THESIS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

Epitaxial Graphene Technology for Quantum Metrology

TOM YAGER



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Quantum Device Physics Laboratory Department of Microtechnology and Nanoscience - MC2 Chalmers University of Technology SE-412 96 Göteborg, Sweden Phone: +46 (0)31-772 1000

Cover: False colour optical microscopy image of selectively patterned Hall bar devices on a pre-characterised SiC/G substrate.

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Abstract

Graphene grown on silicon carbide by high-temperature annealing (SiC/G) is a strong contender in the race towards large-scale graphene electronics applications. The unique electronic properties of this system lead to a remarkably robust and accurate Hall resistance quantisation of 0.1 parts per billion, making SiC/G devices highly desirable for the endeavour of quantum resistance metrology. However, major challenges for this technology remain, such as control of the charge carrier density and reproducibility of material growth and device properties.

The main aims of the work presented in this Thesis are to understand and improve the performance and reproducibility of SiC/G devices for quantum Hall resistance metrology. Moreover, in this work we developed further understanding of material issues such as the homogeneity of SiC/G for applications in quantum metrology, and ultimately wafer scale electronics.

By correlating the nanoscopic growth features of SiC/G with electron transport measurements, we were able to reveal the wafer scale electronic homogeneity of monolayer graphene grown on SiC. We developed disparate gating methods to enable quantum Hall effect at lower magnetic fields (B = 2-5 T) and to study electron transport close to charge neutrality, useful for metrology. We investigated the role of the reconstructed SiC morphology and bilayer graphene inclusions on the reproducibility of nominally monolayer graphene quantum Hall devices, and reveal the important consequences for quantum resistance metrology.

The above-mentioned studies were assisted by the development of optical microscopy methods to accurately identify single and multilayer domains of epitaxial graphene in addition to the nanoscopic details of the reconstructed SiC surface. This was found to be an important step of rapid and non-invasive quality control leading to improved device performance and reproducibility for quantum metrology applications.

While the focus has been placed on quantum metrology devices, the findings and technologies developed in this Thesis work are readily applicable to investigate other two-dimensional materials and graphene systems, in both research and industrial environments.

Keywords: Epitaxial graphene, silicon carbide, quantum Hall effect, resistance metrology, electron transport, charge neutrality, bilayer graphene, optical microscopy

List of Publications

Appended Papers

This Thesis is based on the work contained in the following papers.

A. Express Optical Analysis of Epitaxial Graphene on SiC: Impact of Morphology on Quantum Transport

T. Yager, A. Lartsev, S. Mahashabde, S. Charpentier, D. Davidovikj, A. Danilov, R. Yakimova, V. Panchal, O. Kazakova, A. Tzalenchuk, S. Lara-Avila, and S. Kubatkin *Nano Letters 13, 4217* (2013).

B. Wafer-Scale Homogeneity of Transport Properties in Epitaxial Graphene on SiC

T. Yager, A. Lartsev, R. Yakimova, S. Lara-Avila, and S. Kubatkin *Carbon 87, 409* (2015).

C. High Mobility Epitaxial Graphene Devices via Aqueous Ozone Processing T. Yager, M. Webb, H. Grenberg, R. Yakimova, S. Lara-Avila, and S. Kubatkin Applied Physics Letters 106, 063503 (2015).

D. Low Contact Resistance in Epitaxial Graphene Devices for Quantum Metrology

T. Yager, A. Lartsev, K. Cedergren, R. Yakimova, V. Panchal, O. Kazakova, A. Tzalenchuk, K. H. Kim, Y. W. Park, S. Lara-Avila, and S. Kubatkin *AIP Advances, vol. 5, no. 8* (2015).

Other Contributions

E. Tuning Carrier Density Across Dirac Point in Epitaxial Graphene by Corona Discharge

Lartsev, T. Yager, T. Bergsten, A. Tzalenchuk, T. J. B. M. Janssen, R. Yakimova, S. Lara-Avila, and S. Kubatkin *Applied Physics Letters 105, 063106* (2014).

F. Phase Coherence and Energy Relaxation in Epitaxial Graphene Under Microwave Radiation

V. Eless, T. Yager, S. Spasov, S. Lara-Avila, R. Yakimova, S. Kubatkin, T. J. B. M. Janssen, A. Tzalenchuk, and V. Antonov *Applied Physics Letters, 103, 093103* (2013).

G. Quantum Hall Effect and Quantum Point Contact in Bilayer-Patched Epitaxial Graphene

Chua, M. Connolly, A. Lartsev, T. Yager, S. Lara-Avila, S. Kubatkin, S. Kopylov, V. Fal'ko, R. Yakimova, R. Pearce, T.J.B.M. Janssen, A. Tzalenchuk, and C. G. Smith *Nano Letters 14, 3369* (2014).

H. Hot Carrier Relaxation of Dirac Fermions in Bilayer Epitaxial Graphene

J. Huang, J. A. Alexander-Webber, T. J. B. M. Janssen, A. Tzalenchuk, T. Yager, S. Lara-Avila, S. Kubatkin, R. L. Myers-Ward, V. D. Wheeler, D. K. Gaskill, R. J. Nicholas *Journal of Physics: Condensed Matter 27, 164202* (2015).

I. Physics of a Disordered Dirac Point in Epitaxial Graphene from Temperature-Dependent Magnetotransport Measurements

J. Huang, J. A. Alexander-Webber, A. M. R. Baker, T. J. B. M. Janssen, A. Tzalenchuk, V. Antonov, T. Yager, S. Lara-Avila, S. Kubatkin, R. Yakimova, and R. J. Nicholas *Physical Review B, vol. 92, no. 7, p. 75407* (2015).

Symbols

- k_B Boltzmann Constant
- a₀ Carbon-Carbon Bond Length
- n Charge Carrier Density
- μ Charge Carrier Mobility
- σ Conductivity
- I Current
- j Current Density
- ω_c Cyclotron Frequency
- s Disorder Parameter
- m^{*} Effective Mass
- σ Electrical Conductance
- n_e Electron Carrier Density
- \vec{E} Electric Field
- e Elementary Charge
- E Energy
- E_F Fermi Energy
- υ_F Fermi Velocity
- γ Gamma Factor
- V_g Gate Voltage
- R_H Hall Coefficient
- ρ_{xy} Hall Resistivity
- V_H Hall Voltage
- n_h Hole Carrier Density
- Intensity Input
- I_{in} Intensity Output
- R_{xx} Longitudinal Hall Resistance
- V_{xx} Longitudinal Hall Voltage
- ρ_{xx} Longitudinal Hall Resistivity
- B Magnetic Field
- l_B Magnetic Length
- τ Mean Free Time
- h Planck's Constant
- t Time
- r_{tip} Tip Radius
- c Speed of Light in Vacuum
- R_{xy} Transverse Hall Resistance
- V_{xy} Transverse Hall Voltage

Abbreviations

AFM	Atomic Force Microscopy
ARPES	Angle Resolved Photoemission Spectroscopy
CMOS	Complementary metal-oxide semiconductor
CVD	Chemical Vapour Deposition
C-Face	Carbon Face of Silicon Carbide $(000\overline{1})$
DIC	Differential Interference Contrast
DOS	Density of States
EBL	Electron Beam Lithography
FLG	Few Layer Graphene
GaAs	Gallium Arsenide
hBN	Hexagonal Boron Nitride
IPA	Isopropanol
LEEM	Low Energy Electron Microscopy
LOR	Lift-Off Resist
KPM	Kelvin Probe Microscopy
μm	Micrometer or Micron (10^{-6} m)
nm	Nanometer (10^{-9} m)
PMMA	Polymethyl-Methacrylate
QED	Quantum Electrodynamics
QHE	Quantum Hall Effect
QHR	Quantum Hall Resistance
SiC	Silicon Carbide
SiC/G	Epitaxial Graphene on Silicon Carbide
Si-Face	Silicon Face of Silicon Carbide (0001)
SiO ₂	Silicon Dioxide
SPM	Scanning Probe Microscopy
STM	Scanning Tunneling Microscopy
RMS	Root Mean Square
UHV	Ultra High Vacuum
Å	Ångström (10 ⁻¹⁰ m)
1LG	Monolayer Graphene
2LG	Bilayer Graphene

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Chapter 1 Introduction

A combination of graphene's exotic electronic properties and the relative simplicity of its production have led to a rapid proliferation to hundreds of research groups across the world [1]. In 2010, two of the leading pioneers of this research, Sir Kostya Novoselov and Sir Andre Geim, were awarded the Nobel Prize in physics for their "groundbreaking experiments regarding the two-dimensional material graphene" [2,3].

