillations,  $\Delta R_{xx}$ , is determined for several integer values of  $\nu$ . d) The damping of  $\Delta R_{xx}$  is found as a function of  $T_l$ . e) Equivalent data is obtained at a low fixed  $T_l$  with high currents. This is compared to the temperature dependence from d) and  $T_e$  is extracted.

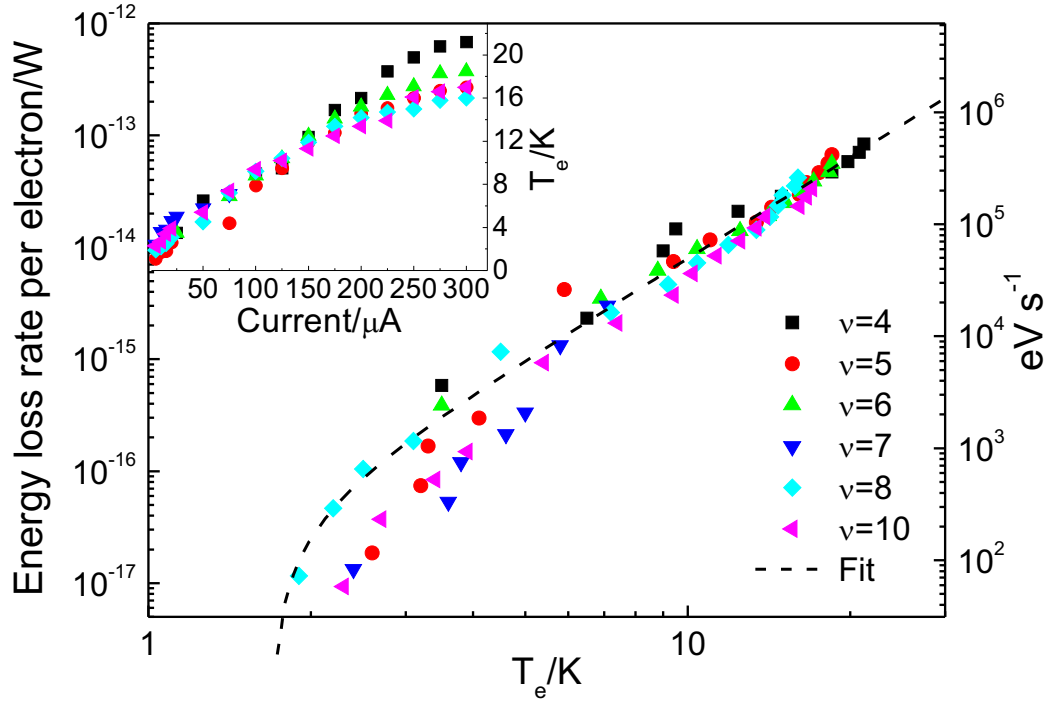


Figure 3.4: Energy loss rates as a function of electron temperature measured at a fixed  $T_L=1.5$  K. The rate follows the expected  $(T_e^3 - T_L^3)$  dependence. Electron temperature is measured as a function of current, shown in the inset.

energy loss times are slightly longer than values for GaAs taken from both electrical and optical measurements [115, 122, 123], and significantly longer than found recently for graphene [112].

### 3.4 High Current Breakdown of the Quantum Hall Effect

The high current induced breakdown of the quantum Hall effect is characterised by a sudden increase from the zero resistivity state and a deviation from the quantised Hall resistance ( $\Delta\rho_{xy}$ ). We will define the point at which breakdown occurs as  $\rho_{xx}$  or  $\Delta\rho_{xy} \gtrsim 1 \Omega$ . High current breakdown is observed by measuring the  $I-V_{xx}$  characteristics of the sample in a four terminal configuration. A series of such  $I-V_{xx}$  traces are shown



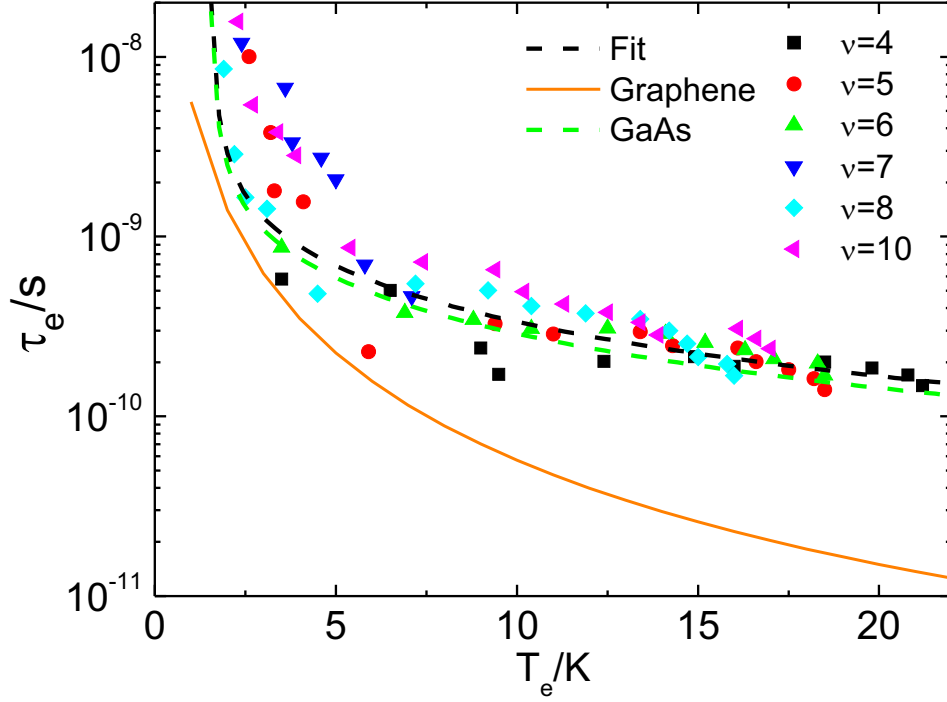


Figure 3.5: Relaxation time as a function of electron temperature as deduced from Equation 3.3. Also shown is  $\tau_e$  for graphene [112] and GaAs at 1.5 K, as deduced from optical [122] and electrical [115, 123] measurements of energy loss rate as a function of electron temperature.

in Figure 3.6 for a  $600\,\mu\text{m}$  wide Hall bar at 1.5 K. Clear quantum Hall breakdown is observed for both  $\nu = 1$  and  $\nu = 2$  as a sudden onset of dissipation. We find critical current values for the two filling factors of  $I_c(\nu = 1) = 145\,\mu\text{A}$  and  $I_c(\nu = 2) = 180\,\mu\text{A}$  (Fig. 3.6).

By contrast the deviation from quantisation of the Hall resistance within the plateau shows a sudden onset at currents, much greater than that of  $I_c$  (Fig. 3.7). Previous investigations of the dependence of  $\Delta\rho_{xy}$  on  $\rho_{xx}$  have shown two different types of phenomena. The first was a linear relationship due to thermal activation,  $\Delta\rho_{xy} = S\rho_{xx}$ , where  $S \sim 0.1$  [124, 125]. The second showed an abrupt drop of a few ppm from quantisation at currents of  $\approx 0.8I_c$  [126], ascribed to delocalisation of electrons and not thermal activation. Our observations clearly differ from both of these but have more in

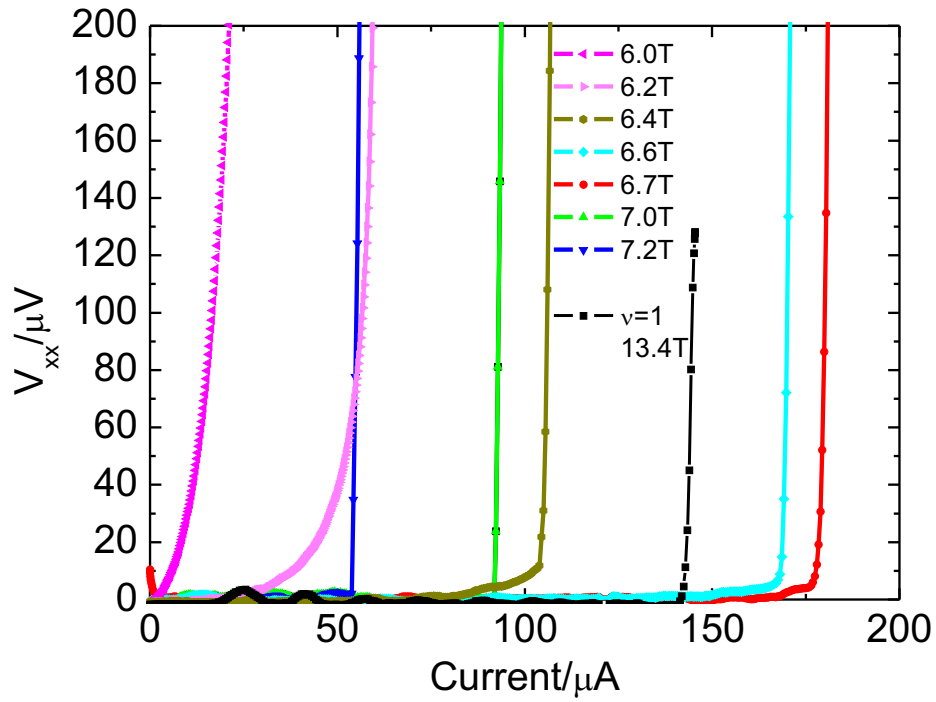


Figure 3.6: The current voltage characteristics for  $\nu = 2$  (colours) and  $\nu = 1$  (black) clearly showing a sudden onset of resistance following a critical current. At magnetic fields below the field of highest breakdown current, the longitudinal voltage dropped is a more gradual increase with increasing current. Above this field a more sudden, step-like increase is observed indicating a different type of phase transition. The small oscillations seen at low currents in the  $\nu = 1$  curve are electrical noise.

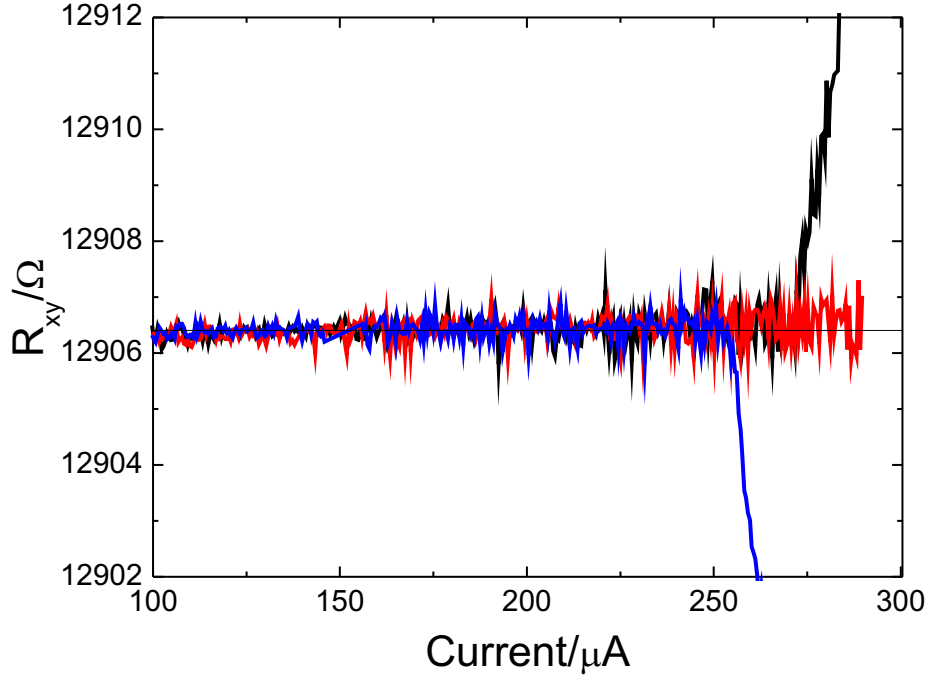


Figure 3.7: The deviation of the Hall voltage from quantised values at  $\nu = 2$  for three magnetic field values corresponding to  $\nu = 1.965$  (blue),  $\nu = 2$  (red) and  $\nu = 2.07$  (black).

common with the abrupt deviation as seen by Kawashima *et al.* [126] as we do not see a linear relationship within the noise levels. The noise levels we observe are relatively large for these measurements as the current and voltage were measured using two separate voltmeters and as such any time delay between either measurement would mean that the current could be mismatched from the voltage.

The magnetic field dependence of the breakdown current, is shown in Figure 3.8a. Due to the macroscopic scale of the sample there are significant inhomogeneities leading to a significant difference in the magnetic field at which the exact occupancy occurs, and this will be greatest in the current direction due to the larger physical separation of the  $V_{xx}$  contacts. A comparison of the magnetic field dependence of the breakdowns of  $\rho_{xx}$  and the Hall deviation for  $\rho_{xy}$  suggest that inhomogeneities in the carrier density probably play a significant role in the behaviour observed. On the high field side of the plateau the breakdown current is very similar for  $\rho_{xx}$  and  $\rho_{xy}$  (Fig. 3.8a). At the same

time the nature of the breakdown is the well known abrupt breakdown with a sudden onset of resistance. By contrast, at lower fields where the  $\rho_{xy}$  quantum Hall current gives considerably larger breakdown values than observed for  $\rho_{xx}$  the resistivity  $\rho_{xx}$  shows a gradual onset (Fig. 3.6). This is consistent with multiple successive breakdowns in regions of progressively increasing carrier density which reach the breakdown condition at lower fields. Further evidence for this comes from measuring the outer contacts which have twice the separation and show a further decrease in the breakdown current. The  $\rho_{xy}$  breakdown current is a maximum, as expected, where the  $\nu = 2$  state is at exact integer occupancy as calculated from the classical Hall coefficient measured at high temperature, whereas the  $\rho_{xx}$  minima are at slightly higher fields and are centered on the peak breakdown current for  $\rho_{xx}$ . From this we can estimate that the inhomogeneous carrier density within a sample may vary by  $\sim 10\%$ .

The inhomogeneity induced difference between the critical current for  $\rho_{xy}$  and  $\rho_{xx}$  can also be observed in the magnetotransport data. Figure 3.9 shows the longitudinal and Hall resistances as a function of magnetic field at high currents, close to or above  $I_C$  for  $\rho_{xx}$ , in  $\nu = 2$  for a  $600\ \mu\text{m}$  wide device. For the highest currents (above  $100\ \mu\text{A}$ ) two transitions are observed in the  $\rho_{xx}$  data. The first is a sudden onset of longitudinal resistance at low magnetic field corresponding to a current induced reduction in the width of the  $\nu = 2$  plateau. A second transition is observed at higher magnetic fields, typically  $\sim 0.2\ \text{T}$  above, where  $d\rho_{xx}/dB$  undergoes a sharp increase. The  $\rho_{xy}$  data clarifies the origin of this transition which correlates exactly with the field at which  $\rho_{xy}$  shows a sudden deviation from quantisation. It is worth noting that even when at  $200\ \mu\text{A}$ ,  $\rho_{xx}$  does not reach zero, the width of the quantised Hall plateau remains finite.

Using three  $600\ \mu\text{m}$  wide Hall bars with carrier densities of  $1.3 \times 10^{11}\ \text{cm}^{-2}$ ,  $2.3 \times 10^{11}\ \text{cm}^{-2}$ , and  $3.3 \times 10^{11}\ \text{cm}^{-2}$  we have studied the field dependence of the peak breakdown current at  $\nu = 1$  and  $2$  (Fig. 3.8b). We find a linear dependence of  $\nu = 1$  breakdown current with magnetic field. The data for  $\nu = 2$  are also consistent with a

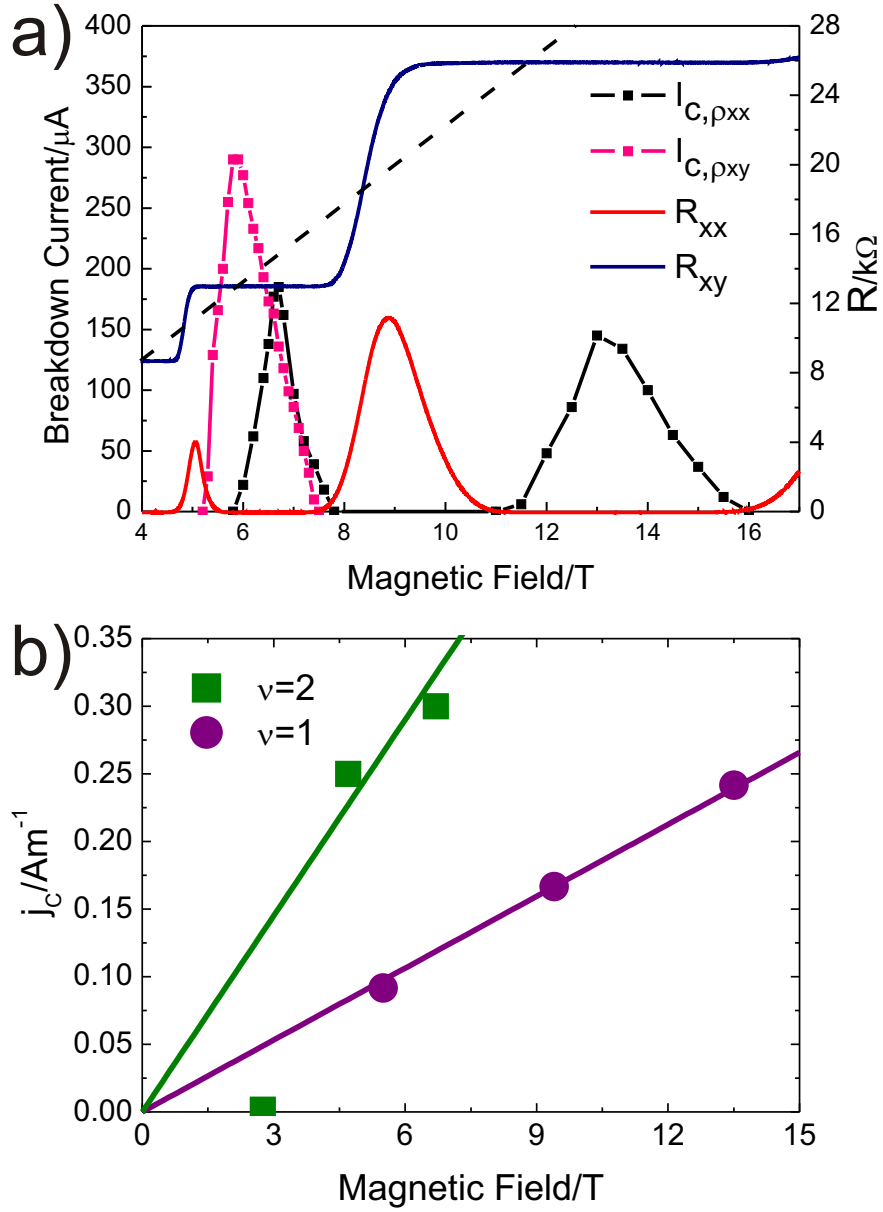


Figure 3.8: a) Field dependence of breakdown currents,  $I_c$ ,  $\rho_{xx}$  and  $I_c$ ,  $\rho_{xy}$ , for a  $600\ \mu\text{m}$  device with carrier density of  $3.3 \times 10^{11}\ \text{cm}^{-2}$  shown with the magnetotransport plot. Dashed black line indicates the predicted classical Hall resistance which crosses the Hall plateau at integer filling factors.  $I_c$ ,  $\rho_{xy}$  could only be plotted for  $\nu = 2$  due to issues with the contact resistance at high magnetic fields, as described in the text. b) The magnetic field dependence of peak breakdown current density for  $\nu = 2$  (dark green) and  $\nu = 1$  (purple) from three  $600\ \mu\text{m}$  Hall bars with carrier densities of  $1.3 \times 10^{11}\ \text{cm}^{-2}$ ,  $2.3 \times 10^{11}\ \text{cm}^{-2}$ , and  $3.3 \times 10^{11}\ \text{cm}^{-2}$ . At the lowest carrier density the  $\nu = 2$  state is not well defined with  $I_c \sim 1\ \mu\text{A}$ .

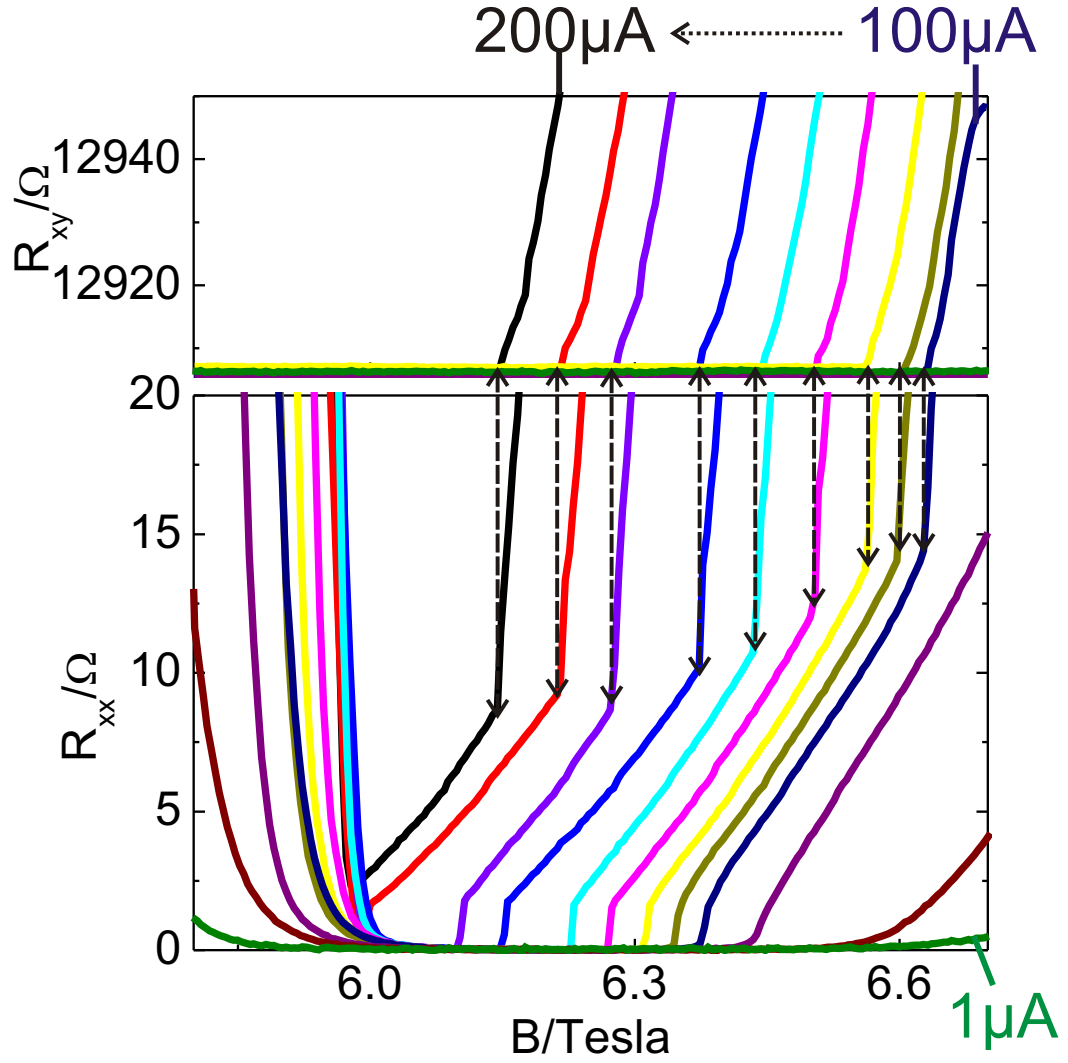


Figure 3.9: Magnetotransport data showing two stages in the onset of longitudinal resistance at high current. There is an initial field at which  $R_{xx}$  exits the dissipationless state. The higher field onset corresponds to the field at which  $R_{xy}$  deviates from quantisation. Also shown for clarity is the low current measurement of  $\nu = 2$  (green)

linear increase with magnetic field, with the exception of the lowest density sample which does not have sufficiently well resolved oscillations to observe quantum Hall behaviour.

One issue encountered was a runaway increase in contact resistance at high currents and high magnetic fields. From two contact measurements it was found that at high fields the voltage dropped at the contacts becomes several times that of the Hall voltage. Due to this effect increasing with magnetic field this meant that we were only able to probe the peak Hall deviation current for  $\nu = 2$  and not  $\nu = 1$ . The contact resistance returns to its original value as the magnetic field is lowered. The origin of this contact resistance is unclear, however in certain models of quantum Hall systems with strong disorder [127] a 2DEG can undergo a phase transition from the quantum Hall state into an insulating state. The sample regions under the contacts could exhibit increased disorder which may allow this transition making the contacts insulating at high fields.

A number of other interesting features and phenomena can be found from the  $I - V_{xx}$  characteristics. Using several sets of connections on a series of samples, a number of different characteristics emerge. One such feature is the hysteretic behaviour observed when the current is decreased after breakdown has occurred (Figure 3.10). This occurs because electrons in the sample heat up during breakdown and remain hot when the applied current is decreased [128].

### 3.4.1 Sample Inhomogeneities

Figure 3.11 shows a series breakdown  $I - V_{xx}$  curves observed in a single  $600\ \mu\text{m}$  wide device. As described above, the zero resistance state persists at low currents followed by a sudden current induced onset of resistance. There are a number of differences between each of the  $I - V_{xx}$  characteristics as the voltage probes are varied. The curves appear to be grouped into pairs. The contact pairs  $BC$  and  $HG$  show the highest breakdown current values, closest to the  $A$  source-drain contact, whereas both  $CD$  and  $GF$ , closer

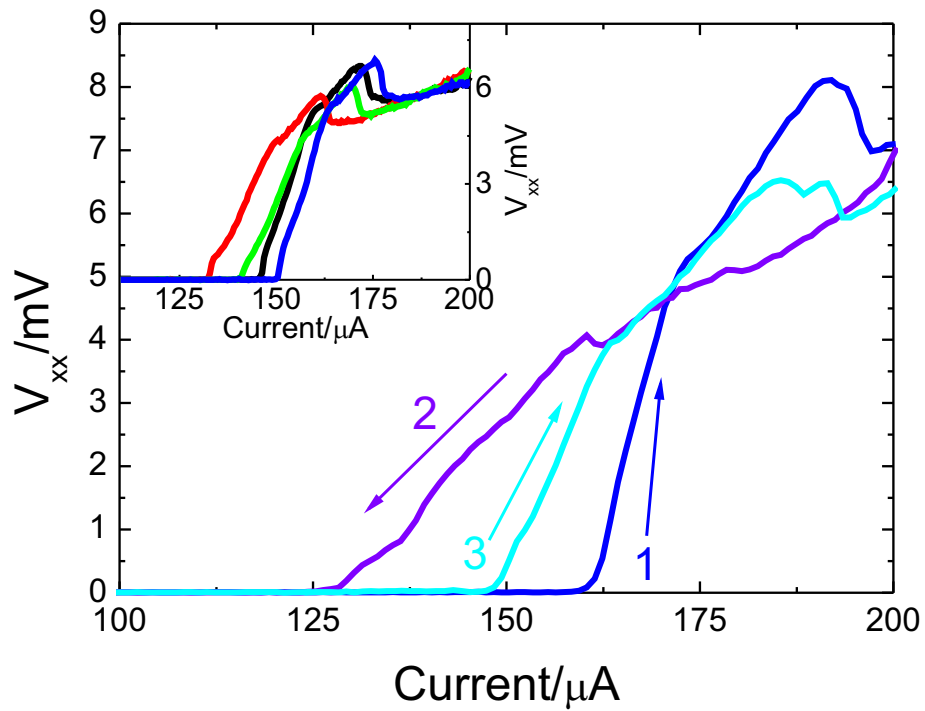


Figure 3.10: Highly hysteretic and non-linear  $I - V_{xx}$  characteristics at 6.5 T in the  $\nu = 2$  plateau as demonstrated by sweeping the current up to 200  $\mu\text{A}$  (1) back to zero (2) then up again (3). Inset: Repeating the measurements several times, each breakdown is different but all show the same underlying features.



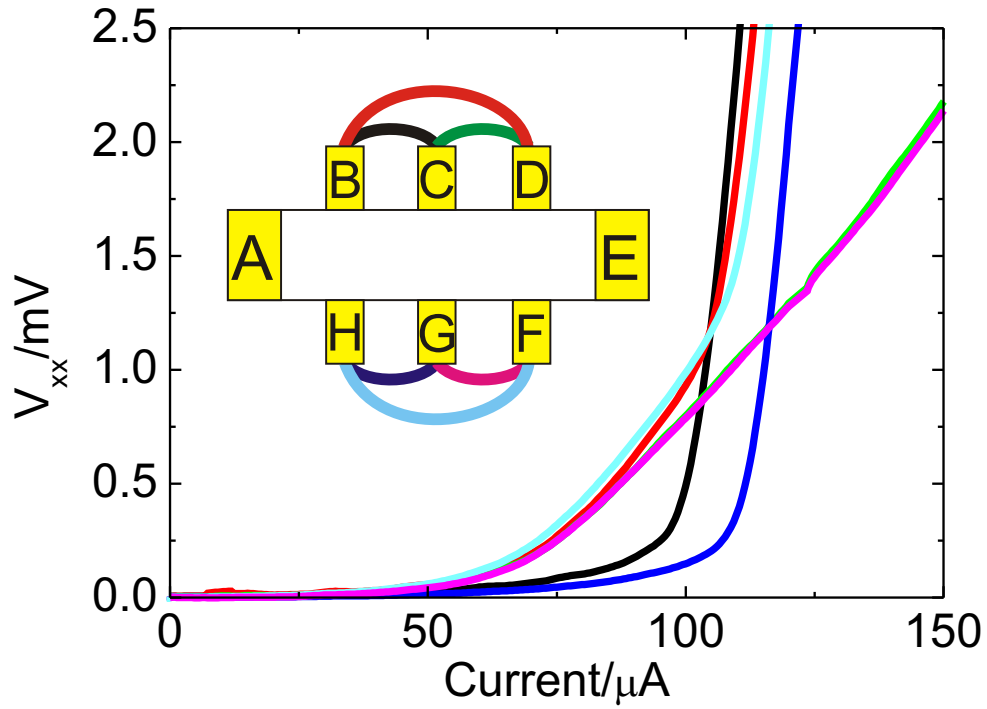


Figure 3.11: I-V characteristics at  $\nu = 2$  for several contacts on the same Hall bar device exemplifying the inhomogeneities often observed in such devices. Inset: The sample geometry and contact positions.

to the  $E$  source-drain contact, show an onset of resistance at much lower currents. Measuring across the entire device using  $BD$  or  $HF$  voltage probes appears, perhaps expectedly, to be a superposition of  $I - V_{xx}$  curves from each end of the device. In such a large device it is clear that carrier density inhomogeneities can cause significant variations in the quantum Hall breakdown characteristics which must be reduced in order to optimise for quantum Hall metrology applications.

### 3.4.2 Geometric Dependence

A number of studies on low mobility samples have shown that the critical breakdown current scales linearly with the Hall bar width [129] consistent with the existence of a critical electric field for the breakdown of the quantum Hall effect. Critical currents in high mobility samples, on the other hand, have been shown to increase sublinearly with

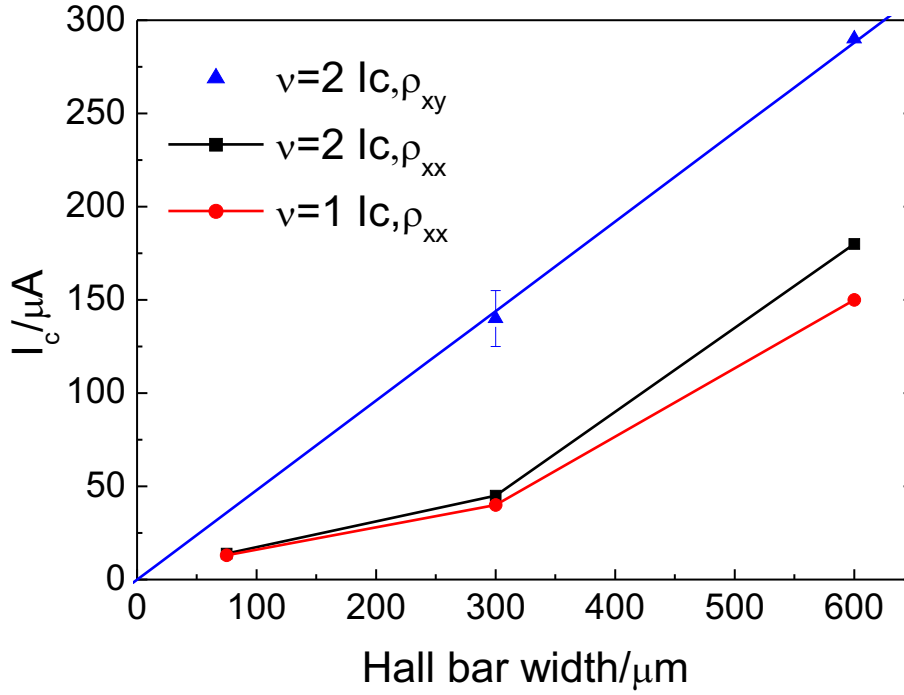


Figure 3.12: Width dependence of maximum Hall deviation current for  $\nu = 2$  (blue) and  $I_c$  for  $\nu = 2$  (black) and  $\nu = 1$  (red). The three widths used were  $75 \mu\text{m}$ ,  $300 \mu\text{m}$  and  $600 \mu\text{m}$ .

width [130]. This leads to the breakdown condition being described as a critical current density across the width,  $W$ , of the Hall bar given by  $j_c = I_c/W$ , which ranges from  $\sim 0.1$ - $1.6 \text{ A/m}$  [129, 130] in GaAs and recently up to  $8 \text{ A/m}$  in exfoliated graphene [112] and  $43 \text{ A/m}$  in polymer gated epitaxial graphene (Chapter 4).

We have studied the width dependence of  $I_c$  in devices of three widths,  $75$ ,  $300$  and  $600 \mu\text{m}$ , all with equal aspect ratios. Figure 3.12 shows that the current for the onset of quantum Hall deviation ( $\Delta\rho_{xy}$ ) increases with increasing width resulting in a critical current density of  $0.5 \text{ A/m}$  for the  $600 \mu\text{m}$  device. A study of  $I_c$  from the breakdown of  $\rho_{xx}$  shows lower values than observed from  $\Delta\rho_{xy}$ , and considerably more variability and dependence on contact arrangements which we attribute to both macroscopic and microscopic inhomogeneities in electron density as discussed above.

### 3.4.3 Temperature Dependence

Indium Antimonide quantum Hall resistance standards would offer a distinct advantage over conventional GaAs devices if they could be operated at higher temperatures. To study this, the field was set at the position of maximum breakdown current and the temperature varied. Temperature dependence of the longitudinal  $\rho_{xx}$  breakdown current for both  $\nu = 1$  (14 T) and  $\nu = 2$  (7 T) in a 600  $\mu\text{m}$  Hall bar were studied (Fig. 3.13a). Both plateaux are seen to show very little reduction in breakdown current to well above the Helium-4 temperature of 4.2 K. This compares well to the equivalent temperature dependence observed for GaAs devices. Typical results for a similar GaAs sample [131] with a carrier density of  $2.4 \times 10^{11} \text{ cm}^{-2}$  are also shown in Figure 3.13a for comparison. Whilst GaAs may have higher critical current densities at low temperatures, the breakdown current for the QHE falls much faster with increasing temperature. This means that at 4.2 K, the breakdown current of GaAs is only  $\sim 20\%$  of its low temperature value, whereas for InSb the breakdown current remains at over 85%. We can approximate the temperature dependence [132] of the quantum Hall breakdown current density,  $j_c$ , using

$$j_c = j_c^0 \left( 1 - \frac{T_L^2}{T_c^2} \right). \quad (3.4)$$

Where  $j_c^0$  is the breakdown current density at zero temperature and  $T_c$  is the critical temperature, above which QHE is not observed. We find that while the absolute breakdown current density is higher in GaAs, the critical temperature is higher in InSb with  $T_c \approx 8 \text{ K}$  due to the larger Landau and spin-split energy gaps. In GaAs the value of  $T_c$  has been found to scale with magnetic field at almost exactly 1 K/T [132]. Assuming the same behaviour for InSb based on the results for the linear field scaling of  $j_c^0$  (Figure 3.8b) would suggest a value of  $\approx 1.3 \text{ K/T}$  which is significantly larger than for GaAs but is not scaling linearly with the magnitude of the cyclotron energy.

The most widely accepted theory of the breakdown of the QHE has been described in

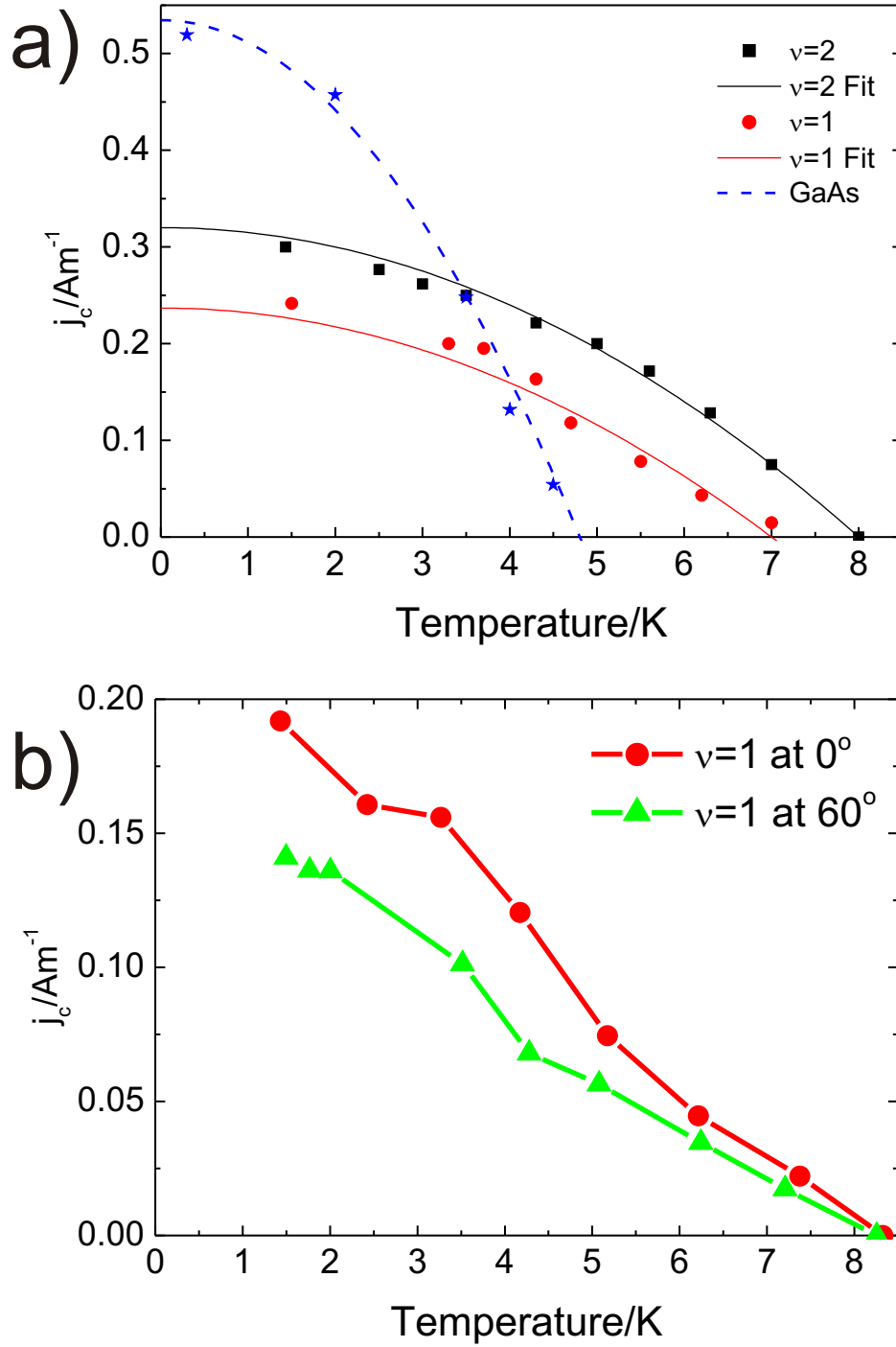


Figure 3.13: a) Temperature dependence of longitudinal breakdown current density for  $\nu = 2$  (6.1 T, black) and  $\nu = 1$  (12.2 T, red) for a  $600 \mu\text{m}$  Hall bar fitted using equation 3.4. Also shown for comparison is the temperature dependence of  $\nu = 2$  in GaAs at 4.8 T (blue dashed) taken from Ref. [131]. b) Temperature dependence of breakdown current density for  $\nu = 1$  perpendicular to the magnetic field (9 T) and at  $60^\circ$  (18 T), taken with a  $75 \mu\text{m}$  device.

the work of Komiyama and Kawaguchi and is based on bootstrap-type electron heating [133, 134]. It predicts that breakdown occurs at a critical electric field,  $E_c$ , which is determined by the energy relaxation time given by

$$E_c = \sqrt{\frac{4B\hbar\omega_c}{2e\tau_e}}, \quad (3.5)$$

assuming a two-fold (spin) degeneracy of the Landau levels. This yields a predicted critical electric field of 27.1 kV/m at 6T using  $\tau_e = 500$  ps, the value at the breakdown temperature of 8 K. This corresponds to a  $\nu = 2$  breakdown current density of 2.1 A/m, compared to the experimental value of 0.5 A/m observed for the  $\rho_{xy}$  deviation. This difference is not surprising as the theory is known to overestimate  $E_c$  by a factor of 2 to 4 when compared to the highest values observed in even the most well optimized wide Hall bars in GaAs[129]. This is probably due to uncertainties in the most appropriate value of  $\tau_e$  which should be used.

#### 3.4.4 Breakdown of spin-split quantum Hall states

The temperature dependence of the breakdown current for  $\nu = 1$  was also studied in a  $75\ \mu\text{m}$  device as shown in Figure 3.13b. InSb is very different from GaAs due to the very high electron g-factor which means that large quantum Hall breakdown currents can also be observed at high temperatures for  $\nu = 1$ , where the separation between the two spin levels is comparable to the Landau splitting for  $\nu = 2$ . The breakdown currents for  $\nu = 1$  are only slightly smaller than for  $\nu = 2$ , which means that  $E_c(\nu = 1)$ , is significantly ( $\sim 60\%$ ) higher than for  $\nu = 2$  and the quantum Hall effect persists up to similar temperatures. In GaAs at low enough temperatures ( $< 0.5$  K) in a given sample  $E_c(\nu = 1)$  is found to be equivalent to  $E_c(\nu = 2)$  [135].

The spin splitting is known to be significantly enhanced by rotating the sample

relative to the magnetic field direction [8]. Integer filling factor occurs at a specific magnetic field perpendicular to the surface of the 2DEG. As such, by rotating the sample the total magnetic field can be increased whilst maintaining the same filling factor. Figure 3.13b shows a comparison for two measurements with the same perpendicular field for a narrow channel sample ( $75\mu\text{m}$ ) with the sample at  $0^\circ$  and  $60^\circ$  to the applied field. The total magnetic field is therefore doubled for  $\nu = 1$ . While the spin splitting increases between  $0^\circ$  and  $60^\circ$  by a factor close to 2, the breakdown current for  $\nu = 1$  actually falls. We attribute this to a mixing of energy levels in the quantum well which leads to additional breakdown mechanisms, possibly due to coupling to bulk and higher energy states.

### 3.5 Summary

We have observed quantum Hall effect in the narrow band-gap InSb/AlInSb system. We have shown that the large cyclotron energy leads to the quantum Hall effect persisting to higher temperatures than seen for GaAs, although the maximum value of the critical current is somewhat smaller due to the lower energy loss rate. We have shown that the high current breakdown can be observed for spin-polarised quantum Hall states at  $\nu = 1$ , and that the critical breakdown field is higher than that at  $\nu = 2$ . Deviation from Hall quantisation at high electric fields is abrupt and is shown to occur at currents much greater than those required to see longitudinal dissipation which is related to the presence of significant carrier density inhomogeneities in the samples.