Graphene is an atomically thin, two-dimensional honeycomb lattice of carbon [4]. Whilst this material was investigated theoretically [5–8] and also, to some extent, experimentally [9–11] during the 20th century, a single layer of graphene was not conclusively isolated and studied until 2004 [12]. This was achieved by a simple mechanical exfoliation technique (i.e. scotch tape) used to cleave individual graphene sheets from bulk graphite (e.g. a pencil trace) [4,12]. Once isolated, individual graphene flakes were transferred to the surface of dielectric substrates where they were identified by interference enhanced optical microscopy and their thickness was analyzed using atomic force microscopy [12–16]. Experimental demonstrations of graphene's unique electronic structure soon followed, with magnetotransport measurements and the observation of the half-integer quantum Hall effect [14,17].

Since the discovery of graphene, its interesting physical properties have fascinated scientists and engineers, leading to the idea that the wonder materialgraphene has the capability of leading to a revolution in technology similar to the one by plastics in 20th century. As of today, arguably the only real application where graphene has truly outperformed any previously known technology is in quantum Hall resistance metrology [18–22]. In the quantum Hall effect (see Chapter 2), a relatively simple measurement of electrical resistance yields the ratio of two fundamental constants of nature; the electron charge, e, and Planck's constant, h [23,24]. The unique electronic properties of graphene result in an exceptionally robust quantum Hall effect [14,17] achievable at relatively low magnetic fields [21,25] and even at room temperature [26].

The first precision measurements of the graphene quantum Hall resistance were reported in 2008 on exfoliated graphene flakes [27]. However, the precision of resistance quantisation was limited to 15 parts per million, inferior to similar measurements for previously established semiconductor materials of choice such as gallium arsenide (GaAs). Subsequent measurements for large area epitaxial graphene, grown on silicon carbide substrates (SiC/G), found the resulting resistance plateaus to be extremely well defined [18,19]. This was found to be due to a combination of the rich interplay between graphene and the silicon carbide substrate, low contact resistances and large quantum Hall breakdown currents for the devices [20,28]. Consequently, SiC/G materials have surpassed the metrological performance of the previous material of choice, GaAs, enabling precision resistance measurements accurate to 0.1 parts per billion [19].

Whilst epitaxial graphene on silicon carbide has become an established material for quantum metrology, there exist substantial challenges in the reproducibility of its electronic device properties. For quantum Hall devices, irreproducibility can arise due to aspects of either the material (e.g. SiC/G morphology) or the devices (e.g. high contact resistance). The challenge of device reproducibility is further exacerbated for the extension to wafer scale applications, such as quantum Hall arrays [29,30], where the full quantisation of each and every device is vital to their successful implementation for quantum metrology. Furthermore, systematic investigations of the SiC/G device system are required for the advancement of quantum Hall metrology measurable under relaxed experimental conditions [21].

Thesis Outline and Scope

The main aims of the work presented in this Thesis are to understand and improve the performance and reproducibility of SiC/G devices for quantum Hall resistance metrology [Papers A, C, D]. While the focus has been made on quantum metrological devices, the findings and technologies developed in this work are readily applicable to investigate graphene and other two-dimensional materials, in both research and industrial environments. The contents of the Thesis are described below.

Chapter 2 outlines a theoretical description of graphene crystals, their resulting electronic properties and consequences for magnetotransport. This is followed by a review of common graphene production methods, with a more in-depth discussion of epitaxial graphene materials grown by high temperature annealing on the surface of silicon carbide substrates.

Chapter 3 introduces the optical and scanning probe microscopy methods used to characterise and provide quality control on SiC/G materials prior to the fabrication of Hall bar devices. The presence and role of polymer resist residuals, resulting from

electron beam lithography, and an overview of the post-fabrication cleaning of graphene devices are discussed.

Chapter 4 describes a systematic investigation of the charge carrier density and mobility of SiC/G devices. Electronic device properties are characterised under different environmental conditions and high and low doping regimes. Magnetotransport measurements are correlated with microscopy of the material to reveal the impact of surface morphology and layer inhomogeneity on the variability of charge transport properties.

Chapter 5 reveals the effect of SiC/G growth features on the achievement of reproducible quantum Hall effect in these systems. The challenges of achieving accurate Hall quantisation and low contact resistances suitable for metrology are discussed.

Finally, Chapter 6 summarises the main results of the Thesis, presents the appended papers in a wider context and provides a future outlook to this field of study.

Chapter 2 Concepts

Carbon structures exist in a wide variety of structural forms each exhibiting varied and often exceptional mechanical, electronic and optical properties. Elemental carbon allotropes can be found with various dimensionalities from quasi-zero and onedimensional Buckminster fullerenes [31] and carbon nanotubes [32] to threedimensional diamond and graphite. Graphene is a single, atomically thin twodimensional layer of graphite that has been found to exhibit a range of unique and extraordinary properties [5,13,33,34]. In this Chapter the structural and electronic properties of monolayer and bilayer graphene are introduced as well as their influence in quantum magnetotransport measurements. This is followed by a review of state of the art graphene production methods, with particular emphasis devoted to epitaxial graphene materials that are explored in further detail throughout this Thesis.

2.1 Graphene Fundamentals

2.1.1 Crystal Structure of Monolayer Graphene

In its two-dimensional geometry, each carbon atom forms sp² covalent σ -bonds with its three nearest neighbour atoms, equally distributed in-plane with an angle of 120° [35]. Since the electronic structure of a carbon atom is 1s² 2s² 2p², the remaining unbound p_z orbital forms a π -bond out of plane. These electrons are delocalised over the graphene crystal, similar to well-understood aromatic molecules such as benzene. The resulting honeycomb crystal structure for graphene can be constructed theoretically as a triangular Bravais lattice with a two atom basis [5]. In real space, the vectors between nearest neighbour carbon atoms are given by

$$\boldsymbol{\delta}_{1} = \frac{a_{0}}{2} \left(\hat{x} + \sqrt{3} \, \hat{y} \right), \quad \boldsymbol{\delta}_{2} = \frac{a_{0}}{2} \left(\, \hat{x} - \sqrt{3} \, \hat{y} \right), \quad \boldsymbol{\delta}_{3} = \frac{a_{0}}{2} \left(- \, \hat{x} \right), \tag{1}$$

where $a_0 = 1.42$ Å is the length of a carbon-carbon bond (Figure 2.1). The resulting primitive unit cell contains two equivalent sublattices, A and B. The two-dimensional translational lattice vectors for the unit cell may be defined in Cartesian coordinates as

$$\boldsymbol{a_1} = \frac{a_0}{2} \left(3 \, \hat{x} + \sqrt{3} \, \hat{y} \right), \qquad \boldsymbol{a_2} = \frac{a_0}{2} \left(3 \, \hat{x} - \sqrt{3} \, \hat{y} \right), \tag{2}$$

and in reciprocal space, the lattice vectors can be defined by

$$\boldsymbol{b_1} = \frac{2\pi}{3a_0} \hat{k}_x + \frac{2\pi}{\sqrt{3}a_0} \hat{k}_y, \quad \boldsymbol{b_2} = \frac{2\pi}{3a_0} \hat{k}_x - \frac{2\pi}{\sqrt{3}a_0} \hat{k}_y.$$
(3)