## Chapter 4

# Phase-space of the breakdown of the quantum Hall effect in epitaxial graphene

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We report the phase-space defined by the quantum Hall effect breakdown in polymer gated epitaxial graphene on SiC (SiC/G) as a function of temperature, current, carrier density, and magnetic fields up to 30 T. At 2 K breakdown currents ( $I_c$ ) almost two orders of magnitude greater than in GaAs devices are observed. The phase boundary of the dissipationless state ( $\rho_{xx} = 0$ ) shows a  $(1 - (T/T_c)^2)$  dependence and persists up to  $T_c > 45$  K at 29 T. With magnetic field  $I_c$  was found to increase  $\propto B^{3/2}$  and  $T_c \propto B^2$ . As the Fermi energy approaches the Dirac point, the  $\nu = 2$  quantized Hall plateau appears continuously from fields as low as 1 T up to at least 19 T due to a strong magnetic field dependence of the carrier density.

## 4.1 Introduction

The quantum Hall effect (QHE) observed in two-dimensional electron gases is defined by vanishing longitudinal resistivity,  $\rho_{xx} = 0$ , and a quantised Hall resistance,  $\rho_{xy} = h/\nu e^2$  for  $\nu = \text{integer}$ . Ever since its first observation[13] in silicon the QHE has been used as a quantum electrical resistance standard which has been most extensively developed using GaAs devices [136]. In recent years since the first isolation of graphene and the observation of the integer QHE [23, 25], the attention of quantum Hall metrology labs has turned to graphene as a potentially more readily accessible resistance standard capable of operating at higher temperatures and measurement currents with lower magnetic fields. This is in part due to its large cyclotron energy gaps arising from the high electron velocity at the Dirac point. Recent experimental work [112] has also shown that it has high electron-phonon energy relaxation rates, an order of magnitude faster than in GaAs heterostructures, which play an important role in determining the high current breakdown of the QHE. In particular polymer gated epitaxial graphene on SiC has been shown to be an exceptional candidate for metrology [86, 111] and the universality of quantisation between it and GaAs has been shown to be accurate within a relative measurement uncertainty of  $8.6 \times 10^{-11}$ [28].

If epitaxial graphene is to be used as a quantum resistance standard it is important to understand the experimental limits which confine the phase-space in which the accurate, dissipationless QHE can be observed. Such a phase-space is determined by the temperature,  $T$ , carrier density,  $n$ , magnetic field,  $B$ , and current,  $I$ . The breakdown of the QHE is defined as the point where deviations from quantisation,  $\Delta\rho_{xy}$ , can be observed and this is strongly correlated with the point where  $\rho_{xx} \neq 0$ . A linear relationship of  $\Delta\rho_{xy}/\rho_{xy} = S\rho_{xx}$  is typically observed in GaAs [125] and recently in graphene [137], with typical values of  $S = 0.1$  [136], therefore measurement of the  $I - V_{xx}$  characteristics in the quantum Hall regime will also determine the maximum current available while



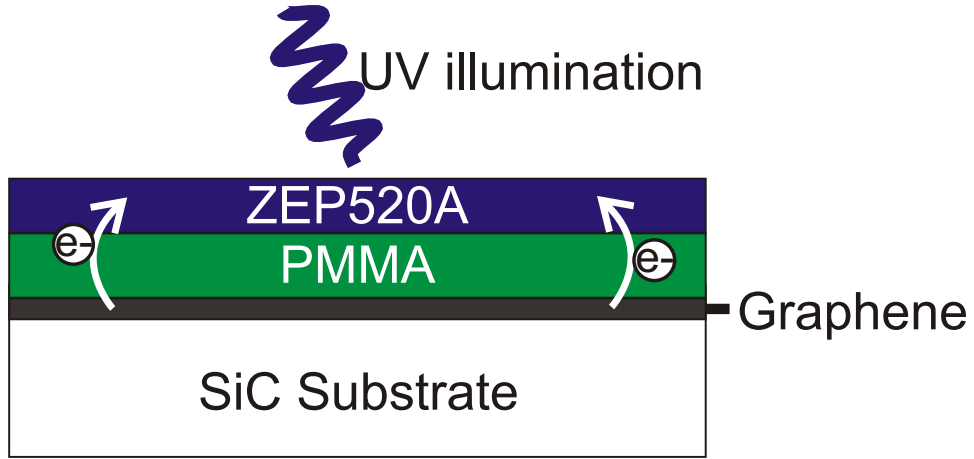


Figure 4.1: Electrochemical gating technique: UV illumination of the ZEP520A creates electron acceptor states, charge is then transferred from the graphene through the PMMA layer.

maintaining a quantised  $\rho_{xy}$ . At high currents a sudden onset of longitudinal resistance is observed above a critical current  $I_c$  [27, 111, 136]. Modelling the breakdown using the bootstrap electron heating (BSEH) model from Komiyama and Kawaguchi [29] which looks at the balance between the rate of increase of energy input and electron energy loss has been reasonably successful.

In GaAs and InSb the temperature dependence [131, 132] (Chapter 3) of  $I_c$  has been shown to be of the form

$$I_c(T) = I_c(0) \left( 1 - \frac{T^2}{T_c^2} \right), \quad (4.1)$$

where  $T_c$  is the temperature at which  $I_c = 0$ , leading Rigal *et.al.* [132] to draw parallels with a phase diagram as predicted by the Gorter-Casimir two-fluid model for superconductors. We will show that this also describes the temperature dependence of  $I_c$  very well in epitaxial graphene and will examine the magnetic field dependence of  $T_c$ , providing further support for the description of the dissipationless quantum Hall regime in terms of a phase diagram. The quantum Hall effect has already been reported in graphene at room temperature using magnetic fields of 45 T [138], however the plateaus did not show exact quantization as the resistivity was still finite ( $\sim 10\Omega$ ). In this

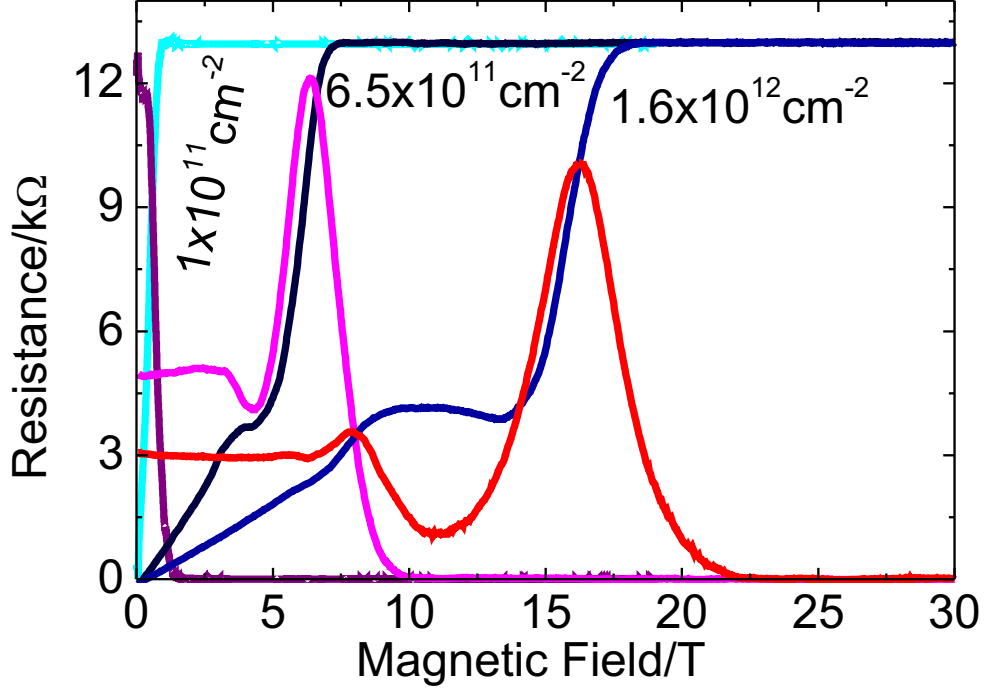


Figure 4.2: Magnetotransport data taken from both extremes of the carrier density range, as well as an intermediate density.

work we address the formation of the zero-resistance state which corresponds to the dissipationless current flow needed to maintain the full quantum Hall condition.

## 4.2 Experimental Configuration

Two devices were studied, prepared from epitaxially grown graphene on the Si-terminated face of SiC. Each device was lithographed using an e-beam and oxygen plasma etching into an eight leg Hall bar geometry ( $W/L = 4.5$ ) with widths of  $W = 5\mu\text{m}$  and  $W = 35\mu\text{m}$  for Sample 1 and Sample 2 respectively. Samples were electrically connected with large area Ti-Au contacting (Section 2.2). A polymer gating technique using room temperature UV illumination was used to vary the electron density from  $1 - 16 \times 10^{11} \text{ cm}^{-2}$  as described in Ref. [85] (Fig. 4.1). D.C. magnetotransport and  $I - V$  data were taken using magnetic fields from a 21 T superconducting solenoid and

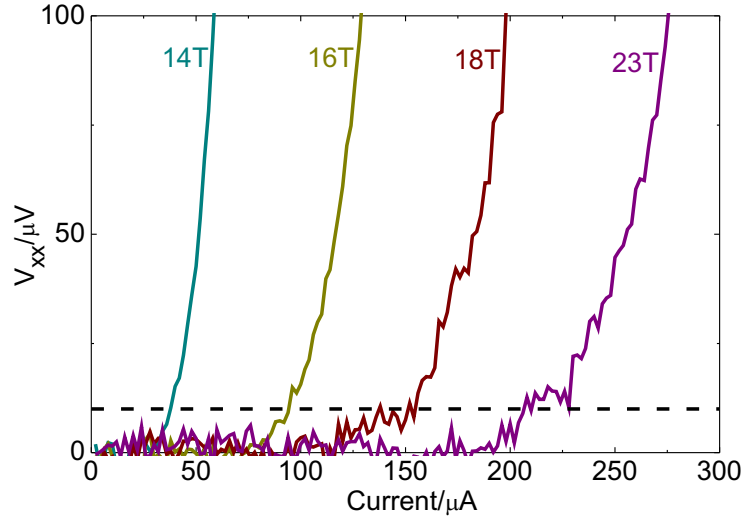


Figure 4.3: a)  $I - V_{xx}$  characteristics of Sample 1 at 2.0 K, with a breakdown condition of  $V_{xx} = 10 \mu\text{V}$ , giving a maximum critical current density  $j_c = 43 \text{ A/m}$  at 23 T.

a 30 T 20 MW resistive-coil magnet at the LNCMI Grenoble. Magnetotransport data is shown in Figure 4.2 for three carrier densities from the minimum to the maximum.

### 4.3 Magnetic field dependent critical current

Figure 4.2 shows magnetotransport data for Sample 1 with  $n_{B=0} = 6.5 \times 10^{11} \text{ cm}^{-2}$ . We observe Shubnikov-de Haas oscillations in filling factors up to  $\nu = 8$ , and a  $\nu = 2$  quantum Hall plateau beginning at  $B = 8 \text{ T}$  with  $\rho_{xx} = 0$  from  $B = 10 \text{ T}$ . This  $\nu = 2$  state is over 20 T wide and observable all the way up to the maximum magnetic field of 30 T. A series of  $I - V_{xx}$  traces were taken every 1 Tesla along the plateau to investigate the breakdown phenomena. Typical  $I - V_{xx}$  traces are shown in Figure 4.3 at  $T = 2 \text{ K}$ . At 23 T we find  $V_{xx} = 0$  until  $I = I_c = 215 \mu\text{A}$ , where we define the critical breakdown current at  $V_{xx}(I_c) = 10 \mu\text{V}$ , just above the noise-level of our measurements (Fig. 4.3), corresponding to a resistivity of  $\rho_{xx} \approx 0.01 \Omega$ , consistent with a quantization accuracy of better than 1 in  $10^7$ . Such a high breakdown current for a device just  $5 \mu\text{m}$  wide,

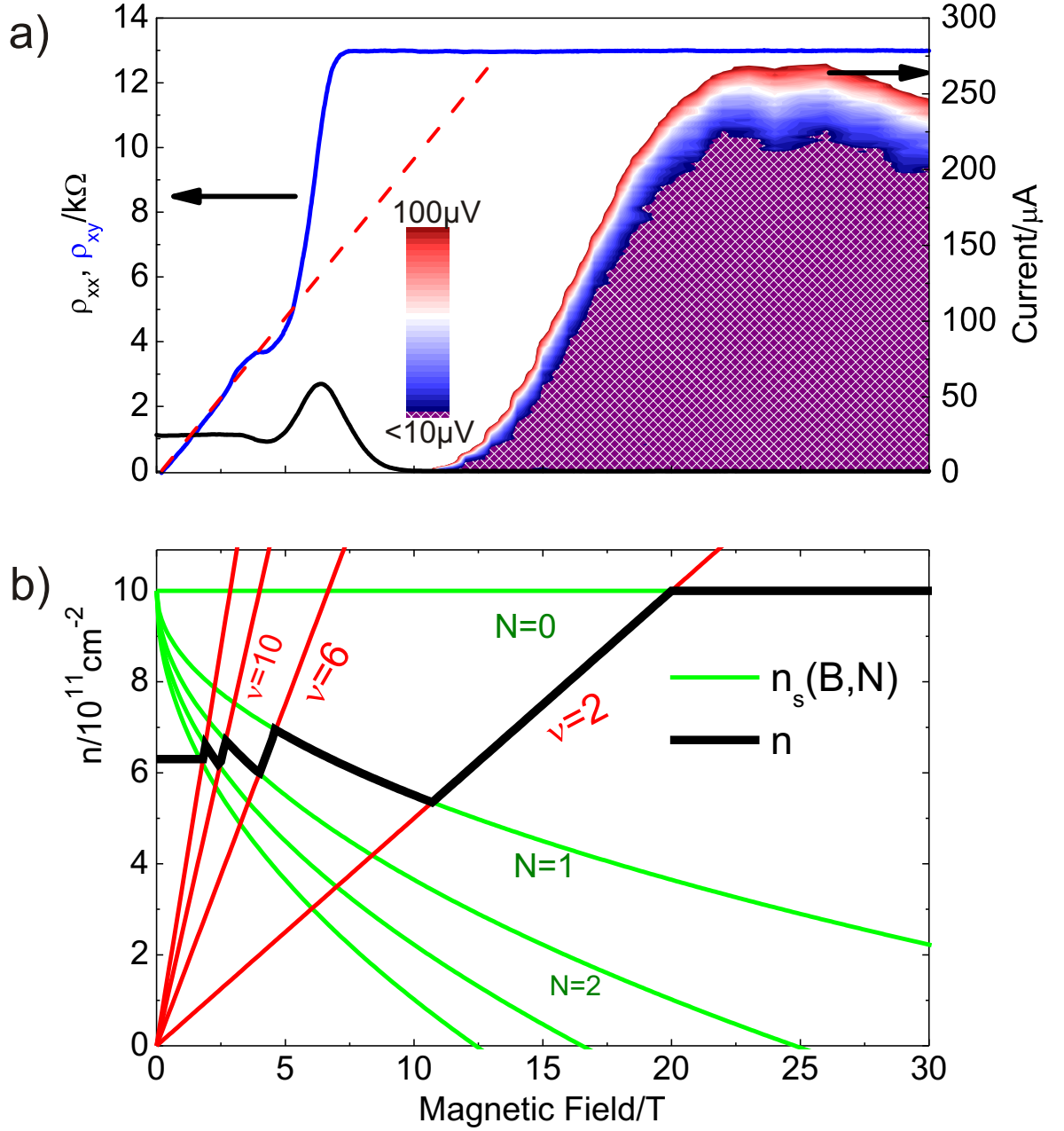


Figure 4.4: a) Combined magneto-transport ( $\rho_{xy}$  (blue),  $\rho_{xx}$  (black)) data and  $I - V_{xx} - B$  contour plot, the hashed region represents  $V_{xx} < 10\mu\text{V}$ , the dissipationless quantum Hall regime. The red dashed line is the extrapolation of the low field Hall coefficient. The magnetic field at which it intersects  $\rho_{xy} = h/2e^2$  is the expected field of integer filling factor  $\nu = 2$ . b) Magnetic field dependence of the carrier density (black), following lines of constant filling factor (red) while  $E_F$  lies between Landau levels, and following the charge transferred from surface donors in SiC,  $n(B, N)$  (green), while the Landau levels fill, from the model in [111].

giving a critical current density of  $j_c = 43 \text{ A/m}$ , is truly exceptional in comparison to even the most well optimised GaAs devices ( $j_c^{\text{GaAs}} \sim 1\text{-}2 \text{ A/m}$ ). The full set of  $I - V_{xx}$  traces are plotted in Figure 4.4a as a contour plot. The hashed region is the phase space where the dissipationless QHE is observed. The critical current  $I_c$  increases along the plateau with a peak around 23 T.

## 4.4 Charge Transfer Model

Traditional semiconductor quantum Hall systems show a very sharp peak in  $I_c$  centered at integer filling factor (Chapter 3). However, the peak breakdown current occurs at fields much greater than  $\nu = 2$  calculated from the zero-field carrier density (Fig. 4.4), and changes very little in magnitude over a wide range of fields. This is due to the strong magnetic field dependence of the carrier density in epitaxial graphene grown on Si-terminated SiC described by the charge balance equation relating the carrier density from the substrate  $n_s$  and from the gate  $n_g$  [139] (Fig. 4.5)

$$\gamma[A - 4\pi e^2 d(n_s + n_g) - E_F] = n_s + n_g, \quad (4.2)$$

where  $A$  is the difference in work function between undoped graphene and the SiC donor states,  $E_F$  is the Fermi energy and  $\gamma$  is the density of donor states. The carrier density transferred to the gate is found from the gate capacitance  $C$  and the applied voltage  $V_g$  using  $n_g = CV_g/e$ . Carriers are transferred to the graphene from the surface donor states of the SiC which are assumed to have a constant density of states. The charge transfer,  $n_s(B, N)$  is proportional to the difference between the workfunction of the graphene and the SiC and is dependent on magnetic field, according to

$$n_s(B, N) = n_\infty - \frac{\gamma \hbar v_F \sqrt{2N} / \lambda_b}{1 + e^2 \gamma / c_c}, \quad (4.3)$$

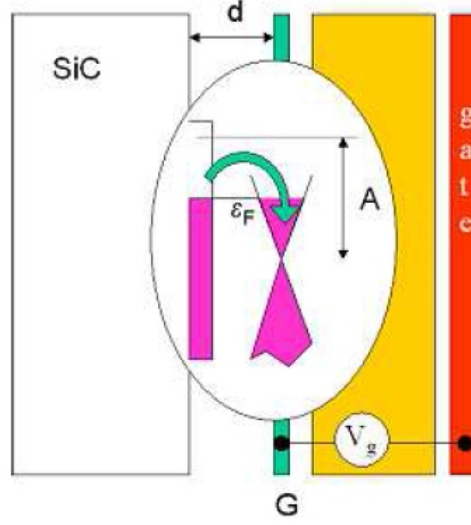


Figure 4.5: Charge transfer model between SiC and gated graphene (G), adapted from [140].

where  $c_c = 1/4\pi d$  is the classical capacitance per unit area, with  $d = 0.3 \text{ nm}$  being the distance between the SiC donor layer and the graphene (Fig. 4.5),  $\lambda_b = \sqrt{\hbar/eB}$ , and  $n_\infty$  is the predicted maximum carrier density when the work function of the graphene matches that of the donor states, as determined by

$$n_\infty = \frac{A\gamma}{1 + e^2\gamma/c_c} - n_g. \quad (4.4)$$

This causes the unbroadened Landau levels to be completely filled over a wide range of magnetic fields [111], particularly when the Fermi Energy  $E_F$  is between the  $N = 0$  and  $N = 1$  Landau levels as in the region above 11 T in Figure 4.4b. Assuming that the peak  $I_c$  occurs at  $\nu = 2$ , the data shown in Figure 4.4a suggests that the carrier density has increased to  $n = 1.1 \times 10^{12} \text{ cm}^{-2}$  by 23 T. In addition, the slow decrease of  $I_c$  suggests that, contrary to the theoretical prediction (Fig. 4.4b),  $n$  is still increasing. As a result the breakdown current is relatively independent of magnetic field, above 23 T, which adds to the convenience of epitaxial graphene as an electrical resistance standard.

## 4.5 Low Carrier Density Phase Diagram

At the lowest carrier density studied using Sample 2 ( $n_{B=0} \sim 1 \times 10^{11} \text{ cm}^{-2}$ ), the  $\nu = 2$  state (Fig. 4.6a) begins at  $B = 1 \text{ T}$  and persists up to the maximum field studied for this sample of  $19 \text{ T}$ . The breakdown current shown in Figure 4.6a is negligible at low fields ( $B < 3 \text{ T}$ ) but rapidly increases reaching a peak at  $B = 7 \text{ T}$ , suggesting a carrier density of  $n_{B=7\text{T}} = 3.5 \times 10^{11} \text{ cm}^{-2}$ . At  $7 \text{ T}$ ,  $I_c = 140 \mu\text{A}$ , giving  $j_c = 4 \text{ A/m}$  for this  $35 \mu\text{m}$  wide device. Importantly, from an applications perspective,  $I_c \sim 100 \mu\text{A}$  by  $5 \text{ T}$ , a magnetic field which is readily accessible with simple benchtop magnets and where a current of  $100 \mu\text{A}$  has been shown to be sufficient to obtain an accuracy of a few parts in  $10^{11}$  when comparing  $2h/e^2$  in graphene and GaAs [28]. Applying the charge transfer model [139] the magnetic field for peak breakdown is accurately predicted (Fig. 4.6b) but above this no further increase in carrier density is expected due to the finite density of donor states. However, the data suggest that the carrier density is still increasing, as the breakdown current has only decreased by a factor of 1.8 by  $19 \text{ T}$ . The discrepancy between the data and the theory is probably due to the influence of Landau level broadening which is not included in the original model [139]. In typical semiconductor 2DEGs [136] (Chapter 3), breakdown currents show a triangular behaviour with a plateau width (defined by  $I_c(\nu)/I_c \geq 0$ ) of  $\Delta\nu/\nu \sim \pm 0.2$  (Fig. 3.8). Assuming a level degeneracy ( $\eta$ ) of 4 for the  $\nu = 2$  plateau due to the valley and spin degeneracies in graphene, this should correspond to a total plateau width of  $\Delta\nu = \pm 0.8$ , and  $I_c$  should halve at  $9 \text{ T}$  ( $\nu = 1.6$ ). This is consistent with results reported for exfoliated graphene [141]. By contrast the slow decrease in  $I_c$  seen in Figure 4.6a suggests that the occupancy remains  $\nu \geq 1.6$  up to  $19 \text{ T}$ . Given that  $\nu = hn/B_z e$ , the carrier density has therefore increased to  $n \geq 7 \times 10^{11} \text{ cm}^{-2}$ , at  $19 \text{ T}$ .

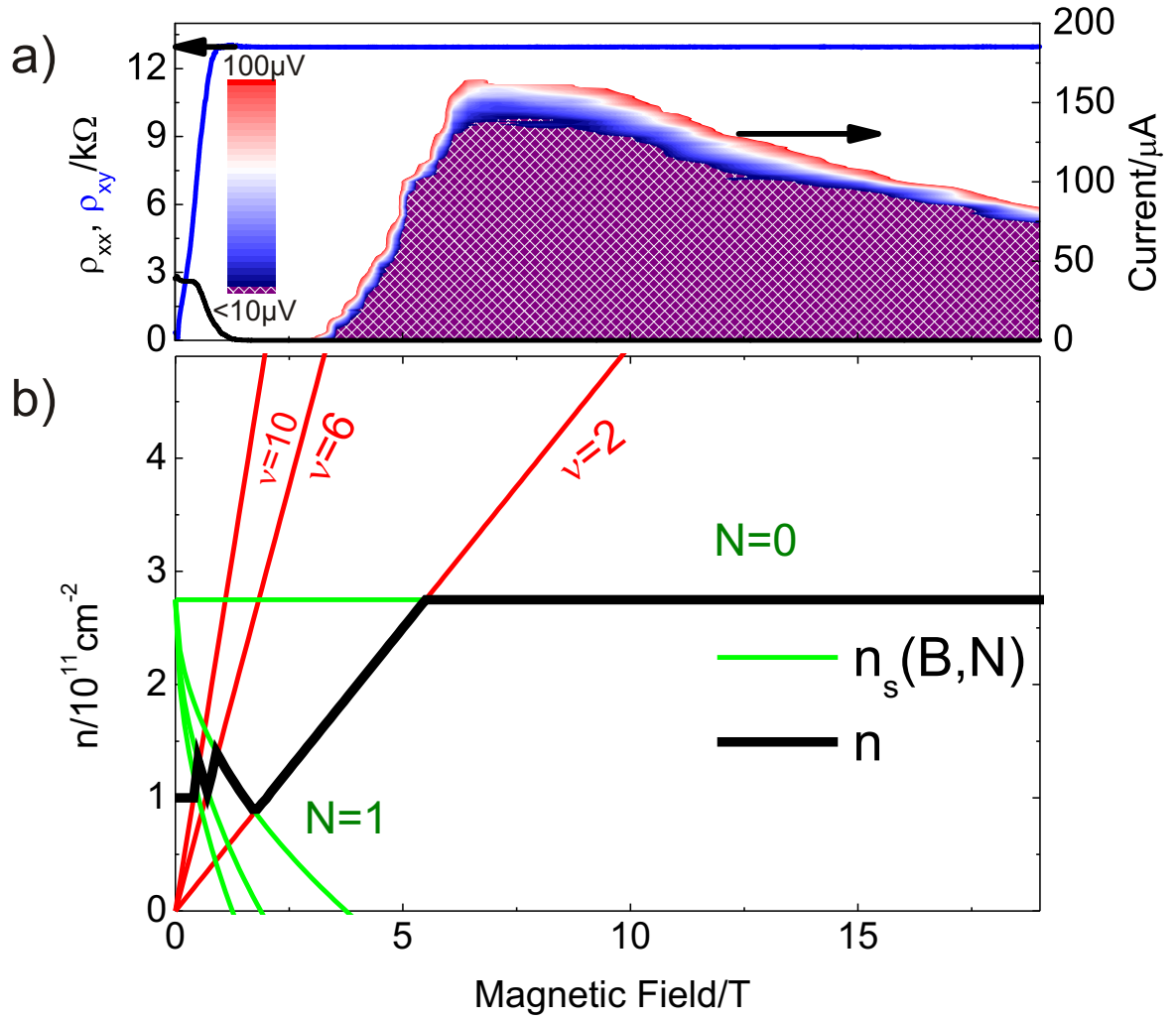


Figure 4.6: a) Magnetotransport ( $\rho_{xy}$ (blue) and  $\rho_{xx}$ (black)) and corresponding  $I - V_{xx} - B$  contour plot for the  $35\mu\text{m}$  wide device at  $T = 1.5 \text{ K}$  where the hashed region represents  $V_{xx} < 10\mu\text{V}$ , the dissipationless quantum Hall regime. b) Theoretical prediction of magnetic field dependent carrier density from Ref. [139].



## 4.6 Arrhenius Analysis

An Arrhenius analysis of the activated conductivity at higher temperatures (75 to 100 K), above the variable range hopping (VRH) regime [142, 143], was used to estimate the magnetic field dependence of the Fermi energy,  $E_F$ . The temperature dependence of  $R_{xx}$  was measured at elevated temperatures (Fig. 4.7). We then fit the temperature dependence of  $R_{xx}$  (Fig. 4.7b) to

$$R_{xx} \propto \exp\left(\frac{-2\Delta}{k_b T}\right) \quad (4.5)$$

The activation gap  $\Delta$  measures the separation of  $E_F$  from the conducting states  $E_\mu$  of the nearest Landau level ( $N = 1$  for  $B < 7$  T,  $N = 0$  for  $B > 7$  T), where  $\Delta = |E_\mu - E_F|$ . The temperature regime of 75 to 100 K was selected as it was the lowest regime at which this fit holds throughout the plateau.

Figure 4.8, shows  $\Delta$  and the value of  $E_F$  which has been deduced by assuming that it is midway between the two Landau levels at 7 T where  $\nu = 2$ . At low fields  $E_F$  corresponds to the approximately constant value of 40 meV deduced from the low field carrier density. Above 2.5 T the carrier density begins to increase due to the charge transfer from the substrate which keeps the Fermi energy in the gap between  $N = 1$  and  $N = 0$ , and the system enters the dissipationless quantum Hall state. Above 7 T  $E_F$  begins to fall slightly but appears pinned close to a constant energy of  $E_F \sim 40$  meV suggesting that there may be a specific surface impurity level close to this value. This suggests that the  $\nu = 2$  plateau could extend up to higher fields still until the extended states of the symmetry broken  $N = 0$  state pass through the pinned Fermi level.

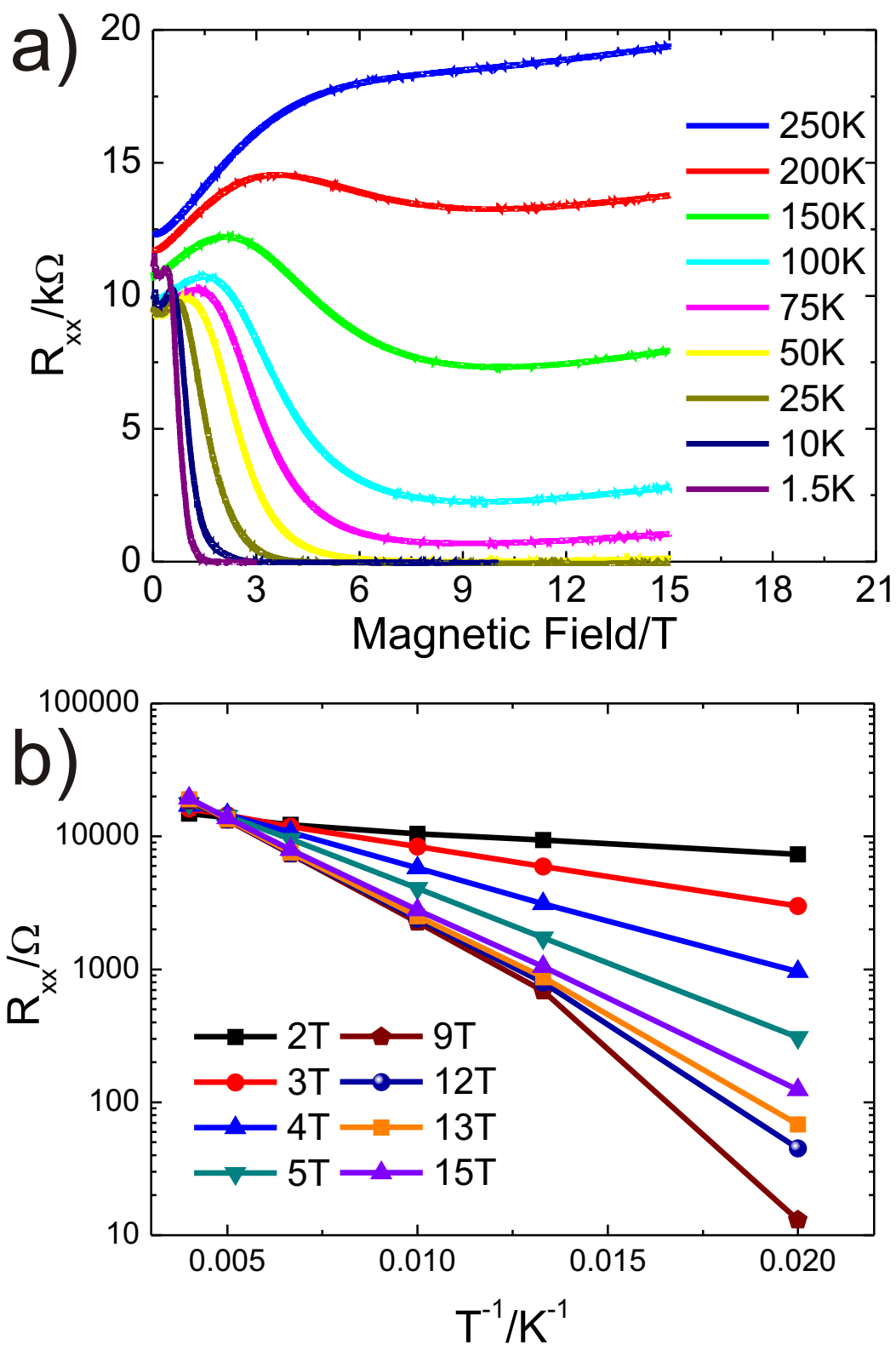


Figure 4.7: a) Magnetotransport data from 1.5 K to 250 K. b) Resistance as a function of inverse temperature. Linearity of the plots indicates thermal activation. At 9 T below  $T = 75$  K the plot deviates from linearity, which may indicate a change from thermal activation to variable range hopping.

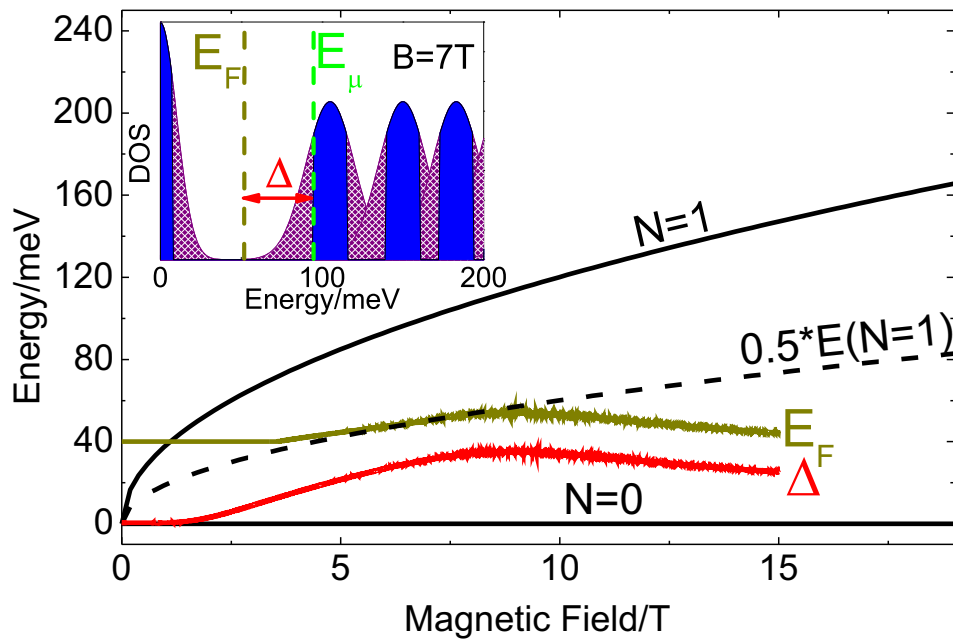


Figure 4.8:  $\Delta$  as a function of magnetic field and the resulting  $E_F$  as calculated from the Arrhenius analysis. Inset) The measured value of  $\Delta$  is the energy difference between the Fermi energy (yellow) and the nearest extended states (blue), also known as the mobility edge.

## 4.7 Temperature Dependence

High temperature ( $T > 4$  K) operation is also highly desirable for an accessible resistance standard. We have studied the temperature dependence of the dissipationless phase for several carrier densities for the peak  $I_c$  at  $\nu = 2$ , except for the highest carrier density of  $n = 1.6 \times 10^{12} \text{ cm}^{-2}$ , at 29 T as the maximum  $I_c$  was just beyond our maximum field. Figure 4.9a shows that Equation 4.1 also describes the temperature dependence of  $I_c$  for the dissipationless state very well in epitaxial graphene. In addition to the analogy with superconductors [132] this form has also been suggested by Tanaka *et al.* [131] based on a model which predicts this behaviour from a temperature-dependent mobility edge caused by the temperature dependence of the tunneling probabilities from localised to extended states at the centre of the Landau levels.

Experimentally, only limited evidence exists for the dependence of  $T_c$  on magnetic field with values for GaAs [131, 132] of  $T_c/B \approx 1 \text{ K/T}$  for B values of 4.8 to 7.7 T at  $\nu = 4$  and  $T_c \propto 1/\nu$ , while for InSb  $T_c = 8 \text{ K}$  at 6.1 T (Chapter 3). It is therefore surprising that for graphene we see a strong superlinear scaling, as shown in Figure 4.9b with a best fit of approximately  $T_c \propto B^2$ , which extrapolates to  $T_c = 111 \text{ K}$  at 45 T. The rate of increase of the cyclotron energy gap between the  $N = 1$  and  $N = 0$  Landau level is sublinear, given by  $E_N = \text{sgn}(N) \times c^* \sqrt{2e\hbar B|N|}$ , where  $c^*$  is the electron velocity. This sublinear behaviour of  $E_N$  on  $B$  would suggest a weaker overall field dependence of  $T_c$  on  $B$ . In epitaxial graphene the magnitude of the disorder is significant, meaning that the activation energy gap ( $\Delta = |E_\mu - E_F|$ ) is not simply  $E_0 - E_1$ . In  $\nu = 2$ ,  $\Delta$  has a large offset due to level broadening, as described above. The energy gap  $\Delta$  has been shown to increase more rapidly than the cyclotron energy with magnetic field [142] due possibly to smaller broadening for the  $N = 0$  Landau level which is topologically protected [23].

Novoselov *et al.* [138] claimed to have observed “room temperature quantum Hall

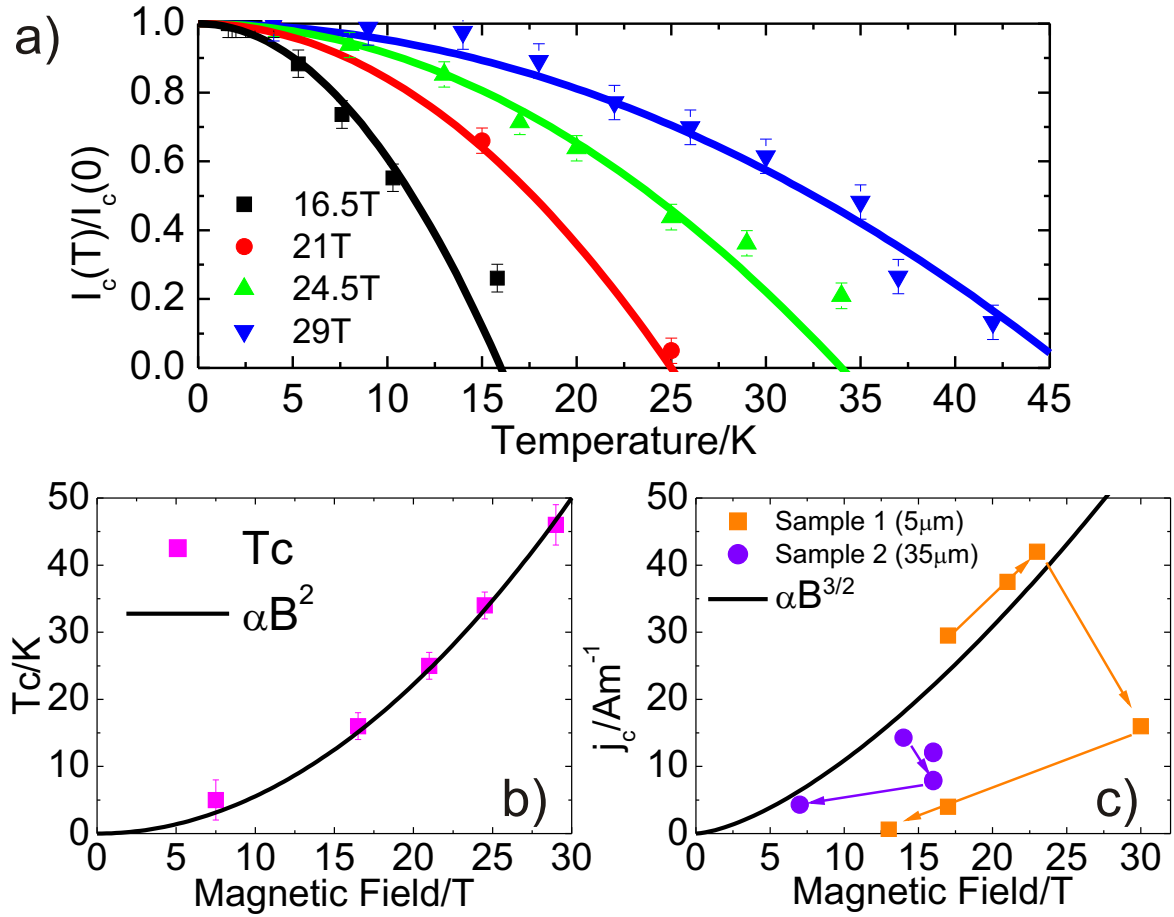


Figure 4.9: a) Normalised temperature dependence of breakdown current at several magnetic fields, fitted with Equation 4.1. (b) The magnetic field dependence of  $T_c$ , with a best fit of  $0.055 \times B^2$ . (c) The magnetic field dependence of the peak  $j_c$  for the two Hall bars with the sequence of illumination shown by arrows. Sample 2 in particular shows significant degradation after prolonged UV exposure.

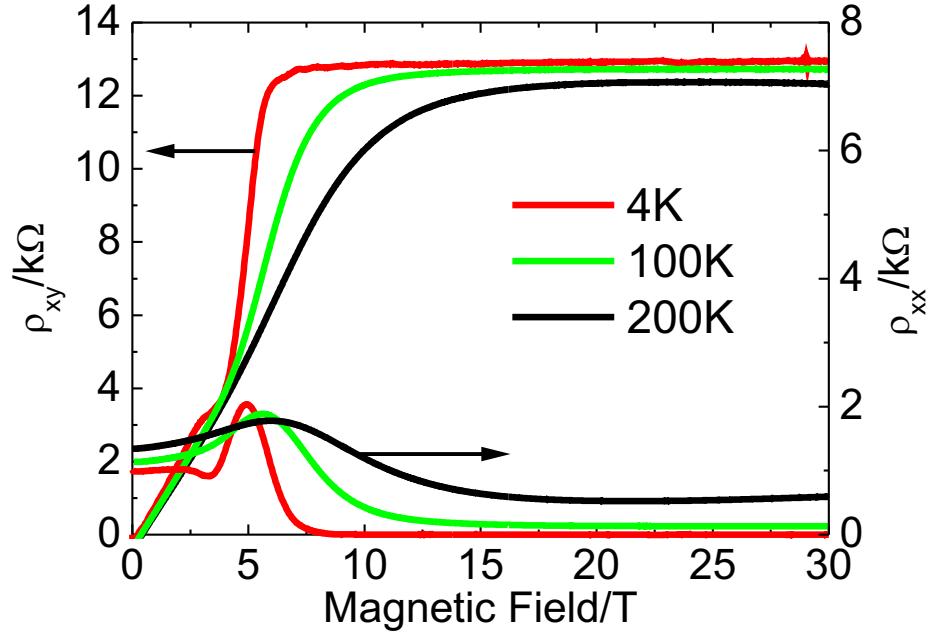


Figure 4.10: Hall resistance as a function of magnetic field. Even at 200 K,  $\rho_{xy}$  shows signs of quantisation, however, due to the finite  $\rho_{xx}$  the true dissipationless state has broken down, which explains the apparent room temperature observation of the QHE at high magnetic fields.

effect in graphene”, whereas we do not. Clearly there is a discrepancy with our results which can easily be explained due to the stringency of our condition for breakdown. Figure 4.10 shows magnetotransport at elevated temperatures. By first inspection the Hall resistance appears quantised, however the quantisation is weak due to the finite  $\rho_{xx}$  in the plateau.

By contrast  $I_c$  has been extensively studied and is well known experimentally to scale as  $B^{3/2}$  [27, 131, 136] as predicted by several of the models for breakdown [29] which include factors for the cyclotron energy and the inverse magnetic length. Figure 4.9c shows the values for  $j_c = I_c/W$  at  $\nu = 2$  for both samples after each UV illumination. The highest values observed for Sample 1 are also consistent with a  $B^{3/2}$  dependence. However, there is considerable degradation in the observed values after extended UV illumination, which is thought to introduce significant spatial inhomogeneities which are

likely to reduce  $j_c$ . Interestingly despite the differences in  $j_c$  values the same samples produced the very clear systematic dependence of  $T_c$  shown in Figure 4.9, supporting the phase diagrammatic picture of the dissipationless state. It should be noted that the values are significantly higher for the  $5\ \mu\text{m}$  Hall bars and there is some evidence that quantum Hall breakdown current densities are larger for smaller Hall bar widths [136, 144].