Figure 2.1: Left: Graphene honeycomb structure comprising of A and B sublattices. Right: Corresponding reciprocal lattice of graphene. Adapted from [36]

The corresponding reciprocal lattice is hexagonal with four high symmetry points, Γ , M, K and K'. The two points K and K' at the corners of the graphene Brillouin zone are also known as the Dirac points, and can be defined by

$$\boldsymbol{K} = \frac{2\pi}{3a_0}\hat{k}_x + \frac{2\pi}{3\sqrt{3}a_0}\hat{k}_y, \quad \boldsymbol{K}' = \frac{2\pi}{3a_0}\hat{k}_x - \frac{2\pi}{3\sqrt{3}a_0}\hat{k}_y.$$
(4)

These Dirac points are most important for determining the low energy electronic properties of graphene [36], described in the following section.

2.1.2 Electronic Structure of Monolayer Graphene

In condensed matter systems, the electronic and optical properties emerge from crystallographic ordering of the lattice [37]. The electronic band structure of graphene can be theoretically calculated in the tight-binding approximation model [5–7]. In this model, it is assumed that the graphene crystal is formed by a periodic lattice of strong ionic potentials with valence electrons strongly bound to their ion [38]. The electron wavefunction of the crystal can be calculated by the linear combination of Bloch function states, summed over the whole lattice.

For the case of graphene, there are two inequivalent lattice sites A and B. Since the carbon atoms on sublattice sites A and B are energetically identical, the onsite energies can be stated as $\varepsilon_A = \varepsilon_B = 0$ [39]. The energetic hopping parameters $t_{AB} = t_{BA} = t$, between neighbouring atoms, A and B, are predominantly determined by the Coulomb interaction. The resulting eigenvalues of the Schrodinger equation are given by

$$det(\widehat{H}_k - E\widehat{1}) = \begin{pmatrix} -E & tf_k \\ tf_k^* & -E \end{pmatrix} = 0, \qquad (5)$$

where $\hat{1}$ is the unity matrix, and f_k is

$$f_k = 4\cos\left(\frac{k_x 3a_0}{2}\right)\cos\left(\frac{k_y \sqrt{3}a_0}{2}\right) + 4\cos^2\left(\frac{k_y \sqrt{3}a_0}{2}\right).$$
(6)

The resulting energy dispersion of graphene can be expressed as

$$E_k = \pm t \sqrt{1 + 4\cos\left(\frac{k_x 3a_0}{2}\right)\cos\left(\frac{k_y \sqrt{3}a_0}{2}\right) + 4\cos^2\left(\frac{k_y \sqrt{3}a_0}{2}\right)}.$$
(7)

In this tight-binding model, the band structure is symmetric around zero energy for electrons and holes and the valence band touches the conduction band at the inequivalent points K and K' (Figure 2.2). The model can also be extended to second



Figure 2.2: Electronic dispersion for monolayer graphene. Expansion around the K points for low energies reveals the linear Dirac spectrum. Adapted from [36]

nearest neighbour hopping, with the subsequent calculations resulting in a small electron-hole asymmetry and the introduction of so called trigonal warping [36,40,41].

The low energy dispersion spectrum, most relevant for charge neutral graphene, can be found by expanding the full spectrum around the Dirac points [5] such that:

$$\boldsymbol{k} = \boldsymbol{K} + \boldsymbol{q} , \qquad \text{where } \boldsymbol{q} \ll \boldsymbol{K} . \tag{8}$$

This leads to the linear dispersion relation of graphene stated simply as

$$E_k = \pm \hbar v_f |\boldsymbol{q}| \,, \tag{9}$$

where \hbar is the reduced Planck constant and v_f is the Fermi velocity. In these tight binding calculations, this Fermi velocity is determined by the lattice constant, $a_0 = 1.42$ Å, and the hopping parameter, $t \approx -2.5$ eV [5,42], leading to a value of

$$v_f = \frac{3|t|a_0}{2\hbar} \approx 10^8 \text{cm s}^{-1} \approx \frac{c}{300}.$$
 (10)

where c is the speed of light in a vacuum. In this low energy limit, the effective Hamiltonian can be described by

$$\widehat{H}_{k} = \hbar v_{f} \begin{pmatrix} 0 & q_{x} - iq_{y} \\ q_{x} + iq_{y} & 0 \end{pmatrix} = \hbar v_{f} \boldsymbol{\sigma}. \boldsymbol{q} , \qquad (11)$$

where $\boldsymbol{\sigma} = (\sigma_x, \sigma_y)$ are Pauli spin matrices. In the case of graphene, this term relates to a pseudospin describing the two non-equivalent sublattice sites A and B. The

resulting Hamiltonian is analogous to the Dirac equation for relativistic massless fermions but with the speed of light reduced to the Fermi velocity in graphene [8,43]. This unusual electronic behaviour allows the exploration of exotic quantum relativistic phenomenon in a simple and controllable bench-top experiment. This was evocatively summarised in 2005 by Andre Geim: "QED comes out of a pencil trace." [44].

2.1.3 Crystal Structure of Bilayer Graphene

In the case that two or more graphene layers are vertically stacked, the composite monolayer electronic properties are substantially modified by the introduction of interlayer hopping. Stacking of graphene layers occurs by van der Waals attraction, with an interlayer separation distance of 3.35 Å. Bilayer graphene, comprising of two stacked monolayer graphene crystals is a unique and interesting electronic system in between monolayer and bulk graphite [42].

Bilayer graphene stacking leads to a total of four inequivalent lattice sites for the carbon atoms; A1, B1, A2, and B2. Here the letter denotes the individual A and B atoms whilst the number refers to the two graphene layers [45]. There are several different stacking possibilities for the two graphene layers. The orientation of the crystals is described in terms of the vertical overlap of the A and B atoms of each crystal layer. These stacking orientations for bilayer graphene can include AA, AB (Bernal) and turbostratic stacking.

In the AB stacking configuration, the second layer of graphene is rotated by 60 degrees with respect to the first (Figure 2.3) [46]. The result is that the A1 sublattice sites of the first layer are vertically aligned with the B2 sites of the second layer. At the same time, the A2 and B2 sublattice sites are vertically aligned either above or below the center of the carbon ring of the other layer. Consequently, in this stacking configuration, there is significant out of plane hopping between vertically aligned atoms of sublattice, but negligible out of plane hopping for atoms of the other sublattices. This inequivalence leads to a disruption of the linear dispersion of



Figure 2.3: Bilayer graphene with AB stacking. structure comprising of A and B sublattices. Adapted from [46]

monolayer graphene, leading to a parabolic dispersion for bilayer graphene [45].