## 4.8 Unconventional Geometric Effects

The breakdown of the quantum Hall effect is governed by the current density,  $j_c = I_c/W$ , where  $W$  is the width of the Hall bar. By applying the current using a pair of Hall probes across the device (Fig. 4.11) the effective width, which is perpendicular to the current, is increased thus reducing the Hall electric field. This leads to a dramatic increase in the critical current to over 1 mA (Fig. 4.11), which now shows extremely sudden onset of longitudinal resistance in an almost instantaneous phase transition.

## 4.9 Calculating the energy loss time

One of the key components of the bootstrap electron heating (BSEH) model of the breakdown of the quantum Hall effect (discussed further below) is the characteristic electron-phonon relaxation (energy loss) time,  $\tau_e$ . This can be extracted by measurements of the Shubnikov–de Haas (SdH) oscillations, using the same method as those described in Chapter 3. At low applied currents SdH oscillations are damped by an increasing lattice temperature,  $T_L$ . However, at fixed, low, lattice temperatures the oscillations may also be damped by the application of high currents which raises the electron temperature,  $T_e$ , above  $T_L$ . By comparing the  $T_L$  dependence of the SdH oscillations with those at high currents,  $T_e$  can be extracted for a given current (Fig. 4.12a). From this, the power dissipation (energy loss rate) per electron is found as a function of electron temperature

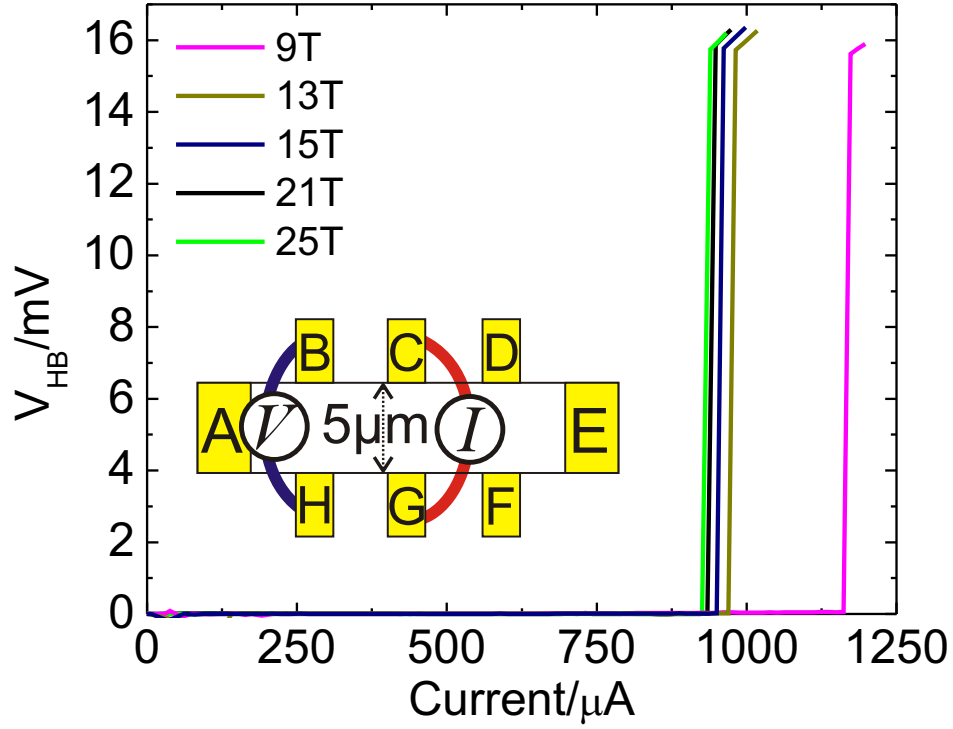


Figure 4.11:  $I_{CG} - V_{BH}$  characteristics of the  $5 \mu m$  wide device. Using this unconventional geometry, where the current is applied across the bar, remarkably high values of  $I_c$  are observed.

and is shown in graphene at low temperatures ( $T_e < 100$  K) to be of the form [98, 145]

$$P = \alpha(T_e^4 - T_L^4), \quad (4.6)$$

where  $\alpha$  is carrier density dependent ( $\alpha \propto n^{-1/2}$ ) [145] as predicted theoretically for graphene [146]. The energy loss time associated with the energy loss rate is given by Equation 3.3 [98, 146]. Since  $\tau_e \propto (PE_F)^{-1} \propto n^{-1/2}n^{1/2}$ , this results in an effectively constant energy loss time as a function of carrier density for a given electron temperature. The value of  $\tau_e$  used in the BSEH model discussed below was taken from the model described in Ref. [98], which is a good fit at high temperatures (Fig. 4.12b) for the samples studied with values given by

$$\tau_e = \frac{A}{T_e^2} + \tau_0, \quad (4.7)$$



where  $A = 5.7 \times 10^{-9} \text{ K}^2\text{s}$  and  $\tau_0 = 1 \text{ ps}$  was included in Ref. [98] to account for the saturation of the electron energy loss time at high temperatures.

The electron temperature at which the energy loss time was extracted was taken as  $T_e = T_c$ , so as to best characterise the carriers at breakdown. Due to the  $T_e^4$  dependence of energy loss rate,  $\tau_e$  is strongly dependent on the choice of  $T_c$ . For example  $\tau_e$  calculated for the breakdown at the lowest carrier density (7 T) can vary by a factor of two by changing  $T_c$  by  $\pm 1 \text{ K}$ .

Baker et al. also showed there to be a decrease in  $\alpha$ , and hence an increase in  $\tau_e$ , by a factor of  $\sim 1.7$ , when comparing measurements at high magnetic fields (from SdH oscillations) versus those at low magnetic fields ( $< 0.1 \text{ T}$ ) from the temperature dependence of the weak localisation peak centred at  $B = 0$  [145]. No further systematic changes were found as a function of magnetic field (and Landau level index) in the high field regime, hence we assume that  $\tau_e$  is independent of magnetic field at higher fields. It is possible that in the fully quantised quantum Hall state, the energy loss time may change, which may explain the systematic over-estimation of the theoretical critical current density  $j_c$  described below.

## 4.10 Bootstrap Electron Heating

The most widely accepted theory for the QHE breakdown is the bootstrap electron heating model proposed by Komiyama and Kawaguchi [29] in which the quantum Hall state becomes thermally unstable above a critical Hall electric field where the rate of change of electron-phonon energy loss rate becomes less than the rate of increase of input power. This predicts a critical breakdown electric field of

$$E_c = j_c \rho_{xy} = \sqrt{\frac{4B\hbar\omega_c}{\eta e \tau_e}}, \quad (4.8)$$

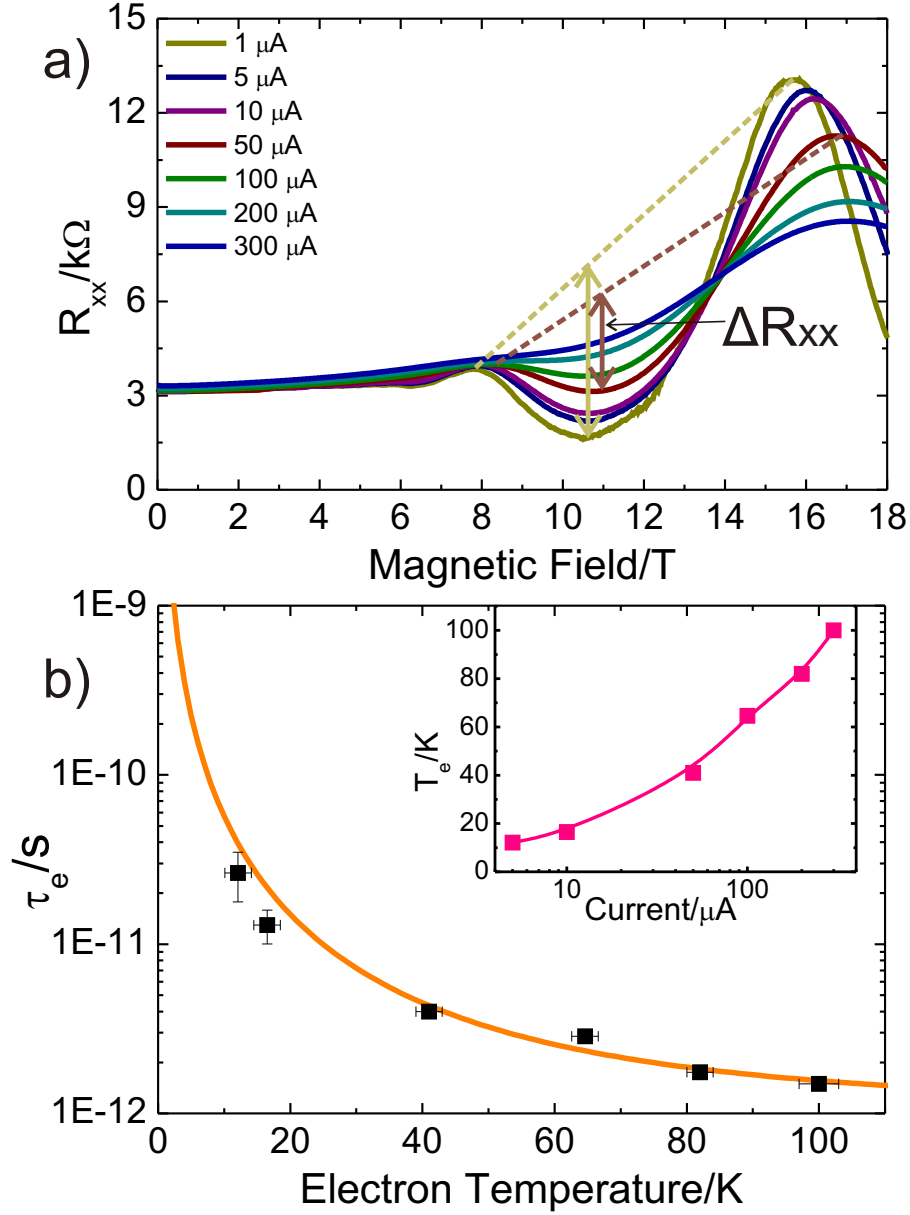


Figure 4.12: a) Shubnikov–de Haas oscillations in epitaxial graphene (Sample 1) at 2 K. The oscillations are damped due to high applied currents up to 300  $\mu A$ . b) Electron–phonon relaxation time,  $\tau_e$ , as a function of electron temperature extracted from the data set in (a) (black squares). Also shown is the theoretical model (orange line) as described in [98] (Equation 4.7). Inset: The electron temperature as a function of current.

| Material      | $\hbar\omega_c$<br>(meV) | $\tau_e$<br>(ps) | $j_c$ (A m <sup>-1</sup> )<br>Theory[29] | $j_c$ (A m <sup>-1</sup> )<br>Experiment | width<br>( $\mu$ m) |
|---------------|--------------------------|------------------|------------------------------------------|------------------------------------------|---------------------|
| GaAs (7T)     | 12                       | 100 [115]        | 2.9                                      | 1.4                                      | 35 [131]            |
| InSb (7T)     | 40                       | 500 [Ch.3]       | 2.6                                      | 0.3                                      | 600 [Ch.3]          |
| Graphene (7T) | 105                      | 80 [145]         | 7.3                                      | <b>4.3</b>                               | 35                  |
| (14T)         | 150                      | 30 [145]         | 23                                       | <b>15</b>                                | 35                  |
| (17T)         | 165                      | 16 [145]         | 36                                       | <b>30</b>                                | 5                   |
| (23T)         | 200                      | 6 [145]          | 71                                       | <b>43</b>                                | 5                   |

Table 4.1: Material comparison for QHE breakdown at  $\nu = 2$ .

where  $\tau_e$  is a characteristic electron–phonon energy relaxation time. Recently much experimental [145, 147, 148] and theoretical [146] interest has focused on the way hot electrons lose energy to the lattice in graphene. We use the values of  $\tau_e$ , observed at  $T_c$  as described above, and measured previously from the damping of Shubnikov–de Haas oscillations in GaAs [115] and InSb (Chapter 3, Fig. 3.4), to calculate the predicted  $j_c$  for  $\nu = 2$  and compare these to conventional semiconductor 2DEGs in Table 4.1. The theoretical and experimental values for  $j_c$  in graphene are considerably larger, as compared for example to InSb, which has the lowest effective mass of the III–V semiconductors,  $m^* = 0.02 m_e$  [11]. At 7 T the cyclotron energy gap is 105 meV for graphene, compared to 40 meV in InSb, however we find an order of magnitude increase in critical current density for graphene over InSb. This is mainly a result of the factor 6 difference in  $\tau_e$  between the two systems. The increase of  $T_c$  with field (Fig. 4.9b) causes  $\tau_e$  to decrease and the dependence of  $j_c$  on magnetic field to be superlinear (Fig. 4.9c).

## 4.11 Summary

In summary, we have investigated the phase space in which the dissipationless quantum Hall state exists for epitaxial graphene. The data support the idea that this system can be described in terms of a phase diagram for the dissipationless state where the

temperature dependence of the critical current follows a behaviour  $\propto (1 - (\frac{T}{T_c})^2)$  as seen in GaAs and InSb quantum Hall systems, providing strong evidence that this is a general feature of the quantum Hall state for a wide range of magnetic fields, temperatures and different materials. We demonstrate that both the critical temperature and current are strongly magnetic field dependent and that at high fields critical current densities can be more than a factor 30 larger than previously observed in other systems. The physical origin of the exceptionally large values of  $j_c$  observed appears to be a combination of the large cyclotron energy gap in graphene and the fast electron-phonon relaxation of hot carriers. In epitaxial graphene, charge transfer from the carbon layer between the graphene and the SiC substrate also leads to a strongly magnetic field dependent carrier density and an exceptionally wide  $\nu = 2$  plateau due to charge transfer from surface impurities followed by pinning to a constant energy associated with a surface impurity level.

## Chapter 5

Hyperspectral imaging of exciton  
dynamics in individual carbon  
nanotubes controlled by high  
magnetic fields

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This chapter describes low temperature (4.2 K) micro-photoluminescence ( $\mu$ PL) studies of high purity individual semiconducting single walled carbon nanotubes (SWNTs) in magnetic fields up to 30 T. We observe ultra-narrow emission linewidths with a FWHM  $< 80 \mu\text{eV}$ . Using these narrow linewidths we study in detail the effects of high magnetic fields on the exciton fine structure. In pristine SWNTs the dark exciton is clearly resolved at  $B < 1$  T with a consistent zero-field splitting of  $\Delta_x = 2 \text{ meV}$  between the dark and bright exciton for (8,6) tubes. High intensity laser irradiation creates an additional dark-bright pair of bound spin singlet exciton states with an increased zero-field splitting of  $\Delta_x^{\text{bound}} = 7 \text{ meV}$ . Multiple magnetically activated emission sidebands are observed in a number of individual SWNTs which we attribute to the magnetic brightening of previously dark localised quenching sites, which may explain the apparent variability of  $\Delta_x$  observed within single chiralities in early individual SWNT magnetospectroscopy. Imaging of individual SWNTs in high magnetic field confirms that these sidebands originate from spatial localised states in previously dark segments of the tube.

## 5.1 Introduction

Since their discovery [35] the exceptional optical [100] and electronic [149] properties of single-walled carbon nanotubes (SWNTs) have been of particular interest for the study of fundamental physics as well as for potential applications. The band structure of SWNTs is calculated from the graphene band structure using the zone-folding approximation and may be semiconducting or metallic depending on the direction and diameter of folding (chirality) [150]. Photoluminescence (PL) and photoluminescence excitation (PLE) spectroscopy experiments on semiconducting SWNTs facilitate the study of a rich variety of 1D exciton physics. The narrow diameter of SWNTs leads to strongly bound excitons due to large Coulomb interaction. A combination of electron and hole spin and the presence of two degenerate valleys at the  $K$  and  $K'$  points means the predicted excitonic spectrum of a semiconducting single walled SWNT consists of a spin-singlet manifold of 4 states with just one optically active (bright) state, and 12 optically forbidden (dark) triplet states.

A magnetic flux threading a SWNT will modulate the band-gap due to the addition of an Aharonov-Bohm phase to the circumferential component of the electron wavefunction. Due to symmetry breaking in the magnetic field the previously dark even parity spin-singlet exciton state becomes optically active and the odd-even parity splitting can be observed directly [32]. The value of the zero-field splitting energy between the dark and bright spin-singlet exciton states is essential for elucidating the fine excitonic structure of semiconducting SWNTs. Zero-field splitting energies of  $\Delta_x = 1$  to 8 meV have been observed from low field PL of individual SWNTs [151–153] and from high field ensemble measurements [154–161].

The strong interaction of SWNTs with the local environment has led several recent studies to focus on the role of extrinsic effects such as surface charge trapping and defects. In this Chapter we demonstrate that by studying the magneto-optical properties

of individual SWNTs it is possible to identify both the intrinsic and impurity induced defects and to control these with high intensity optical excitation and high magnetic fields.

## 5.2 Experimental

A chirality selected solution of individualised semiconducting SWNTs was prepared using polymer wrapping techniques [49] described in Chapter 2. Low temperature micro-photoluminescence ( $\mu$ PL) measurements were taken with the sample immersed in helium gas at 4.2 K (Chapter 2).

Two geometries were used to determine the magnetic field effects. Faraday geometry was used where the surface of the substrate is perpendicular to the magnetic field. Using a mirror at  $45^\circ$ , Voigt geometry, in which the light propagation vector  $\mathbf{k}$  is perpendicular to the direction of the magnetic field and the surface of the sample, was used to test the effects of flux threading the SWNTs. Polarised excitation was used to selectively excite SWNTs aligned on the substrate in the direction of the magnetic field due to a large depolarisation effect [31].

## 5.3 Finding a Pristine Tube

The PL excitation wavelength was initially set to 720 nm to correspond to the predominantly (8,6) nanotubes and extensive  $x,y$  scans were performed to identify isolated single nanotubes which emit at a single wavelength. Figure 5.1a shows a typical large area PL image where a piezo-stage was used to scan the position of the excitation and a spectrum was taken for each pixel of the map. These maps contain a great deal of information including the chirality of nanotubes, position, bundling and specific energy levels. The



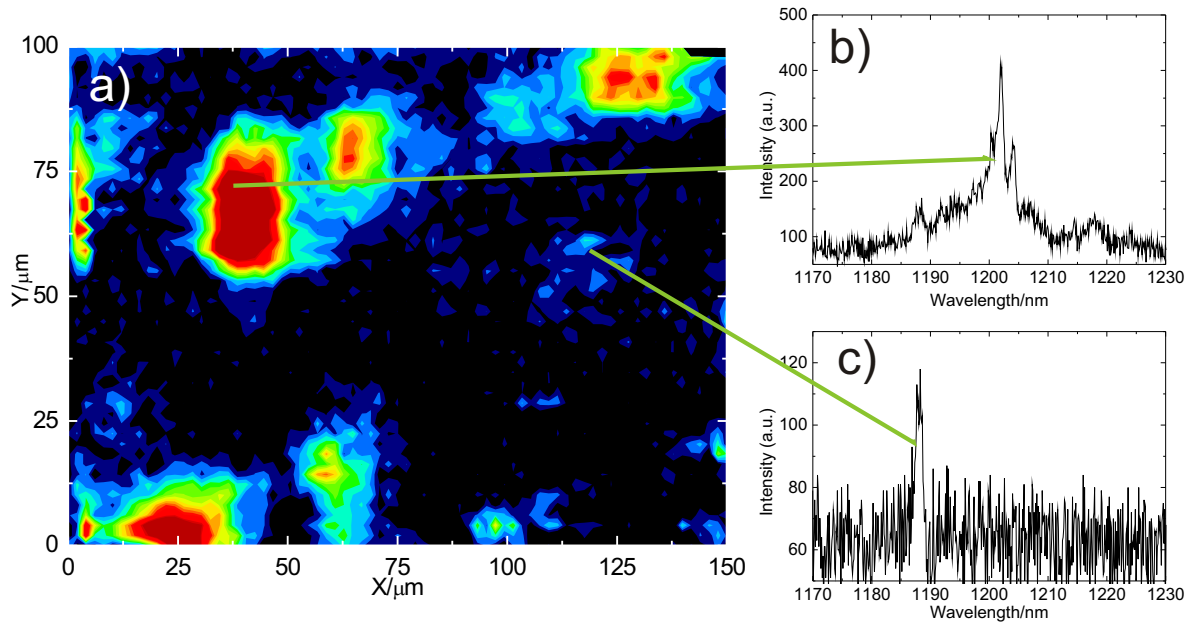


Figure 5.1: a) Spatial PL mapping: Emission intensity as a function of position with spectra shown for a bundle (b) and an isolated individual tube (c).

integrated emission intensity was plotted as a function of position. Two types of features can be observed: large areas of high intensity emission and smaller sections of relatively low intensity emission. Figure 5.1b shows a spectrum taken from the centre of one of the large area features. It is clear that the spectrum is comprised of a large number of emission peaks with energy distributed around 1200 nm. This is characteristic of a bundle of carbon nanotubes, where the number of peaks is an indication of the number of nanotubes contained within the bundle. Figure 5.1c shows the spectrum from an isolated bright region which shows a single bright emission peak. This is a signature of an individual, isolated, SWNT.

## 5.4 Single Tube Photoluminescence

Figure 5.2 is a comparative study of the PL and PLE spectroscopy of ensemble and individual SWNTs. By varying the excitation wavelength we may probe the resonance

in absorption in the  $E_{22}$  transition whereas the emission spectrum details the  $E_{11}$  transition, corresponding to the bright odd-parity spin singlet ( $KK$  and  $K'K'$ ), which we label as  $X^b$  for clarity. Figure 5.2a is the PLE map of a solution of PFO wrapped (8,6) SWNTs in O-xylene at room temperature. The FWHM of  $E_{22}$  and  $E_{11}$  are found to be 53 meV and 29 meV respectively. For comparison, PLE maps of several individual (8,6) SWNTs taken at 4.2 K are shown in figure 5.2b. The linewidth of the  $E_{22}$  absorption remains broad [162],  $\sim 50$  meV whereas the FWHM of  $E_{11}$  narrows by typically two orders of magnitude.