In the case of AA stacking, lattice sites A1 are situated above lattice sites A2, and lattice sites B1 are situated above lattice sites B2 for the two graphene layers. Epitaxial graphene grown on SiC ($000\overline{1}$) is found to exhibit turbostratic stacking where graphene layers are ordered stochastically following neither AA nor AB crystallographic ordering [47]. For AA stacking and turbostratic stacking, the equivalence of sublattice sites A and B remain unbroken and therefore the linear dispersion of monolayer graphene is preserved, leading to monolayer graphene-like features for a multilayer graphene system [48].

In the case that a small twist angle exists between graphene layers, stacking orientations smoothly alternate in lateral dimensions between AA and AB stacking [49,50]. This results in a Moiré pattern for the carbon structure, with a superlattice geometry dependent on the twist angle. For small twist angles less than 1° and for large twist angles between 10-30° the linear dispersion of monolayer graphene is preserved [51]. Between 2-10° the linear dispersion remains but with a renormalised Fermi velocity. Twist angles of approximately 1.5° have been theoretically predicted to lead to flat dispersion bands, further stimulating interest in the research community [51–54].

2.1.4 Electronic Structure of Bilayer Graphene with Bernal Stacking

The electronic structure of bilayer graphene can be theoretically derived, following a similar nearest neighbour tight binding approach as for monolayer graphene, with the addition of the possibility to hop between the layers [35,45,55–57]. This interlayer hopping is represented by the perpendicular hopping parameter, t_{\perp} . For the case of AB stacked graphene bilayers, interlayer hopping is most likely between the vertically stacked sublattice sites, A1 and B2, leading to a modification to the monolayer graphene Hamiltonian:

$$\widehat{H}_{k} = \begin{pmatrix} 0 & tf_{k} & t_{\perp} & 0 \\ tf_{k}^{*} & 0 & 0 & 0 \\ t_{\perp} & 0 & 0 & tf_{k}^{*} \\ 0 & 0 & tf_{k} & 0 \end{pmatrix}.$$
(12)

The resulting eigenvalues of the Schrodinger equation are given by

$$det(\hat{H}_{k} - E\hat{1}) = \begin{pmatrix} -E & tf_{k} & t_{\perp} & 0\\ tf_{k}^{*} & -E & 0 & 0\\ t_{\perp} & 0 & -E & tf_{k}^{*}\\ 0 & 0 & tf_{k} & -E \end{pmatrix} = 0,$$
(13)

$$|tf_k|^4 - 2|tf_k|^2 E^2 - t_\perp E^2 + E^4 = 0.$$
⁽¹⁴⁾

This leads to four solutions to the resulting energy dispersion:

$$E_k = \pm \frac{t_\perp}{2} \pm \sqrt{t_\perp^2 + 4|tf_k|^2} \,. \tag{15}$$

There are two parabolic bands, meeting at $E_k = 0$ in addition to two extra bands at higher energies (Figure 2.4). The system can be described as metallic, with electron-hole symmetry. At low energies the Hamiltonian is given by

$$\widehat{H}_{k} = \frac{1}{2m^{*}} \begin{pmatrix} 0 & (q_{x} - iq_{y})^{2} \\ (q_{x} + iq_{y})^{2} & 0 \end{pmatrix},$$
(16)

where m^* is the non-zero effective mass of charge carriers in bilayer graphene, with a corresponding dispersion relation of:

$$E_k = \pm \frac{\hbar^2 |\boldsymbol{q}|^2}{2m^*}.$$
⁽¹⁷⁾

In contrast to monolayer graphene, the inequivalence between the A and B atomic sites can be used to break the degeneracy between the on site energies of the graphene sublattices, leading to the opening of a small energy gap (band gap) in the presence of perpendicular electric fields (Figure 2.4) [58,59]. The unique properties of AB stacked bilayer graphene make this system a material of interest both for fundamental research and technological applications [60].



Figure 2.4: Electronic dispersion for bilayer graphene assessed by angle resolved photoemission spectroscopy (ARPES). Perpendicular electric fields result in a band gap opening for AB stacked bilayer graphene. Adapted from [58].

2.2 Magnetotransport Techniques

2.2.1 Charge Transport and Field Effect

The charge transport properties of electronic devices can be described by a combination of charge carrier density and mobility. In the classical Drude model of diffusive transport [61,62] charge transport is described in terms of ballistic particles with a mean free time before collisions, $\Delta t = \tau$. The generalised Ohm's law, $\vec{j} = \sigma \vec{E}$, expresses current in terms of the conductivity and electric field. This conductivity can be expressed as a function of electron charge carrier density and mobility as follows:

$$\sigma = en\mu, \qquad (18)$$

where, *e*, is the electron charge, *n*, is the charge carrier density, and μ , is the device mobility. The device mobility is determined by

$$\mu = \frac{e\tau}{m^*},\tag{19}$$

where m^* is the effective mass of the charge carriers. For the case of graphene:

$$E = m^* v_f^2 , \qquad (20)$$

and therefore

$$\mu = \frac{e\tau}{m^*} = \frac{ev_f^2 \tau}{E}.$$
(21)

2.2.2 Hall Effect

First discovered in 1879, the Hall effect is a powerful method to characterise the electronic properties of materials [63,64]. Important material parameters such as resistivity, mobility, and significantly, the charge carrier density can all be extracted from such Hall measurements, obtained at low magnetic fields.

When an electron is situated in crossed magnetic and electric fields, it experiences a perpendicular Lorentz force:

$$\boldsymbol{F}_{\boldsymbol{L}} = \boldsymbol{e}(\boldsymbol{E} + \boldsymbol{v} \times \boldsymbol{B}) , \qquad (22)$$

where *E* is the electric field, *B* is the magnetic field and *v* is the electron velocity. In the case of a two-dimensional electronic system in a perpendicular magnetic field, *B*, a transverse Hall voltage, V_{xy} , is generated perpendicular to both the current density,



Figure 2.5: Schematic of four-terminal resistance measurements on a 6-legged graphene Hall bar.

 j_{xx} , and magnetic field, B_z (Figure 2.5) [65]. The two-dimensional resistivity can be expressed in tensor form as

$$\boldsymbol{\rho} = \begin{pmatrix} \rho_{xx} & \rho_{xy} \\ \rho_{yx} & \rho_{yy} \end{pmatrix}$$
(23)

For perpendicular magnetic fields, $\rho_{xx} = \rho_{yy}$, $\rho_{xy} = -\rho_{yx}$.

The resulting transverse Hall resistivity, ρ_{xy} , is given by the expression

$$\rho_{xy} = \frac{V_{xy}}{I_{xx}} = \frac{B_z}{ne},\tag{24}$$

This transverse resistivity is geometry independent and can equivalently be written as $\rho_{xy} \equiv R_{xy}$. For two-dimensional systems, the longitudinal resistivity depends on the device width, *W*, and length, *L*, as follows:

$$\rho_{xx} = \frac{W}{L} \frac{V_{xx}}{I_{xx}}.$$
(25)

The charge carrier density and Hall mobility can be approximated as follows:

$$n = \frac{B_z}{eR_{xy}}, \qquad \mu_H = \left|\frac{R_{xy}}{\rho_{xx}}\right|. \tag{26}$$

The sign of the measured transverse resistance, with respect to the measurement geometry, can be used to determine the majority charge carriers in a device (i.e. electrons or holes).

It is important to note that the Hall mobility is a composite measurement of two different device regions. The transverse resistivity leads to an assessment of the charge carrier density in the vicinity of the Hall crosses, whereas four-terminal resistivity measurements assess the geometry contained within the Hall bar channel (Figure 2.6). In the case of material inhomogeneity, this characterisation method can



Figure 2.6: Schematics showing approximate device regions characterised by Hall measurements. (a) The transverse Hall resistivity is used to characterise the charge carrier density within the geometry of the Hall crosses (blue). (b) Four terminal resistivity measurements assess the longitudinal resistivity within the Hall bar channel (green).

lead to significant uncertainty in the determination of device mobility. The role of device inhomogeneity is explored in further detail in Chapter 4.