We demonstrate that this is a particular property of emission from individual SWNTs and that strong inhomogeneous broadening still exists from an ensemble of SWNTs with the same chirality [163]. Using a spatial PL map taken on a  $225 \times 225 \mu\text{m}$  area we have analysed the distribution of emission energies from 156 (8,6) SWNTs. All of the individual SWNT showed single narrow emission lines, but when a histogram is compiled of all emission energies this is centered around the peak observed from solution measurements with a width corresponding to an inhomogeneous distribution of  $\sim 20$  meV. A few individual tubes were selected for high resolution studies, several of which demonstrated exceptionally narrow  $E_{11}$  emission linewidths down to a resolution limited  $76 \mu\text{eV}$  (FWHM) (Fig. 5.3c) collected in a 20 second acquisition, with no evidence that the emission wavelength varies as the excitation is scanned along the length of the tube. Such narrow linewidths correspond to an  $E_{11}$  exciton lifetime-broadening of over 30 ps [55]. We attribute the increased lifetimes to the use of PFO wrapping purification and low dispersion densities which electronically decouple the SWNTs from the local environment and each other. This represents an improvement in linewidth of an order of magnitude compared to previous single SWNT  $\mu\text{PL}$  studies [151, 162, 164], and opens the way to new studies of exciton properties for applications such as quantum information processing [165].

The very large difference between the homogeneous and inhomogeneous linewidths

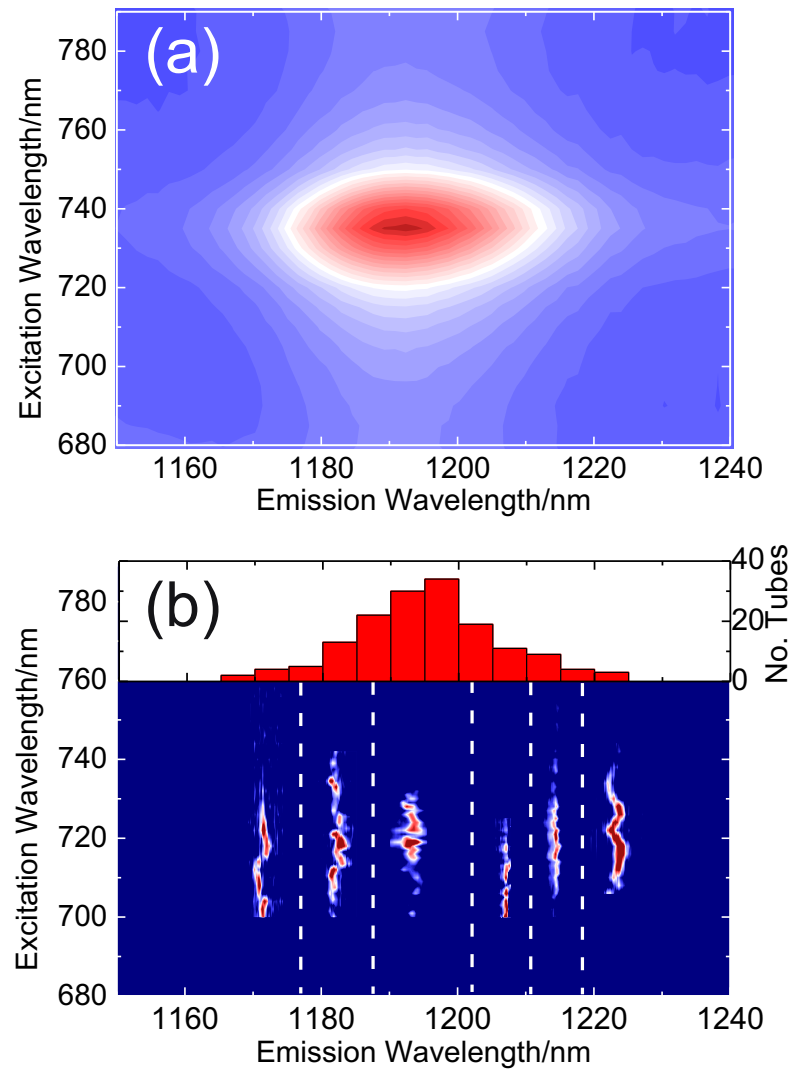


Figure 5.2: Photoluminescence excitation spectroscopy of a) an ensemble of (8,6) SWNTs in solution at room temperature and b) six individual (8,6) SWNTs at 4 K. (b, inset): Energy distribution of 156 (8,6) SWNTs taken from a  $225 \times 225 \mu\text{m}$  spatial PL map.

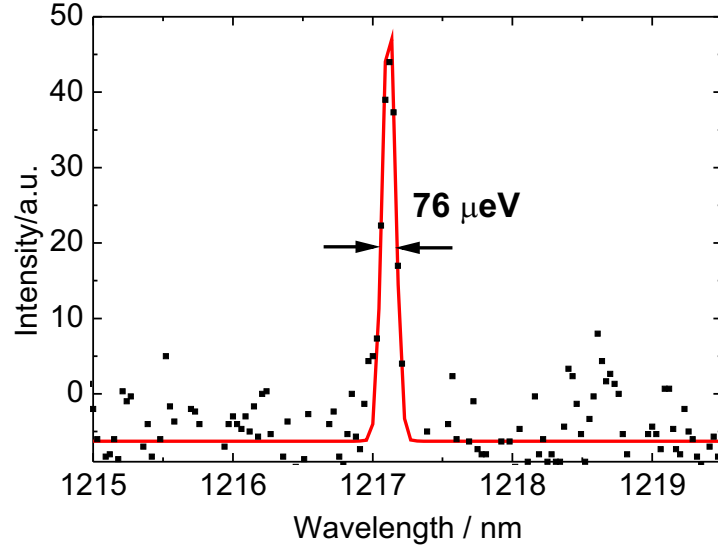


Figure 5.3: An ultranarrow example from an individual SWNT with FWHM of  $76 \mu\text{eV}$ .

observed in the ensemble suggests that the mechanism for light emission in SWNTs must be associated with long lived excitons in a low energy state. It also suggests that any individual SWNT has sufficiently long exciton lifetime and diffusion length to emit from probably only a single emission site governed by the local energy landscape of that individual tube.

## 5.5 Brightening the Dark Exciton

Introducing a magnetic flux threading the SWNT breaks the symmetry in a controlled manner and alters the composition of the exciton states [32] so that the previously dark even-parity spin singlet exciton,  $X^d$ , becomes bright. A finite zero-field splitting,  $\Delta_x$ , is predicted between these states. At higher fields the two states split linearly up and down in energy as a function of magnetic field. In a single particle model the Aharonov-Bohm shift ( $\Delta_{AB}$ ) is given by[150]

$$\frac{\Delta_{AB}}{E_g} = \pm \left( \frac{3\pi d^2 B}{4\phi_0} \right), \quad (5.1)$$

where  $\phi_0 (= h/e)$  is the magnetic flux quantum,  $E_g$  is the band gap,  $d$  is the diameter of the SWNT, and  $\pm$  correspond to the bright and dark states respectively. Including the exciton binding energy gives  $E_b$  and  $E_d$ , for the exciton states  $X^b$  and  $X^d$ , as [151]

$$E_{b,d} = E_0 \pm \frac{\sqrt{\Delta_x^2 + 4\Delta_{AB}^2}}{2}. \quad (5.2)$$

with the main transfer of intensity between the two states occurring by  $\Delta_x = 2\Delta_{AB}$ .

Figure 5.4a shows a typical magnetic field dependence of the PL from an isolated (8,6) SWNT in Voigt geometry excited with a relatively low power density of  $0.1 \text{ mW}/\mu\text{m}^2$ , at 720 nm. At this power density there is a exciton occupancy of  $\sim 2$  within the nanotube, calculated using a typical length of SWNT of  $1 \mu\text{m}$  from AFM characterisation (although tube lengths  $> 5 \mu\text{m}$  are not uncommon), assuming the SWNT absorption cross section observed by Schoppler *et al.* [166] and 30 ps exciton lifetime. At zero magnetic field a single bright emission peak is observed. When the magnetic field is applied an additional peak brightens at lower energy with a splitting given by  $\Delta_x = 1.9 \text{ meV}$ . Due to the narrow linewidths the two states in many SWNTs are clearly resolvable even at fields  $B < 1 \text{ T}$ . There was no significant difference in linewidth between the bright state and dark state in the SWNTs tested. Fitting the magnetic field dependence of several tubes gives an average value for the zero field splitting of  $\Delta_x = 2 \text{ meV}$  for (8,6) SWNTs. In contrast to the large variability reported previously, we see consistency within  $\pm 20\%$  tested over several tubes. At low excitation powers and low temperature, the higher energy bright state becomes energetically unfavourable and the previously dark state becomes the dominant emission for  $B > 3 \text{ T}$  (Fig. 5.4a). A further low energy peak is also observable at high fields, the origin of which will be discussed below. In previous work ensemble measurements have deduced values for (8,6) ( $d = 0.96 \text{ nm}$ ) chirality tubes: temperature dependent intensity measurements give  $\Delta_x = 2.6 \text{ meV}$  [158], magnetic brightening measurements gives  $\Delta_x = 4 \text{ meV}$  [160], and pulsed high field PL

measurements give  $\Delta_x = 7.9 \text{ meV}$  [156]. Direct observation of  $\Delta_x$  in individual SWNTs in previous measurements shows large variability from tube to tube of up to  $\pm \sim 100\%$  of the mean [151, 152]. It has also been shown that  $\Delta_x$  can be strongly dependent on the local environment of the SWNT with an increase of  $\sim 30\%$  in strained SWNTs embedded in polymer films [160]. We attribute much of this variability to the influence of defect bound excitons, which we discuss below.

## 5.6 Dark Excitons Under High Laser Powers

Increasing the excitation power density to  $0.5 \text{ mW}/\mu\text{m}^2$  effectively heats the SWNT [167], enabling the bright state to be observable up to  $B > 8 \text{ T}$  as shown in Figure 5.4b. This allows us to show that the Aharonov-Bohm shift follows the predicted magnetic field dependence up to  $30 \text{ T}$ , with a coefficient for (8,6) tubes of  $\Delta_{AB} = \pm 0.35 \text{ meV/T}$  consistent with theoretical predictions and experimental observations from ensemble measurements [154, 160, 161], although there is some evidence of an increase in  $\Delta_x$  due to carrier heating. The overall consistency of the data and its agreement with theory lead us to conclude that this behaviour is characteristic of the free exciton states.

## 5.7 Quantum Confined Stark Effect

In addition we see features which suggest the dynamic modification of the exciton states (blinking and spectral diffusion) associated with fluctuating local charge in the wrapping polymers. Figure 5.5a shows the time evolution of the emission of the SWNT described above at  $10 \text{ T}$ , taken with  $5 \text{ second}$  resolution for  $500 \text{ seconds}$ . At  $\lambda = 1193 \text{ nm}$  the even-parity spin singlet is observable at a constant wavelength. At longer wavelengths an additional peak is clearly resolved, with fluctuating intensity and spectral diffusion,  $\sim 0$  to  $10 \text{ nm}$  (several  $\text{meV}$ ) below the dark state. Figure 5.7 shows that the intensity

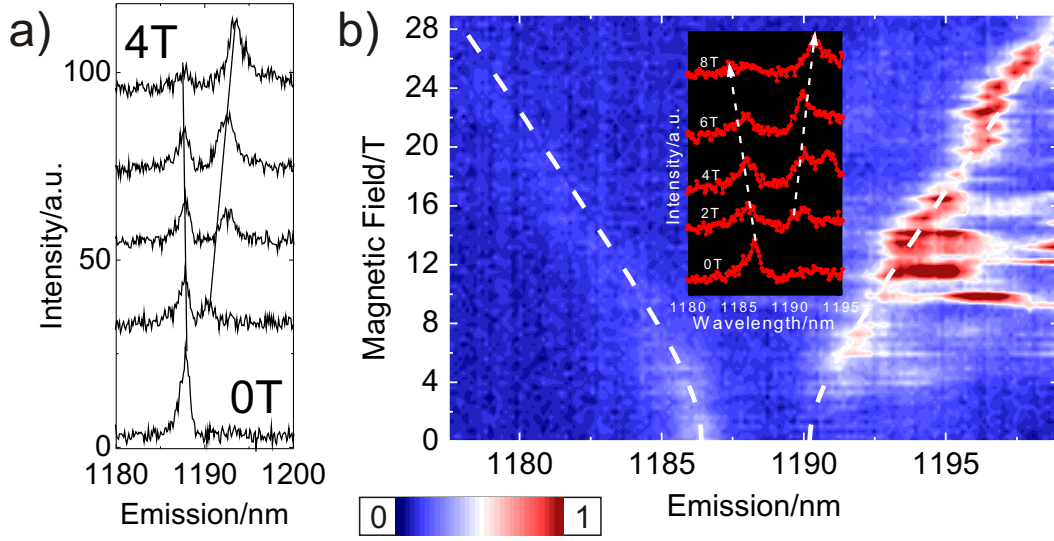


Figure 5.4: Magnetic field dependent emission from an isolated (8,6) SWNT at low excitation power (a) and high excitation power (b). White dashed lines indicate the fitting with Equation 5.2. Inset: Cross sections showing the evolution of the two states to high fields.

of the two peaks is anti-correlated with a correlation coefficient of  $r = -0.28$ , where  $-1 < r < 0$  or  $0 < r < 1$  for anticorrelated and correlated data respectively. Such behaviour has been observed by Matsuda *et al.* [164] in single SWNTs, attributed to a quantum-confined Stark effect [168], which causes a redshifted emission peak due to fluctuating local charges, which are photoinduced in the surfactant wrapping the nanotube. We therefore attribute the longer wavelength emission peak to the quantum-confined Stark effect, as labelled in Figure 5.5a.

## 5.8 Laser Induced Bound Exciton States

Recently, some experimental and theoretical works have moved from the intrinsic properties of SWNTs to studying the extrinsic phenomena which affect them. Much experimental work has focused on, for example, the effects of high intensity laser irradiation on the optical properties. High intensity laser irradiation has been shown to induce blink-

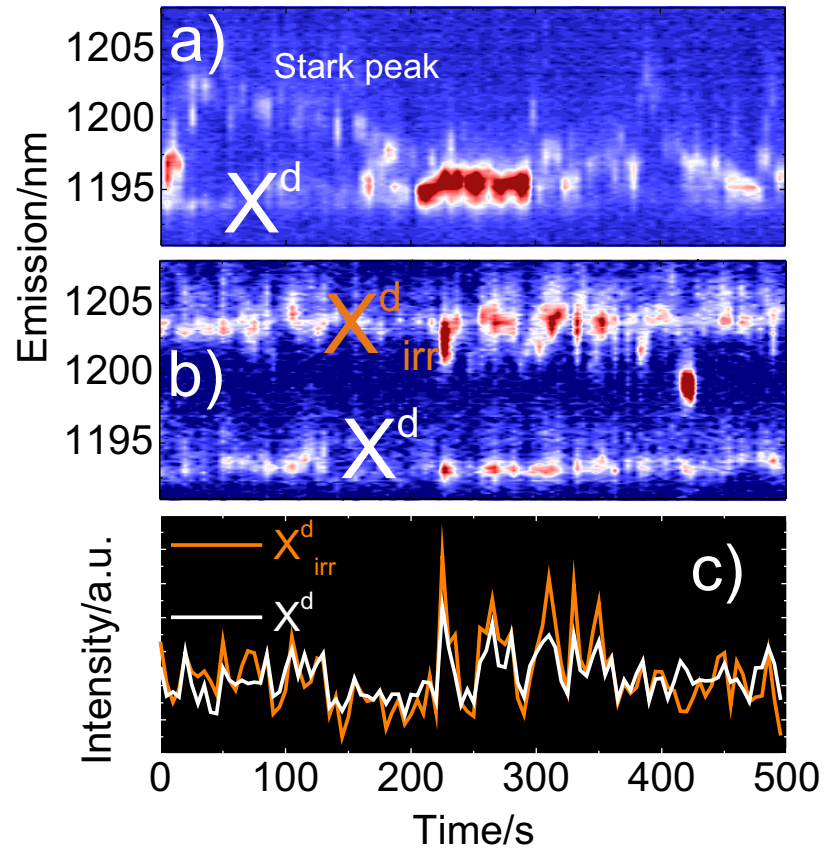


Figure 5.5: Time series of emission at 10 T before (a) and after (b) high intensity irradiation. c) Intensity of  $X^d$  and  $X_{irr}^d$  as a function of time showing correlated emission from the two states.



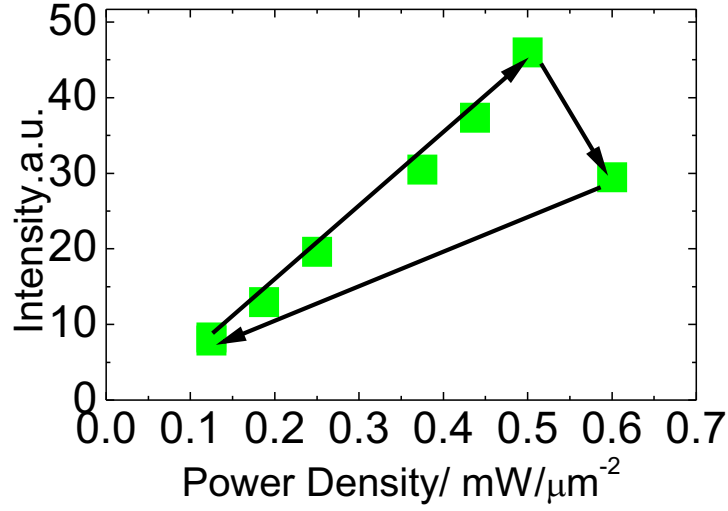


Figure 5.6: Intensity of SWNT emission at increasing excitation power density, the intensity dramatically reduces above  $0.5 \text{ mW}/\mu\text{m}^2$ .

ing [169] and reduce quantum efficiency [170]. Additional deep-level photoluminescence peaks have been observed which are attributed to light induced molecular deposition on air-suspended single SWNTs [170], defect induced brightening of dark triplet excitons [171], and trions in hole doped SWNTs [172].

Laser excitation at 720 nm was increased stepwise from  $0.1 \text{ mW}/\mu\text{m}^2$  to  $0.6 \text{ mW}/\mu\text{m}^2$  at the same position as the spectra in Figure 5.4 were taken and the sample was irradiated for 1 minute at each power. Emission intensity, at 10 T increased linearly with excitation power until a critical power density was reached above  $0.5 \text{ mW}/\mu\text{m}^2$  at which the emission dramatically decreased (Fig. 5.6). When the power is reduced again, an additional pair of a bright and a dark, magnetically brightened, peaks appear at lower energies, labelled  $X_{irr}^b$  and  $X_{irr}^d$ , as seen in Figure 5.8a. The new transitions are also well described by Equation 5.2 with  $\Delta_{AB} = 0.35 \text{ meV/T}$ , but now the binding energy  $\Delta_x$  has increased to 7 meV, the mid-point  $E_0$  is red shifted by 10 meV and the magnetic brightening of the new dark state is considerably greater (Fig. 5.6a, with  $I_{irr}(20 \text{ T})/I_{irr}(0 \text{ T}) \sim 10$ ).

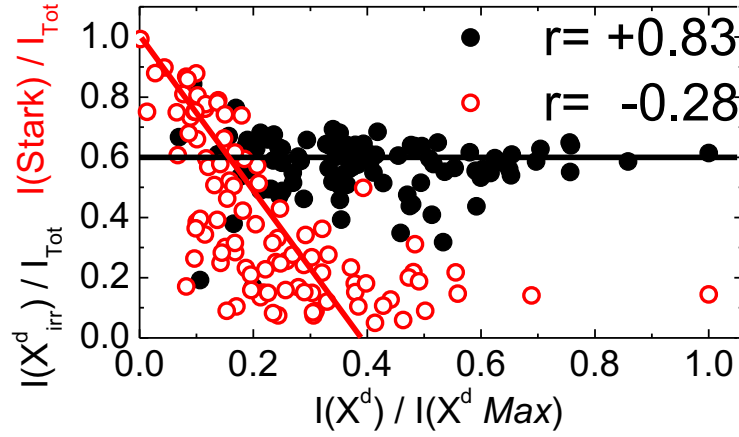


Figure 5.7: Analysis of the emission time series before (red - Stark effect) and after (black -  $X^d_{irr}$ ) irradiation. The relative intensity of the two dominant peaks are plotted as a function of the intensity of  $X^d$ .

A time series at 10 T (Fig. 5.5b) shows that the behaviour has completely changed. The two peaks still show blinking, but unlike the Stark effect peak the intensity of the new magnetically brightened state is strongly correlated ( $r = 0.83$ ) with the original dark state as shown in Figure 5.5c and Figure 5.7. This intensity correlation is strong evidence that both dark states,  $X^d$  and  $X^d_{irr}$  originate from the same single nanotube, which has its emission controlled by the fluctuations in its non-radiative emission rate.

Figure 5.9, compares the magnetic brightening of emission intensity [156, 158, 160] compared before,  $X^d$  and after irradiation  $X^d_{irr}$ . We find that the intensity before irradiation increases by a factor of  $I(20\text{ T})/I(0\text{ T}) \sim 3$ , a factor common to the majority of SWNTs we have studied. The post-irradiated SWNT however, increases by  $I_{irr}(20\text{ T})/I_{irr}(0\text{ T}) \sim 10$ . The high magnetic fields used here also allowed us to see high magnetic field suppression of emission, above 20 T (Fig. 5.9). This effect has been found in stretched films [160], but was previously not well understood. We may now attribute this to the activation of lower lying states, as discussed below.

The high intensity irradiation clearly has dramatic irreversible effects on the proper-

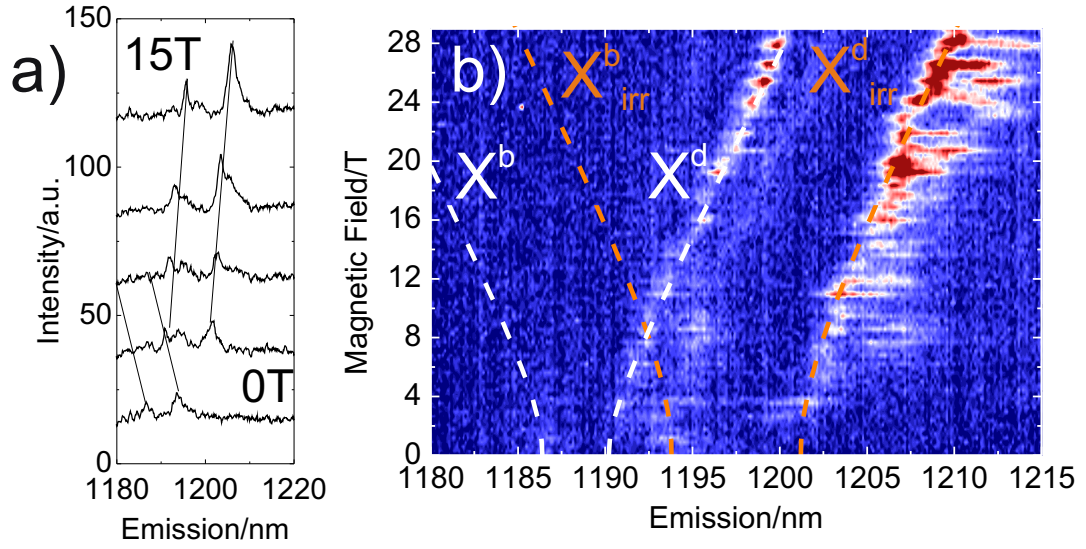


Figure 5.8: a) Cross sections from (b), where (b) shows the magnetic field dependent emission after irradiation using low intensity excitation. White and orange dashed lines show fits to the original and irradiation induced bound excitons respectively.