2.2.3 Integer Quantum Hall Effect

At high magnetic fields and low temperatures, the linearity of the Hall effect can break down, leading to a quantisation of the transverse Hall resistance in rational fractions of the von Klitzing constant $R_K = h/e^2 \approx (25.8 \text{ k}\Omega)$, where *h* is the Planck's constant and *e* is the elementary charge. This Hall quantisation is accompanied by a simultaneous vanishing of the longitudinal resistivity within the device. This effect is the so-called quantum Hall effect, discovered in 1980, for which the Nobel Prize in physics was awarded to Klaus von Klitzing in 1985 [23,66].

The quantum Hall effect emerges from Landau quantisation of charge carriers in two dimensions. Under strong perpendicular magnetic fields, the orbital motion of electrons can become quantised, giving rise to well defined, discrete energy spectrum:

$$E_N = \left(N + \frac{1}{2}\right)\hbar\omega_c\,,\tag{27}$$

where N is an integer (Figure 2.8). The cyclotron energy $\hbar\omega_c$ is proportional to the magnetic field, B and the cyclotron mass, m_c :

$$\hbar\omega_c = \frac{\hbar eB}{m_c}.$$
(28)

The Landau levels are highly degenerate, ideally sharp delta functions. However, in the presence of electronic disorder in the material, these levels become broadened. Between Landau levels, only the states belonging to the occupied levels contribute to



Figure 2.7: Transverse Hall resistance quantisation of the integer quantum Hall effect, measurable for GaAs.

electron transport (Figure 2.7). Therefore the Hall resistivity becomes proportional to the number of occupied levels:

$$R_{xy} = \frac{V_{xy}}{I_{xx}} = \frac{h}{\nu e^2} \approx 25.8 \text{ k}\Omega / \nu , \qquad (29)$$

where ν is an integer representing the number of fully occupied Landau levels. In the case of fully quantised Hall effect, the longitudinal resistance of the material is reduced to zero, since the backscattering process of charge carriers is forbidden.

This quantum Hall effect is a topologically protected two-dimensional state that is unaffected by point like scatterers in the system. The most prevalent description of charge transport in this system is the edge state model [67,68]. In this model, the bulk of the sample becomes insulating due to localisation of the charge carriers. A combination of the high precision, experimental invariance and relative simplicity to measure have made the quantum Hall effect an important tool for quantum resistance metrology [69].

2.2.4 Quantum Hall Effect in Monolayer Graphene

The unique quasi-relativistic electronic properties of monolayer graphene lead to an anomalous half-integer quantum Hall effect, first demonstrated experimentally for exfoliated graphene flakes in 2005 [14,17]. The resulting half-integer filling factors act as a fingerprint for the definitive identification of graphene. Since charge carriers in monolayer graphene behave as massless Dirac fermions, the cyclotron energy and Landau level spacing between the zeroth and first levels are larger than for conventional massive semiconductors [70]. This increases the robustness of the quantum Hall effect in graphene, allowing its observation under more relaxed



Figure 2.8: Schematic illustration of the Landau level spacing for (a) two-dimensional electron gases and (b) massless Dirac fermions. After [70].

experimental conditions such as higher temperatures or lower magnetic fields [26]. The Landau level spectrum for monolayer graphene is given by:

$$E_N = \pm \hbar \omega_c \sqrt{N} = \pm v_f \sqrt{2e\hbar BN} .$$
⁽³⁰⁾

In contrast to conventional semiconductors, a Landau level occurs at zero energy, and due to the electron-hole symmetry of graphene the level is equally shared between electrons and holes (Figure 2.8). Another notable difference is the \sqrt{N} spacing between Landau levels with respect to the magnetic field.

In the quantum Hall effect for monolayer graphene (Figure 2.9), the transverse



Figure 2.9: Half integer quantum Hall effect for exfoliated graphene. After [17].

conductivity is quantised according to:

$$\sigma_{xy} = g_s g_v \left(N + \frac{1}{2} \right) \frac{e^2}{h},\tag{31}$$

where the spin degeneracy, g_s , and the valley degeneracy, g_s , are both equal to two for graphene. This leads to the following quantisation of transverse resistance:

$$R_{xy} = \frac{h}{4e^2\left(N + \frac{1}{2}\right)}.$$
(32)

The high precision and relative robustness of the quantum Hall effect in graphene makes it an ideal system for quantum resistance metrology [18,19].

2.2.0 Quantum Hall Effect in Bilayer Graphene

Bilayer graphene is another special case of the quantum Hall effect (Figure 2.10) [71]. In contrast to monolayer graphene, charge carriers in graphene bilayers are massive, with four-fold degeneracy, leading to the following transverse resistance quantisation in the quantum Hall effect:

$$R_{xy} = \frac{h}{4Ne^2}.$$
(33)



Figure 2.10: Bilayer graphene quantum Hall effect for exfoliated graphene. Adapted from [71].

2.3 Synthesis of Graphene

In the decade since the first isolation and demonstration of monolayer graphene in 2004, several complementary methods have been developed for graphene production. On a small scale, graphene can be mechanically exfoliated from graphite to form high quality micron sized flakes [4,12]. The principle of this exfoliation method can be scaled up to produce large volumes of small graphene flakes by liquid phase exfoliation. The technique of exfoliating graphene flakes from bulk graphite is not readily scalable to produce large area graphene crystals (i.e. millimeter to meter scales). The most highly developed methods for producing large area graphene crystals are epitaxial growth on silicon carbide [10,72–77] and chemical vapour deposition (CVD) on catalytic substrates [78–80]. Each of these resulting graphene materials is unique, presenting different advantages and technological challenges.

In bulk graphite the honeycomb networks of sp^2 covalent bonds between neighbouring carbon atoms are very strong, however the van der Waals forces of attraction between constituent graphene layers are comparatively weak [81–83]. The ability of graphene planes to glide over each other forms the basis for graphite applications in pencils and lubricants as well as the principles allowing the mechanical exfoliation of single atomic layers [4,12]. The initial 'scotch tape' method of exfoliation is capable of producing extremely high mobility devices ($\sim 10^6$ $cm^2 v^{-1} s^{-1}$) [84] that are highly valuable for fundamental research and for exploring exotic physical behaviour [85-89]. Unfortunately, this method is not directly suitable for industrial scale production and applications. One method for the industrial scale production of graphene flakes is liquid phase exfoliation (LPE), however a number of significant issues remain for quality control of the resulting material [90-94]. Presently the material produced from liquid phase exfoliation is not well suited for precision or high-speed electronics but are likely to find various applications in the short-to-medium term such as in graphene composites [95], solar cells [96] and inks [97].

In the chemical vapour deposition method, large areas of graphene are grown on a heated catalytic substrate (e.g. copper) by flowing gaseous carbon-containing molecules under controlled conditions [79,80,98–100]. Some of the main challenges in the production of high electronic quality graphene by this method are the development of small graphene crystals interrupted by grain boundaries and the transfer process onto insulating substrates [79,101]. These issues may be largely overcome by using low pressure CVD [79,102] and an optimised transfer and encapsulation process using boron nitride [103]. The resulting material can exhibit device mobilities as high as 350,000 cm² v⁻¹ s⁻¹, rivaling those of mechanically exfoliated graphene flakes [104].



Figure 2.11: Schematic of epitaxial graphene growth on the silicon face of SiC. Silicon at the surface sublimates at high temperatures, leaving behind a single electronic layer of graphene.

Epitaxial growth on the surface of silicon carbide (SiC) substrates has proven to be a reliable technique to produce large areas of single crystal monolayer graphene [18,105–108]. At temperatures above 1200 °C, silicon atoms from the SiC surface sublime from the surface [109] leaving a carbon rich SiC surface that recrystallizes to form honeycomb crystal layers of graphene (Figure 2.11). Since SiC is a wide band gap semiconductor, electronic devices can be fabricated without the need for graphene transfer. Consequently, epitaxial graphene is a promising candidate for a range of high performance electronic applications [74,75] and, in particular, for quantum resistance metrology [18–21].

2.3.1 Epitaxial Graphene on Silicon Carbide

Silicon carbide crystals have two polar surfaces that can both lead to graphene growth by silicon sublimation [110,111]. These are named the silicon-terminated face (0001) (Si-face) and the carbon-terminated face (000 $\overline{1}$) (C-face). The dynamics of the graphene growth processes are very different for the two polar faces. An important advantage of the Si-face for the production of monolayer graphene is that the growth kinetics are slower [75,76]. This improves the control of layer thickness and uniformity of growth in comparison with the C-face [47].

The first atomic monolayer of carbon material grown on the Si-face is known as the so-called "buffer layer", "zero layer" or "dead layer" [112–115]. Whilst this layer shares graphenes honeycomb structural lattice, it is usually electrically insulating due to covalent bonds between approximately 30% of its carbon atoms and the SiC substrate (Figure 2.12) [114,116]. The second grown layer of atomically thin honeycomb carbon interacts less strongly with the SiC substrate and is the first electrically conductive graphene layer on SiC (0001). This layer has been shown to be a continuous single crystal, that exhibits graphenes electronic spectral properties and is consequently described as "monolayer graphene" [75]. The accuracy of this description was confirmed by a number of independent groups around 2009 with the



Figure 2.12: Schematic representation of (a) buffer layer and (b) monolayer graphene. After [116].

demonstration of characteristic half-integer quantum Hall effect for macroscopic SiC/G devices [18,105–108]. The electronic continuity of grown monolayer graphene over the uneven reconstructed surface morphology of SiC can be understood by considering that this atomically thin sheet covers and flows over steps on the SiC surface in analogue to a carpet flowing down a staircase [18]. Transmission electron microscope studies of epitaxial graphene cross sections corroborate this interpretation [117,118].

Graphene layers grown on the Si-face are found to be heavily electron doped [58,119–121] due to a complex interaction with the SiC via the buffer layer [122]. Angle resolved photoemission spectroscopy (ARPES) estimates the intrinsic electron doping of pristine monolayer SiC/G to be on the order of $n\sim 10^{13}$ electrons cm⁻² [58,119–121]. In addition to the charge transfer from donor states at the surface, the Fermi level of graphene is pinned to these charge reservoirs [28]. This results in inefficient electrostatic carrier density control of SiC/G, particularly for large area devices (e.g. millimeter-sized). Whilst the strong influence of the substrate may be undesirable for some device applications, such as transistors [123,124] or sensors [125], it also leads to highly robust quantisation of the Hall resistance, making SiC/G (0001) systems exceptionally well suited for quantum metrological applications [20,28].

2.3.2 Surface Reconstruction and Layer Inhomogeneity for SiC/G

Annealing of SiC substrates at high temperatures, required for graphene growth, results in an uncontrollable surface reconstruction and to the formation of a parallel series of steps and terraces [126,127]. A single bilayer of silicon and carbon atoms in the SiC crystal has a height of ~0.25 nm [128–130]. Reconstructed surface steps are found to form in integer multiples of this value due to step bunching. This step bunching is thought to be a consequence of a minimisation of the surface free energy [131], with the lateral spacing and step height determined by a number of factors including the growth kinetics [47,75,132–134], crystal misorientation [75,135] and SiC polytype [18,134]. Whilst there are more than 250

possible polytypes of SiC, the two most reproducibly grown are 4H and 6H, with the number denoting the stacking periodicity and the letter denoting a hexagonal crystal symmetry.

The monolayer graphene growth process on the Si-face is not perfectly selflimiting [136,137]. This results in the formation of bilayer and multilayer graphene domains that grow primarily in the vicinity of surface steps and other SiC defects, such as micro-pipes, where graphene growth nucleates [132,138,139]. The resulting bilayer that grows on the Si-face has been reported to have AB stacking [140]. Whilst this inhomogeneous layer growth is often viewed as disadvantageous, the underlying principal of differential growth rates can also be exploited in order to selectively pattern and grow different graphene geometries [141]. In this way it is possible to produce graphene nanoribbons, directly grown along reconstructed SiC step edges [141–143]. Such nanoribbons are found to be metallic or semiconducting depending on their edge terminations ("zigzag" or "armchair") and their width [144]. It has also been reported recently that, under some conditions, graphene nanoribbons epitaxially grown on SiC can display ballistic transport properties over micrometer length scales [142].

2.3.3 Optical Contrast of SiC/G Layers

Optical microscopy has proved an invaluable tool in the discovery and identification of graphene [12–14]. Since each free standing, undoped graphene layer absorbs only 2.3 % of incident light, the ability to reliably identify monolayer graphene in a standard optical microscope is a challenge [15]. An established method to assist in making graphene layers visible is to transfer them to a substrate with a dielectric layer of carefully chosen thickness (typically 300 nm). When illuminated with light of the corresponding wavelength, this leads a significant contrast enhancement due to optical interference and resonant reflection [15,16]. In this way the optical contrast of graphene layers can be increased by up to an order of magnitude, allowing simple identification in an optical microscope (Figure 2.13).



Figure 2.13: Optical microscopy of graphene. Undoped suspended graphene absorbs 2.3% of incident light (left). On a substrate with a dielectric interference layer the layer contrast can be enhanced up to an order of magnitude (middle, right). Adapted from [12,146]

For epitaxial graphene grown on the surface of SiC, two obstacles exist for the use of standard optical microscopy as an identification method. Firstly, the absence of a dielectric interference layer at the surface of SiC precludes the optical contrast enhancement that occurs on SiO₂ substrates [15]. Secondly, the optical contrast of graphene on SiC is predicted in the Fresnel model to be reduced by almost a factor of two due to the refractive index of the substrate [145].

In the general case of *N* graphene layers, each with an optical absorption $\pi\alpha$ (= 2.3%) [146,147], on a substrate with refractive index n_2 and in a medium n_1 , the reflection intensity, I_r , can be approximated by [148]:

$$I_R = R^2 = \frac{(n_2 - n_1 + N\pi\alpha)^2}{(n_2 + n_1 + N\pi\alpha)^2}.$$
(34)

This leads to a reflection contrast, C_R , (Figure 2.14) between each graphene layer in air (n_1 =1), on a substrate with refractive index $n_2 = n_{SiC} = 2.65$, of

$$C_R^{0,1} = \frac{I_R(N=1) - I_R(N=0)}{I_R(N=0)} = \frac{(n_{SiC} - 1 + \pi\alpha)^2}{(n_{SiC} + 1 + \pi\alpha)^2} - 1 \approx 1.5\%.$$
 (35)

This is modified for the case of optical transmission to:

$$I_T = T^2 = \frac{4n_1n_2}{(n_2 + n_1 + N\pi\alpha)^2},$$
(36)

$$C_T^{0,1} = \frac{I_T(N=1) - I_T(N=0)}{I_R(N=0)} = \frac{(n_{SiC} - 1)^2}{(n_{SiC} + 1 + \pi\alpha)^2} - 1 \approx 1.3\%.$$
 (37)

This reduction in optical contrast has previously proven to be prohibitive for optical microscopy of SiC/G. However, in Chapter 3 we will describe techniques to improve this optical contrast, allowing fast, non-invasive screening of SiC/G materials.