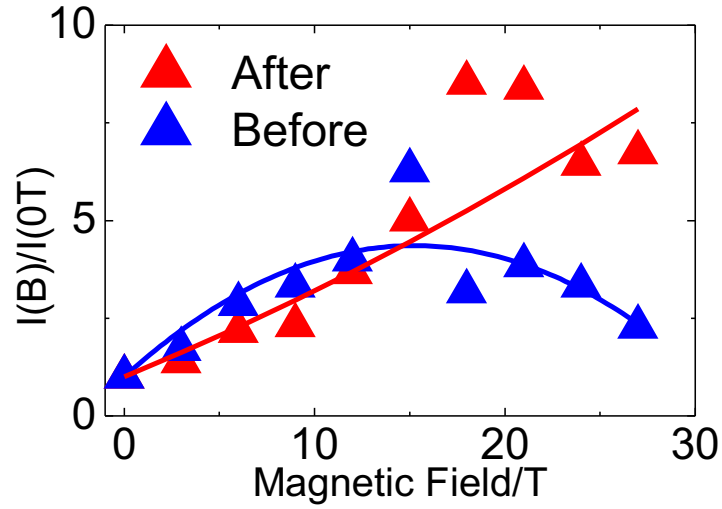


Figure 5.9: Relative brightening of tube emission before and after irradiation as a function of magnetic field.

ties of a SWNT. Using an effective mass theory in the presence of an impurity potential, Tomio and Suzuura have predicted a new pair of lower energy impurity-bound spin singlet exciton states, one bright and the other dark [173]. With an impurity potential on a scale comparable with the tube diameter but  $\gtrsim$  lattice constant, the bound-bright state blueshifts with the free bright state, and the bound-dark state redshifts with the free dark state. We therefore attribute  $X_{irr}^b$  and  $X_{irr}^d$  to bound bright and dark exciton states, respectively. In contrast to the model predicted by Tomio and Suzuura we observe a zero-field splitting between the bright and dark bound exciton states of  $\Delta_x^{bound} = 7$  meV, which is significantly larger than that observed for the unbound exciton states, suggesting that  $\Delta_x$ , which is determined by the strength of the electron-hole exchange interaction, is significantly enhanced at local defect sites. This may explain the variability of splitting found in previous single tube experiments, as the lower quality of tubes studied could lead to spectra dominated by a variety of bound exciton states. The physical origin of such an impurity site may be characterised by the removal of the PFO coating along the tube or the creation of structural defects. Recently Miyauchi *et al.* [174] have shown that deep lower lying exciton states can be induced by oxygen doping of ensembles of (7,5) SWNTs, which they therefore attribute to bound excitons located at structural defects. From the temperature dependence of the emission intensity they have also deduced that a dark state should exist with enhanced values of  $\Delta_x$  of order 10 meV, consistent with our observations.

## 5.9 Additional Magnetically Activated Sidebands

In addition to the behaviour observed in Figure 5.4, many SWNTs exhibit a more complex high field behaviour. The initial regions of the sample were selected for study through spatial PL mapping were those in which we observe a single emission peak at  $B = 0$ . Upon the application of 1 Tesla the  $X^d$  exciton is brightened. As the

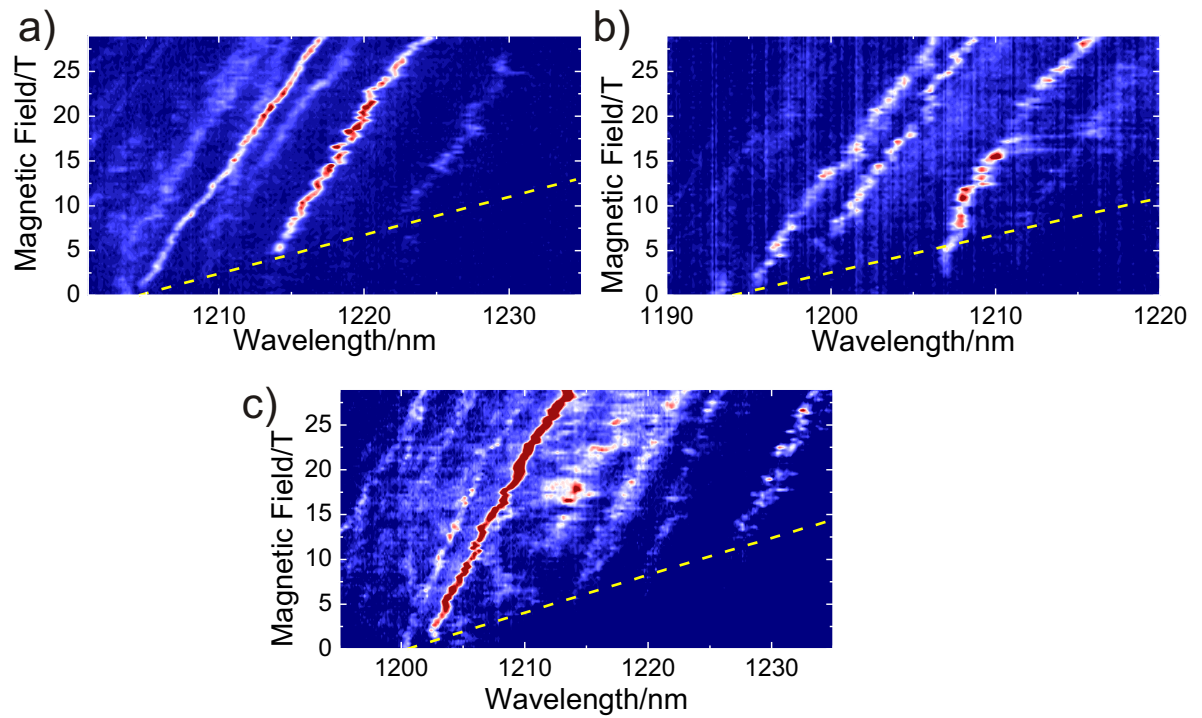


Figure 5.10: Magnetic field dependent emission from three sample positions (a, b and c) which show a single bright emission peak at zero magnetic field. At increased magnetic field further emission peaks are activated. The field required to activate each state is linearly dependent on the magnetic field at 0.5T/meV (yellow dashed line).

magnetic field is increased, further low energy peaks are often seen to become activated. The magnetic field at which each peak becomes activated is linearly dependent on the energy splitting from  $X^b$ , consistent with the condition  $\Delta_x \simeq 2\Delta_{AB}$ . Three examples of such behaviour are shown in Figure 5.10. A common feature of high resolution single SWNT PL imaging is the variability of emission intensity along the tube, where some segments luminesce whilst in other segments the emission is quenched [170, 175]. In addition, a slowly varying energy landscape along a CNT has been observed in high resolution photocurrent spectroscopy [176], where Raman spectroscopy [177] and AFM [178] attributed this variability to the presence of defects and trapped charges. We attribute the multitude of additional emission peaks at high magnetic fields to the magnetic brightening of previously dark shallow impurity states associated with such segments. In order to investigate this hypothesis, high resolution spatial mapping in high magnetic fields were taken as described below.

## 5.10 High Field Imaging

Since the emission of a nanotube may be dominated by its individual local energy landscape, high resolution spatial PL imaging in high magnetic fields is a useful analytical tool. A full photoluminescence emission spectrum is taken at every pixel within the map. Figure 5.11 is the summary of two spatial PL maps over the same  $10 \times 10 \mu\text{m}$  area, one at 0 T the other at 20 T. The spatial dependence of emission is shown for  $B = 0\text{ T}$  in Figure 5.11a. Since the SWNTs, all of (8,6) chirality, emit at slightly different wavelengths (Fig. 5.2) the spatial dependence of each tube may be plotted in different colours by selecting wavelengths. Several tubes can be seen, and as each wavelength window of  $\pm 1\text{ nm}$  some colours have more than one feature. This method allows us to track the redshift and magnetic brightening of several SWNTs at once. The emission wavelength of five SWNTs at 0 T and 20 T are shown in Figure 5.11b.

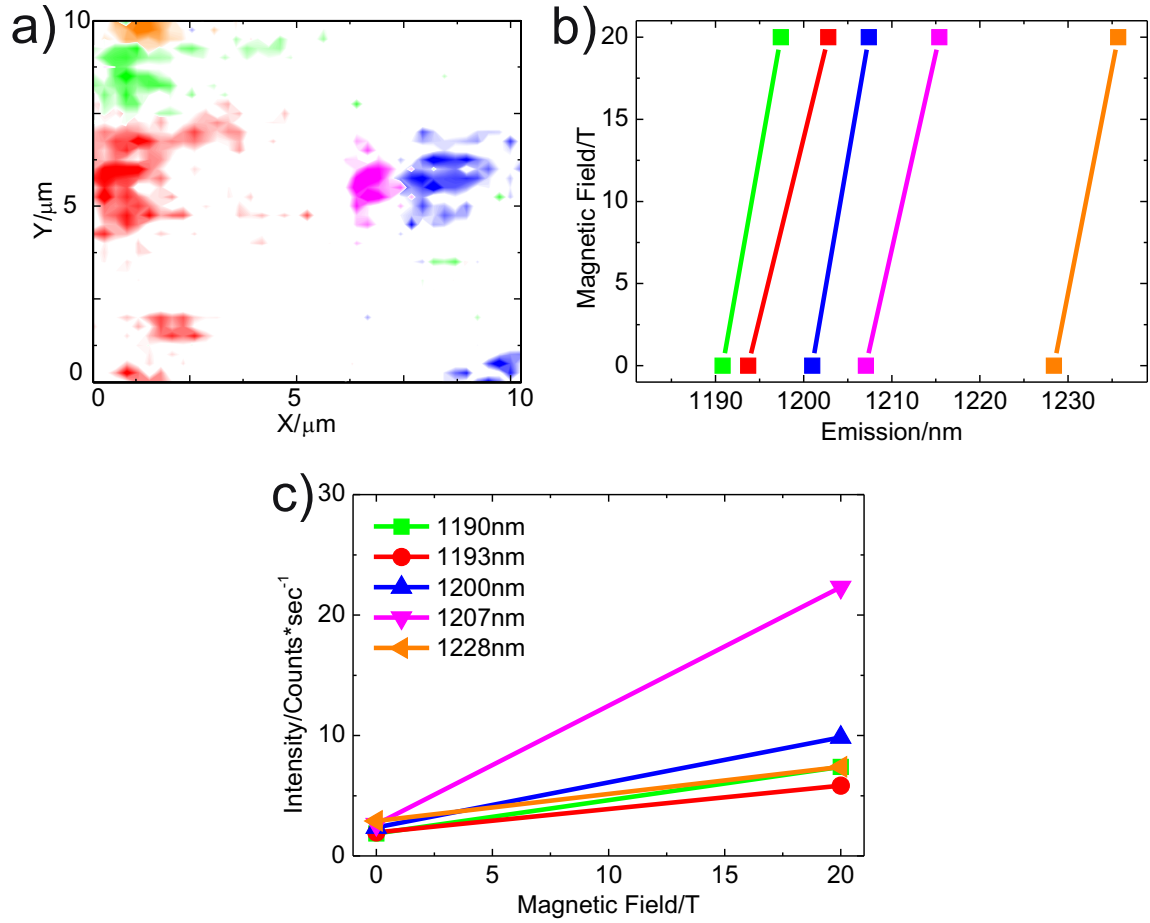


Figure 5.11: a) Spatial PL map at zero magnetic field, colours represent spatial dependence of emission from several (8,6) SWNTs. The map was repeated at 20T and the redshift (b) and magnetic brightening (c) of each tube can be tracked.

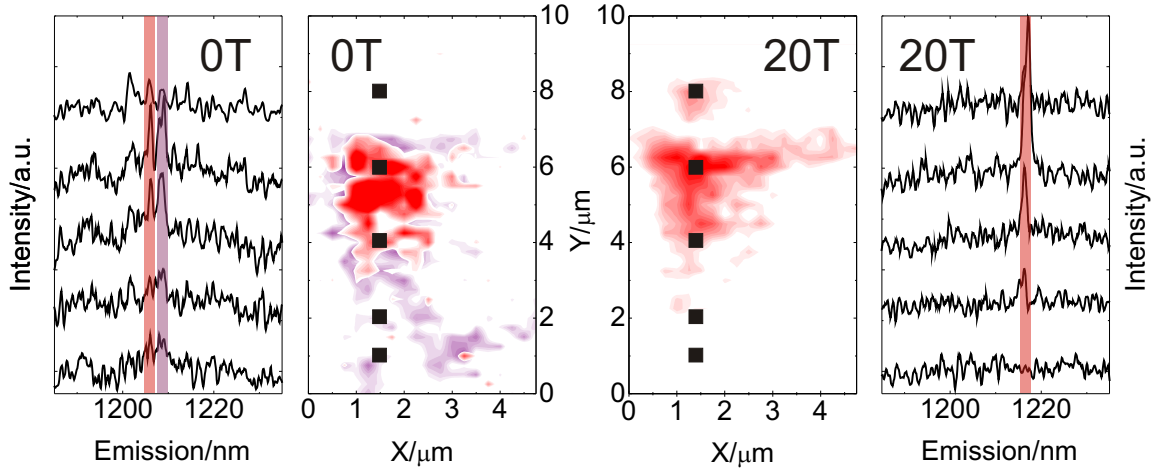


Figure 5.12: Spatial PL maps at 0 T and 20 T covering the same position on the sample. Spectra from the map are shown taken from positions indicated by squares on the map. The highlighted wavelengths represent the wavelength selection corresponding to the colour in the spatial map.

All show a redshift of  $\sim 0.35 \text{ meV/T}$ , suggesting that the polarisation of the excitation is indeed selecting SWNTs aligned in the magnetic field direction ( $y$ -axis). Indeed the  $1200 \text{ nm}$  SWNT (blue) showing the smallest redshift appears to be off vertical in the image (Fig. 5.11), thus having a lower magnetic flux threading the tube. When plotting the magnetic brightening (Fig. 5.11c), the majority of emission lines increase by a factor of  $\sim 3$  at 20 T.

For SWNTs with a length which is longer than the resolution of the  $\mu\text{PL}$  ( $\gtrsim 5 \mu\text{m}$ ) interesting variation of emission can be observed along the tube. Figure 5.12 shows the spatial dependence of emission from an (8,6) tube. At zero magnetic field the emission is characterised by a doublet, where the shorter wavelength peak is emitted from a smaller spatial region of the sample. We interpret this as the emission from the bright state and disorder brightened dark state of the weakly bound free exciton in a weakly disordered SWNT. When a magnetic field is applied the photoluminescence spectrum is dominated by a single bright emission peak which redshifts as expected from the magnetically brightened dark state. The spatial extent of the emission is focused in a



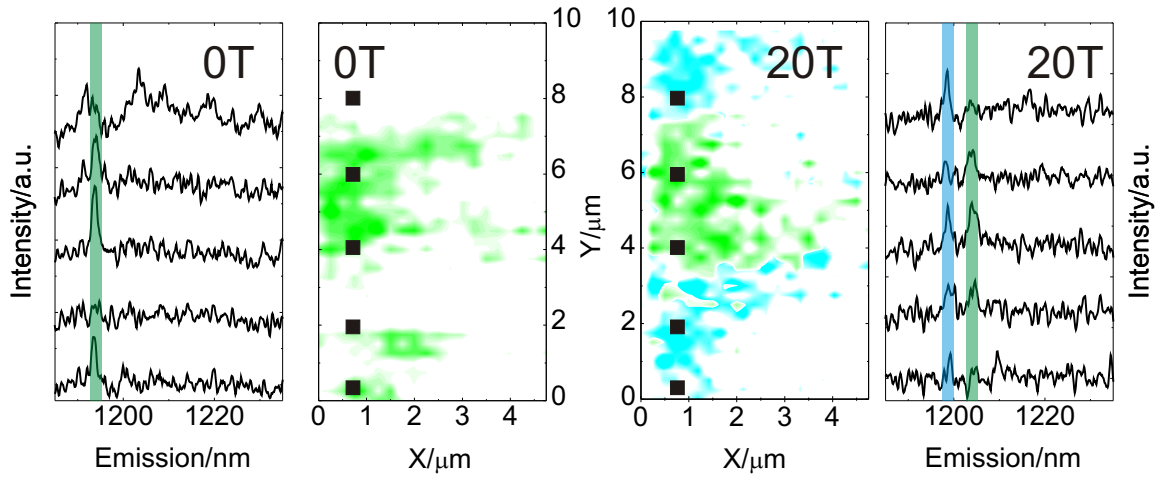


Figure 5.13: Spatial PL maps at 0 T and 20 T including example spectra for clarity. Where at zero magnetic field a single bright emission peak could be observed, a doublet is observed at high magnetic fields.

similar region to the bright exciton state at 0 T. This is further evidence that emission is taking place from a single region within the nanotube due to the local environment. The magnetic field thus enhances the emission from this single region.

Rather different behaviour is shown for the region shown in Figure 5.13, where a single bright emission line is observed at zero magnetic field. A corresponding red-shifted and magnetically brightened emission is observed for the same spatial region, but now a new magnetically activated emission is observed at 5 nm shorter wavelength. This corresponds to spatial regions either side of the zero field emission, and therefore demonstrates that a large contribution to the magnetic brightening comes from the activation of previously dark localised states as described above.

In the most extreme example of spatial mapping, shown in Figure 5.14, large areas of the sample which show no emission at zero magnetic field become bright. A single bright emission state from an (8,7) chirality SWNT is seen at 0 T (orange). Upon the application of 17 T multiple sidebands can be observed. Due to the high spatial and spectral resolution of the mapping we have been able to image the extent of these sidebands.

Two peaks in particular, shown in green and blue in Figure 5.14, are spatially localised at either end of the main 0 T bright emission peak. At zero magnetic field no emission is observed from these sections, whereas magnetic brightening causes these peaks to emit more strongly than the zero field bright state. Quenching sites associated with the ends of SWNTs have been observed [179, 180]. Figure 5.14 and the results shown in Figure 5.13 suggest that there may be a significant contribution to the magnetically brightened defect states approaching the ends of a nanotube.

These results are further evidence towards our previous statement attributing the additional sidebands observed in the magnetic field dependence to bound excitons in previously dark segments of the tube indicated schematically in Figure 5.14. All segments along the tube can contribute both red and blue shifted emission within the wavelength range observed in ensemble measurements (Fig. 5.2).

A broad picture of the life of an exciton in a SWNT emerges where, with no applied magnetic field, long lived highly mobile excitons diffuse freely through a defect and trapped charge induced energy landscape before recombining at a series of local energy minima. Excitons which recombine at sites with no radiative pathways, such as those at defect sites, are quenched. Excitons at these sites may be brightened through the application of a magnetic field threading through the CNT, which are most commonly redshifted by a few to 10's of meV, although may appear at higher energies, as determined by the local energy landscape.

## 5.11 Summary

We have observed exceptional ultranarrow emission from individual PFO wrapped semi-conducting SWNTs at 4 K, resolution limited to  $76\mu\text{eV}$ , showing the PFO purification process yields isolated SWNTs with excellent optical properties. In an applied magnetic

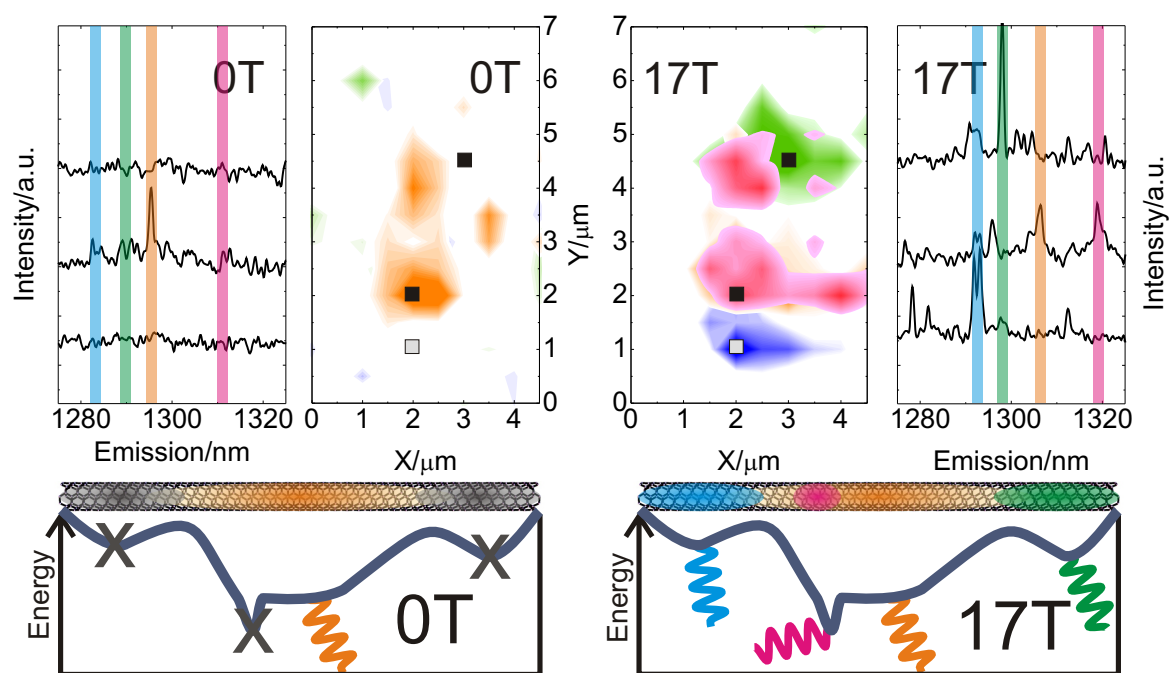


Figure 5.14: Top: Spatial PL map showing a region which has a single bright emission peak at 0 T and a multitude of peaks at 17 T. Some of these peaks originate from spatially localised site which previously showed no emission. Bottom: Schematic energy levels and emission along the CNT with and without applied magnetic field.

field the even-parity spin singlet state is brightening with a consistent zero field splitting of  $\Delta_x = 2 \text{ meV}$  for (8,6) SWNTs which we attribute to the free exciton. The two states split linearly at  $\pm 0.35 \text{ meV/T}$ , with the odd-parity state being visible to 20 T using high excitation powers. At even higher excitation powers SWNTs show irreversible changes in emission both at 0 T and in an applied field, with the optical properties being dominated by bound excitons which show an increased zero-field splitting of  $\Delta_x^{\text{bound}} = 7 \text{ meV}$ , and require higher magnetic fields to achieve optical brightening. Some individual SWNTs showing a single zero field emission peak exhibit multiple sidebands at high magnetic fields which we attribute to the magnetic brightening of a series of progressively more localised sites, suggesting that the local environment is crucial in controlling SWNT emission. Furthermore such bound states appear naturally in SWNTs which, using high spatial resolution scanning PL mapping at high magnetic field, may be imaged. The bound excitons in these spatial maps are characterised by a significant magnetic brightening from localised segments along the tube.