Figure 2.14: Calculated optical transparency for graphene on a dielectric substrate, with refractive index n. For silicon carbide, the refractive index is approximately 2.65.

Chapter 3 Methods

Hall bar devices can be used both as a tool for electrical characterisation of materials and as a platform for quantum metrology. In this Chapter the microfabrication methods to produce Hall bars from epitaxial graphene on silicon carbide are described. Whilst this material can be grown under conditions leading to large area monolayer graphene, the high temperature growth process can also lead to inhomogeneities of the material and surface morphology. For this reason, it can be beneficial to perform surface microscopy prior to fabrication either for the selective alignment of devices to specific surface features or as a form of quality control.

Following microscopy characterisation, Hall bar devices are selectively patterned on the SiC/G substrate by standard electron-beam lithography. Whilst this fabrication method is in some instances capable of producing high performance quantum Hall devices for metrology, it is also found to leave nanometer scale residuals of polymer resist at the graphene surface. Conventional cleaning methods have proven insufficient to fully remove these polymer residuals without also causing substantial damage to graphene, due to a low chemical selectivity between the two organic materials. This Chapter concludes with an overview of the different graphene cleaning methods explored and developed in the Thesis.

3.1 Fast Screening of SiC/G Material

For epitaxial graphene, the surface of silicon carbide reconstructs uncontrollably during high-temperature annealing, leading to the appearance of stepped terraces and nucleation of multilayer graphene domains [126,127]. The electronic properties of graphene devices can be strongly affected by these growth imperfections. Fast, non-invasive quality control is highly desirable for the material, however the identification of nanoscopic SiC/G features has been a significant challenge for microscopy.

In the work presented in this Thesis, epitaxial graphene material was produced by the group of Rositsa Yakimova at Linköping University and Graphensic AB. Monolayer graphene was grown on the silicon-terminated face of 4H-SiC (0001) substrates, by inductive heating to 2000 °C in 1 atmosphere of argon gas pressure. The initial silicon carbide (SiC) material is acquired from Cree Inc. The role of the argon atmosphere is to slow the rate of sublimation of Si atoms, as compared to growth in UHV [76]. Another method used to control the growth mechanism was to confine the SiC in a graphite crucible [149]. The sublimation process was carefully controlled to produce a predominantly monolayer graphene coverage at the SiC surface [75,76].

Established microscopy techniques for identifying and studying graphene on other substrates are not readily transferable to the study of SiC/G devices. For example, Raman spectroscopy [150,151] of SiC/G requires careful calibration and time consuming background subtraction due to a strong signal from the SiC substrate that overlaps with the graphene spectrum [120,152,153]. Another standard microscopy technique for studying SiC/G is low energy electron microscopy (LEEM) [75,154]. Significant drawback of LEEM, however, are the possibilities of radiation induced damage as well as electron beam induced deposition of hydrocarbons present in the vacuum chamber onto the graphene surface [155–157]. A less invasive alternative is scanning probe microscopy (SPM), but this is a slow, micron scale process that is unsuitable for material characterisation at the wafer scale.

Optical microscopy allows the surprisingly simple and accurate identification of graphene domains in epitaxial graphene on silicon carbide (Figure 3.1). Whilst the presence of the SiC substrate is detrimental for contrast imaging [158], an order of magnitude contrast enhancements are possible by a simple digital filtering of the video output of a standard optical microscope and a digital camera. This allows the identification and mapping of individual graphene layers in real time. In addition, optical interference can be used to provide information on the nanoscopic details of the SiC topography. In combination, these techniques make optical microscopy ideal for rapid and non-invasive quality control of as-grown SiC/G.

For optimal uniform illumination with white light, the intensities of different graphene layers are found to occur predominantly in the mid-tones of the intensity spectrum. When the output intensity is linear, it is very challenging to identify the


Figure 3.1: Transmission optical image of 40 μm wide Hall bar, with digital gamma correction.

small (1.3 - 1.5%) contrast between graphene layers on SiC substrates with the naked eye in real-time. By applying non-linear digital filters to the CMOS sensor output, the relative intensities of these mid-tones can be substantially enhanced. One of the simplest, most effective and commonly available intensity filters is known as gamma correction. The gamma factor introduces a power-law non-linearity to the intensity output, I_{out} :

$$I_{out} \propto I_{in}^{\gamma}$$
. (38)

For our microscope setup (see Appendix A), up to an order of magnitude contrast enhancement was achieved by reducing the gamma factor from $\gamma = 1$ (linear output) down to around $\gamma = 0.2 - 0.4$. This simple filter can be applied to the video output in real time, to allow rapid non-invasive characterisation of epitaxial graphene layers, even at the wafer scale (mm) (Figure 3.1).

In addition to identifying individual graphene layers on SiC/G by optical reflection and transmission microscopy, nanoscopic features at the SiC surface can be imaged using optical interference effects (Figure 3.2). One of the most common interference imaging techniques is differential interference contrast (DIC) microscopy [159,160]. In this method, a beam of light is split into a specimen ray and a reference ray. Optical phase shifts due to differential geometric paths lead to



Figure 3.2: Observation of unit high steps in real time by DIC (left) compared with height AFM measured in the same position (right). Adapted from Paper A.

corresponding phase shifts between the reference and specimen rays [161]. The resulting interference leads to a contrast that is dependent on geometric height differences on the sample surface. The DIC method is non-quantitative since the resulting contrast depends only on the relative height differences at the surface.

A more quantitative method for interference imaging is the so-called transport of intensities method where a transmission optical microscope is defocussed by a few micrometers above and below the sample surface, leading to the observation of nanometer high steps as a bright-dark intensity doublet [162–164]. Several images are taken at different focus positions and digitally combined using the transport of intensities method to produce a quantitative 3D height image of the target. For the case of SiC/G, these optical interference methods allow fast identification of the orientation, geometry and spacing of unit-cell high steps on the reconstructed SiC surface, similar to atomic force microscopy.

In summary, optical microscopy of SiC/G can yield similar information to alternative imaging techniques, such as atomic force microscopy and scanning electron microscopy, but with the important advantages of being significantly faster and less invasive. One limit to these optical microscopy methods is the lateral resolution. For our SiC/G material, both the separation between SiC steps and the size of bilayer domain inclusions occur predominantly on the microscale, larger than the lateral resolution limit for visible light. This optical resolution limit describes the ability to distinguish two features with a separation δ , due to optical diffraction [165,166]. It is described by the Rayleigh criterion:

$$\delta \ge 0.66 \frac{\lambda}{NA} \tag{39}$$

where λ is the wavelength and NA is numerical aperture. For optical wavelengths ranging between 390 to 780 nm and typical numerical aperture of around 1.5, the best far-field lateral resolution is around 200 nm [167]. Consequently, the optical microscopy techniques described in this Chapter allow the study of SiC/G homogeneity and defects down to the micrometer (device) scale and up to the millimeter (wafer) scale. They can be used to study the formation of defects and their impact on electronic properties and device performance in a fast and non-invasive way. The techniques also contribute to the effort towards achieving reliable and reproducible wafer scale production of epitaxial graphene.