# Chapter 6

## Conclusions

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### 6.1 Key Results

In this thesis high magnetic field effects were described as observed in low-dimensional systems, namely: graphene, carbon nanotubes, and InSb/AlInSb heterostructures. Magnetotransport measurements of graphene and InSb were used to investigate electron heating and the breakdown of the quantum Hall effect in these low effective mass two-dimensional systems. The relative merits of the two systems as quantum Hall resistance standards were discussed. High magnetic field photoluminescence measurements of individual carbon nanotubes have revealed new details on exciton fine structure and a rich variety of extrinsic effects which make carbon nanotubes a highly sensitive probe to their local environment.

Through studying the electrical current and temperature induced damping of Shubnikov-de Haas oscillations in high mobility InSb/AlInSb heterostructures the electron-phonon energy loss rates were calculated, and found to be slightly slower than those observed

in GaAs over a similar temperature regime (1.5 to 20K). High current measurements at higher magnetic fields revealed that robust quantum Hall states were observed for both even (Landau level) and odd (spin-split) filling factors. For the first time, high current breakdown was observed for the spin polarised  $\nu = 1$  state, moreover the critical electric field was found to be higher than that of  $\nu = 2$ . Increasing the total magnetic field in  $\nu = 1$  using tilted magnetic fields enhances the spin-splitting however due to a mixing of the energy levels this actually results in a decrease in the observed breakdown current. Due to the relatively large area of the devices, inhomogeneities of the carrier density were found. These were shown to have significant effects on the performance of the sample at high currents. The large g-factor and low effective mass leads to large spin-splitting and cyclotron energy gaps respectively. This leads to increased critical temperatures for  $\nu = 2$  (8 K at 6 T) and  $\nu = 1$  (7 K at 12 T) relative to GaAs devices. Ultimately though, the long electron-phonon energy loss time, coupled with sample density inhomogeneities, limit the maximum critical current achievable, and hence limit the potential for an InSb based quantum Hall resistance standard.

Magnetotransport measurements of graphene, grown on silicon carbide, have found the highest breakdown current densities ever reported for the quantum Hall state in any material. Critical current densities of  $j_c = 43 \text{ A/m}$  at 25 T, using a stringent breakdown condition of  $V_{xx} > 10 \mu\text{V}$ , were observed, an order of magnitude larger than even the most well optimised GaAs devices. The dissipationless quantum Hall state is maintained to temperatures  $> 45 \text{ K}$  at 29 T. The temperature dependence of the critical current shows a  $(1 - (T/T_c)^2)$  behaviour, which was observed in GaAs and in this thesis for InSb, suggesting that this is a material independent general behaviour of the quantum Hall state. The work presented here is strong evidence that the dissipationless quantum Hall state should be described as a phase diagram which depends on magnetic field, carrier density, temperature and current. The magnetic field dependence of the breakdown current along the  $\nu = 2$  plateau does not follow the traditional triangular behaviour

observed in InSb (Chapter 3) and in GaAs and Si 2DEGs. This is due to a strongly magnetic field dependent carrier density, arising from the transfer of charge carriers from surface donor states in the underlying substrate. The magnetic field dependence is most extreme for low zero-field carrier densities where an increase in carrier density by a factor of 7 is observed as the magnetic field is increased to 19 T. In collaboration with the National Physical Laboratory, the standards laboratory for the UK, this work is having a direct impact on future graphene based metrology. It has been shown that graphene is an exceptional candidate for high precision, readily accessible electrical resistance standards at low magnetic fields and high temperatures.

The magnetic field dependence of exciton fine structure has been studied in individual carbon nanotubes through micro-photoluminescence. High spectral and spatial resolution at magnetic fields up to 30 T have allowed studies of the optical properties of individual carbon nanotubes to an unprecedented level. Polymer purification has been shown a very suitable process for obtaining individualised carbon nanotubes of excellent optical properties, exemplified by the ultra-narrow emission observed, resolution limited to  $76 \mu\text{eV}$ . Due to this quality, pristine (8,6) chirality CNTs were found to exhibit a consistent zero field splitting,  $\Delta_x = 2 \text{ meV}$ , between the “bright” and “dark” intravalley spin-singlet exciton energy levels. A pristine carbon nanotube was subjected to high intensity laser irradiation dramatically changing its optical properties. An additional bright–dark pair of bound exciton states was created in the nanotube. The bound exciton states exhibit an enhanced  $\Delta_x = 7 \text{ meV}$ , indicating increased electron–hole interaction at a localised laser induced defect site. In addition, many nanotubes exhibit multiple magnetically activated sidebands. Using the results from the irradiated sample, we may attribute these states to naturally occurring localised defect sites along the tube. High resolution spatial mapping at high magnetic fields reveals that in some cases these states can be shown to originate from previously dark spatially localised “quenching” sites which become magnetically brightened.

## 6.2 Future Work and Outlook

As a potential quantum Hall resistance standard InSb showed marginal advantages in some aspects over GaAs but has already now been superseded by graphene. However, the exceptionally large  $g$ -factor and high mobility will still be useful in a variety of applications. The use of InSb in infra-red detectors and thermal imaging systems is already well established. High speed, high mobility transistors are still a possibility for supercomputers, where Intel have shown field-effect transistors operating at over 200 GHz. Unfortunately, the loss of the fabrication facilities and expertise due to cut-backs at QinetiQ, where the highest quality samples (including those described in this thesis) were produced, struck a significant blow for this line of research. Due to the large  $g$ -factor in InSb nanowires, Mourik *et al.* [181] believe that when coupled to a superconductor an exotic class of quasi-particle, known as Majorana fermions which are identical to their own antiparticle, are observed. Majorana fermions, could be of particular interest for the realisation of topologically protected quantum computers. If this proves to be an experimentally viable method of creating and studying Majorana fermions then many exciting prospects lie in store for InSb.

Graphene is undergoing a transition from showing great potential to proving itself in real-world applications. In metrology alone the work presented here shows that graphene is the best known material for electrical resistance standards. The next stage of research for perfecting quantum Hall resistance standards is the fabrication of quantum Hall arrays, where a series of graphene Hall bars are connected together, resulting in a larger measurement current being possible. In addition, using appropriate connections any given fraction (or multiple) of  $h/2e^2$  can be achieved, resulting in a more flexible standard for characterising small (or large) resistances. A significant barrier for this is large scale growth of graphene with uniform electronic properties. The wide  $\nu = 2$  plateau observed for epitaxial graphene at low carrier density in Chapter 4 could



be used to efficiently reduce the strict carrier density homogeneity requirements which normally restrict traditional semiconductor systems. Using a sufficiently high magnetic field and relatively low carrier densities, even significant inhomogeneities could be neglected as all of the devices would be in the quantum Hall regime. The mechanism for the breakdown of the quantum Hall effect due to high currents has long been the subject of much experimental and theoretical interest. The temperature dependence of  $I_c$  indicates that a theoretical, thermodynamics based, model of the breakdown drawing parallels from the two-fluid model of superconductivity could provide interesting insights. Another interesting addition to the work presented here would be the study of the strong temperature dependence of the resistivity of graphene in the quantum Hall state. Two regimes are predicted with separate mechanisms. The first at low temperatures is predicted to follow variable range hopping, which is succeeded by thermal activation at higher temperatures. In order to determine in which temperature regimes these mechanisms operate a precise measure of the resistivity is required over several orders of magnitude of temperature.

Graphene remains the focus of a thriving community in both fundamental research and in a growing number of applications. In 2005, the two seminal graphene research papers from the Manchester [23] and Columbia [25] groups were published back to back in *Nature* and have to date been cited over 12,000 times between them. Eight years of intense research followed and in 2013, with an interesting symmetry, the same two groups published back to back in *Nature* the first observation of Hofstadter's butterfly in monolayer [182] and bilayer graphene [183] on boron nitride superlattices. Graphene continues to excite and surprise.

One of the questions which remain unanswered is the physical origin of the defects or impurities which affect the optical properties of carbon nanotubes. The answer to this would come using a combination of high resolution photoluminescence imaging with even higher resolution scanning probe and electron microscopy, such as atomic force mi-

croscopy, scanning tunnelling microscopy/spectroscopy, scanning electron microscopy and transmission electron microscopy. In order to do this precise alignment marks are required so that a particular identified nanotube can be studied using a variety of techniques. Overall, carbon nanotubes provide an interesting platform to study a great range of physics using optical, electronic and mechanical techniques. There are significant challenges remaining in the growth and/or purification of samples containing a single chirality but progress is being made, in particular in the field of solution processing. The functionalisation of semiconducting carbon nanotubes by polymer wrapping and using their unique optical properties in devices such as flexible organic photovoltaics, photodetectors or light emitters may prove to be one of the key applications of carbon nanotubes. The sensitivity of carbon nanotubes to their local environment, as demonstrated in this thesis, shows that prospects still remain for nanotube based sensors.

Low dimensional nanostructures exhibit a remarkable variety of properties with a great number of uses which have already percolated through, and indeed underpin, the technological world in which we live. The superior mechanical, optical and electronic properties of carbon nanostructures coupled to ever decreasing fabrication costs means that carbon nanotubes and graphene are here to stay.

# Appendix A

## Poster Presentations

This appendix includes posters relating to the work described in this thesis that have been presented at Conferences and Workshops.

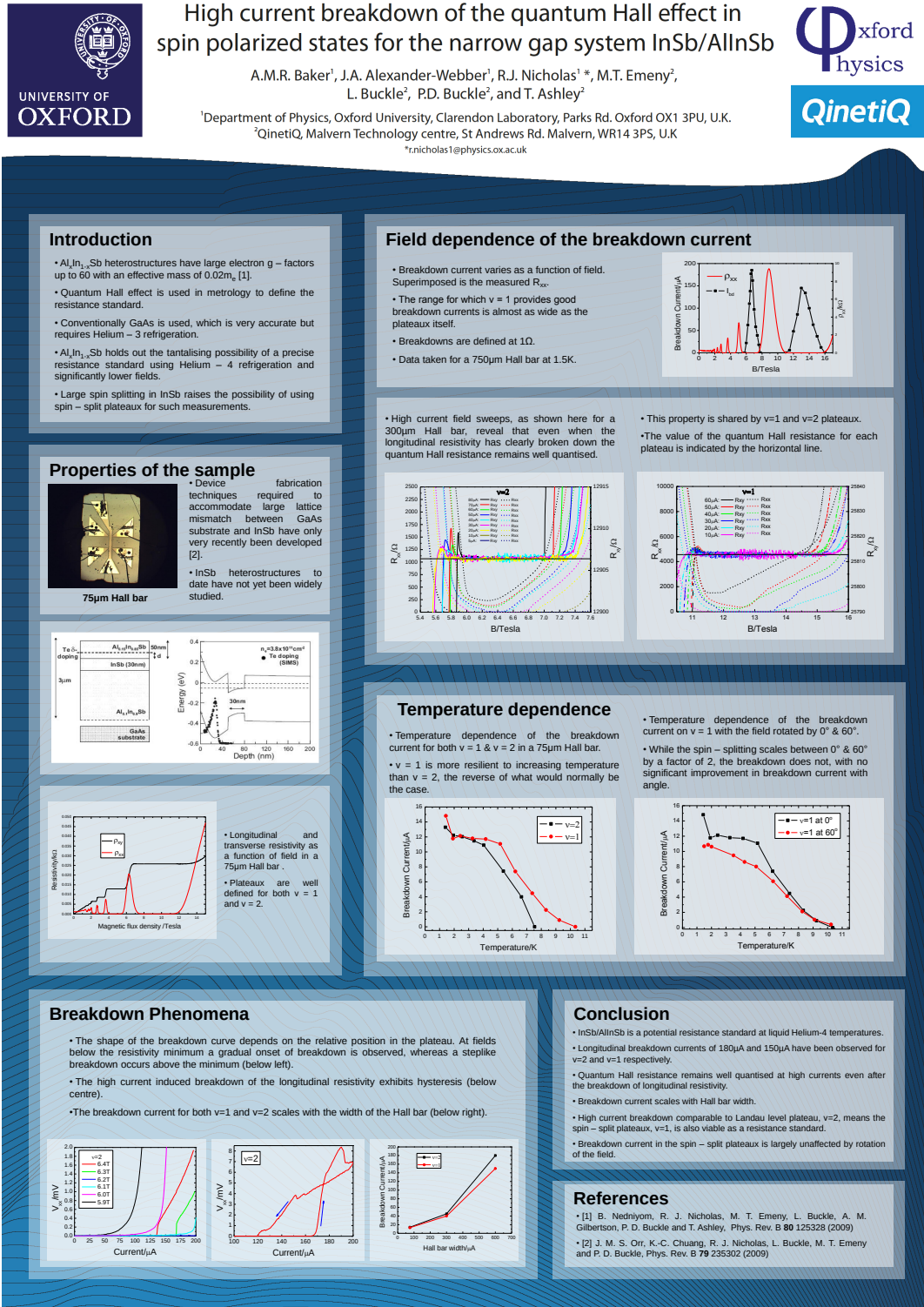


Figure A.1: Poster Presented at the International Conference on the Physics of Semiconductors (2010), Seoul

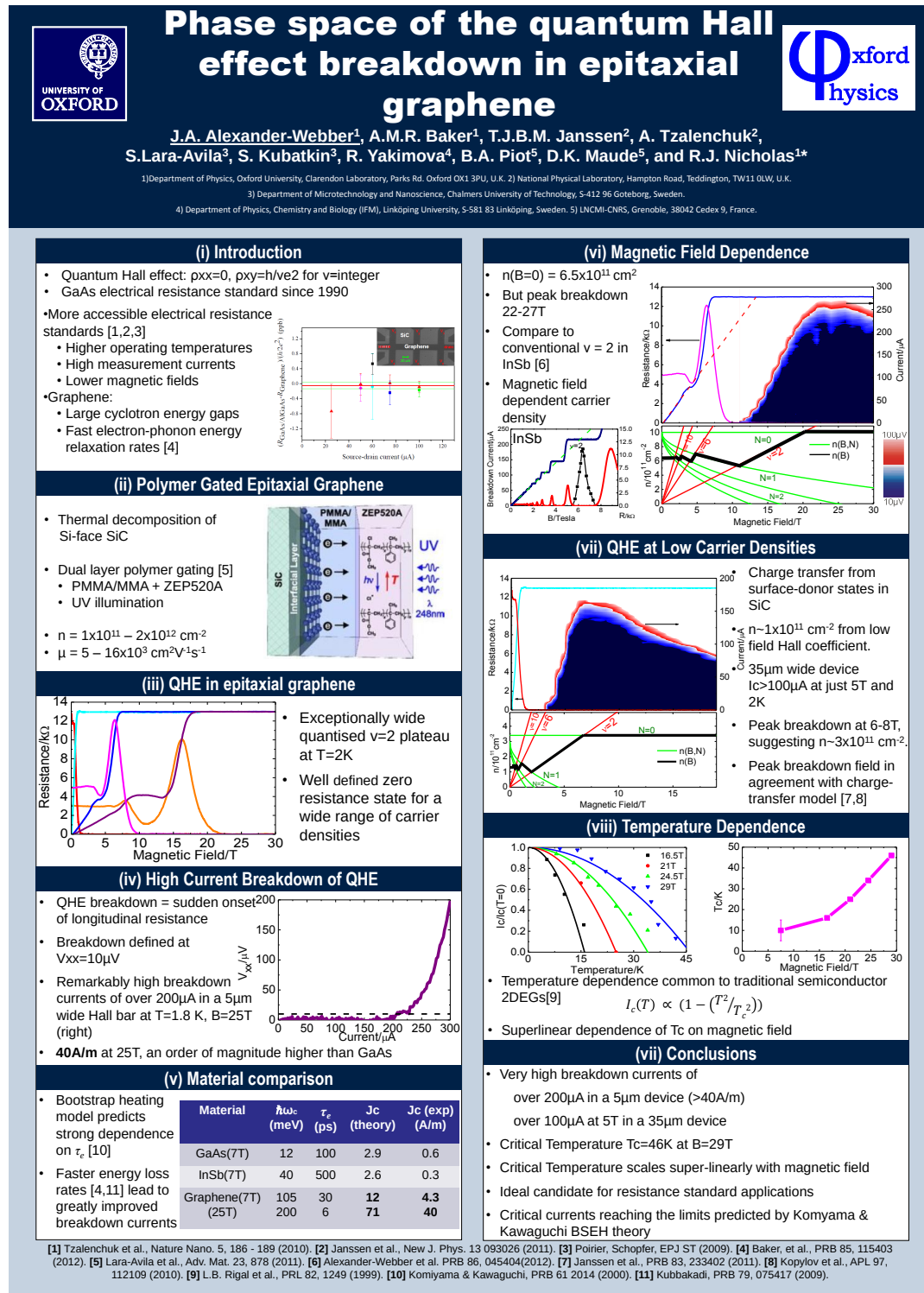


Figure A.2: Poster Presented at the International Conference on the Physics of Semiconductors (2012), Zurich

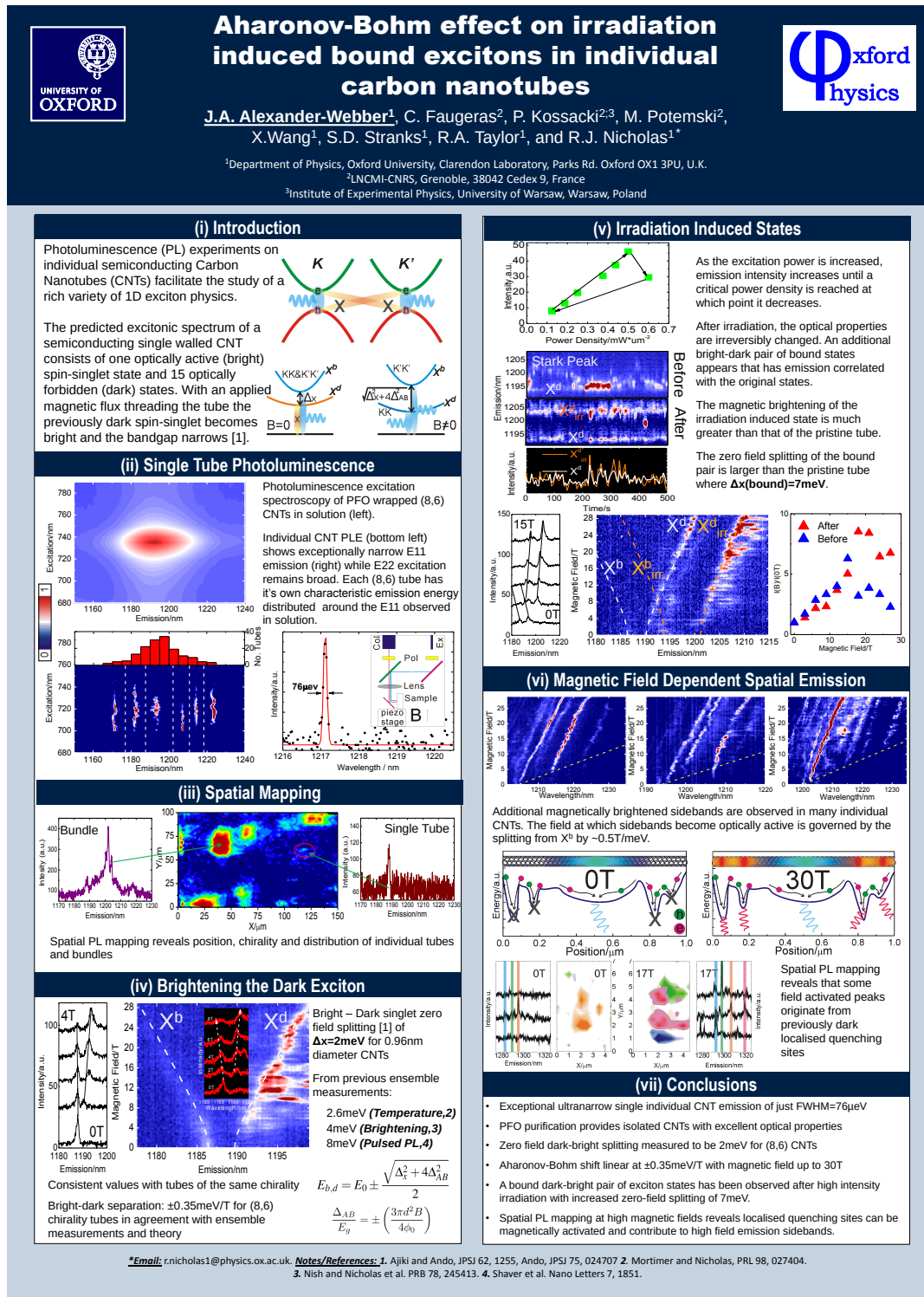


Figure A.3: Poster Presented at the Workshop on Nanotube Optics and Nanospectroscopy (2013), Santa Fe, NM

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