3.2 SiC/G Characterisation by Scanning Probe Microscopy

The surface of both as-grown SiC/G substrates as well as devices was thoroughly investigated by scanning probe microscopy (SPM) techniques as a compliment to optical microscopy. SPM describes a family of high precision surface sensitive microscopy techniques [168]. Since graphene and other 2D materials may themselves be considered as a surface, SPM techniques are inherently suitable for their characterization. Although it is likely that monolayer graphene was successfully produced at least 50 years ago [9], it was not until 2004 that it could be successfully identified with the use of an atomic force microscope and subsequently confirmed by carefully aligning electrical contacts and performing electron transport experiments [4,12,14,17].

In SPM, a nanoscale probe is raster scanned over the surface of a material using 3D piezo-feedback to achieve nanometer precision [169]. The technique was initially developed in 1972 for scanning near-field optical microscopy (SNOM) [170] as a tool to overcome the optical diffraction limit [165,171,172]. This method is still being used to study exotic plasmonic effects in graphene systems [173,174]. The SNOM technique was later adapted to a scanning tunneling microscope (STM) in 1981 where the probe tip is suspended above a metal surface with a feedback control to carefully stabilize an applied tunneling current between the probe tip and surface [175]. Since the tunnel current depends on the exponent of the separation distance, this technique has allowed unprecedented accuracy and precision for surface analysis at the molecular and atomic scale.

In recent years the STM technique has been extended to enable the direct visualization of single molecules and even the structure of their internal covalent bonds [176–179]. For graphene it is possible to directly image the honeycomb atomic structure as well as various defects such as atomic vacancies and grain boundaries [180–183]. The use of STM is limited to electrically conductive materials. Consequently, atomic force microscopy (AFM) was developed soon after in 1985, operating on the basis of van der Waals forces [184]. The widespread

proliferation and availability of scanning probe microscopes in research laboratories has led to their being one of the primary methods for the nanoscale characterisation and study of graphene and other 2D materials. In this Thesis, scanning probe microscopy investigations were performed using a Bruker Dimension ICON AFM.

3.2.1 Atomic Force Microscopy on SiC/G

Atomic force microscopy operates by scanning a sharp probe tip ($r_{tip} = 1-20$ nm) over a sample surface using highly accurate piezodrives to produce high resolution 3D images down to the atomic scale [184]. The probe and surface interact via van der Waals, electrostatic, magnetic and capillary forces [185]. A laser light directed on the probe cantilever reflects onto a photodetector, allowing precise measurement of the tip displacement. The resulting height resolution achievable is on the order of Ångström. Scanning probe microscopy is a relatively slow method, used for imaging micro- and nanoscale surfaces, although the main speed limit on the range of micron per second is set by the feedback electronics. Fast scanning AFMs capable of scanning 30 frames per second are commercially available but are not yet widely distributed [186].

The two most common modes of operation for AFM are tapping and contact modes [184]. In the contact mode, a probe tip is dragged over the sample surface with a feedback control on the applied force. A disadvantage of this method is the possibility of damage to the sample and tip. In tapping mode, the surface damage can be reduced. In this method, the cantilever probe is resonated in the range of around 100-300 kHz over the sample surface. As a result, the probe is only in contact with the surface for a small fraction of the oscillation period, with an adjustable resulting



Figure 3.3: Height AFM image of a reconstructed epitaxial graphene surface with unit cell high steps and ~micron wide terraces. Adapted from Paper D.



Figure 3.4: Height and phase AFM image of a clean 80 μ m × 80 μ m SiC/G surface. The phase image shows a bimodal distribution of monolayer graphene containing micron scale bilayer graphene patches (dark contrast). Bilayer graphene grows along reconstructed SiC steps. The corner squares are AFM alignment markers deposited through a shadow mask in a clean, resist-free, fabrication step.

force applied to the surface [187]. Consequently, tapping mode is the method of choice for delicate samples, such as graphene, where less invasive methods are preferable. Height AFM in tapping mode is a powerful technique for quantitatively mapping surfaces on the nanoscale and has been used in this Thesis to map the reconstructed surface morphology of epitaxial graphene on silicon carbide [18,77]. The presence of this reconstructed surface makes it very difficult to measure graphene thickness by their height. In fact, extra layer growth usually results in a local depression in the substrate, since more silicon atoms have locally sublimated away to liberate the required carbon needed (Figure 3.4).

The phase shift resulting from surface-tip interactions in tapping mode AFM can be exploited to produce high-resolution phase contrast images of a material surface [187,188]. This phase shift occurs due to the delay between the driving oscillation and the output signal and is a measure of the energy dissipation from the probe on the surface. Dissipation can have several different origins such as adhesion and viscoelastic forces [185]. Since the contributing forces are not trivial to distinguish and depend on a number of factors such as the contact area, the method is not quantitative. In the case of SiC/G, phase contrast AFM allows the identification of

monolayer and bilayer graphene domains with high resolution, leading to a bi-modal distribution of their respective phase shifts (Figure 3.4) [189]. A limitation to this technique is the sensitivity to residual dirt on the material surface and as such it requires a pristine clean graphene surface to produce a reliable images.

Kelvin probe microscopy (KPM) is an AFM variant that is highly sensitive to electrostatic forces and is used to map local surface potentials and work functions [190,191]. Feedback voltage applied to the probe tip, scanning above the sample surface in non-contact mode, is used to minimise the electrostatic interaction. For metallic samples this interaction is due to the difference in work functions between the tip and sample (contact potential difference) whereas for insulating material it relates to the surface charge [192]. Several factors can affect this contact potential difference such as the work function of the probe tip, the doping level of the material and the environmental measurement conditions. However, the technique can be quantitative after calibration against a test sample containing materials with well known work functions. Using this technique, the local surface potentials can be measured reliably and quantitatively for bare SiC, buffer layer, monolayer and bilayer graphene on the SiC/G surface [189,193–195].

On SiC/G, tapping height AFM typically shows unit cell high steps, with lateral spacing on the order of $0.5 - 1 \ \mu m$ (Figure 3.3). A number of complementary characterisation techniques, including (optical microscopy, phase AFM, KPM, transport measurements) are performed to demonstrate that a layer of graphene is formed covering the surface of the reconstructed material. Our observations show that although the growth of epitaxial graphene can be predominantly monolayer on SiC (0001), a significant proportion of micron scale graphene bilayer patches can also develop during growth (~ 5-15% bilayer coverage). The relation between these nanoscopic surface inhomogeneities and the resulting charge transport properties are described in greater detail in Chapters 4 and 5.

3.3 Microfabrication of SiC/G Hall Bars

Following the pre-characterisation of the SiC/G material using microscopy, Hall bar devices are fabricated on the mapped substrate by electron beam lithography. The graphene Hall bar devices discussed in this Thesis vary in dimensions ranging from $4 \mu m \times 1 \mu m$ up to 2.5 mm x 1.25 mm.

The standard fabrication procedure (Figure 3.5, Appendix) that was used to pattern graphene Hall bar devices on SiC consists of the following three steps of electron beam lithography (EBL), with a 50 keV acceleration voltage [18,22]. The first step was the production of metal anchors and EBL alignment markers (5nm Ti/ 70 nm Au) through graphene, in direct contact with the silicon carbide substrate. This was achieved by oxygen plasma ashing of lithographically defined regions, followed by metal deposition. The metal anchors improve the adhesion of the contacts layer to



Figure 3.5: This schematic illustrates the three main processing steps used for lift-off fabrication with e-beam lithography. Adapted from [22]

the substrate, making the graphene devices more resilient and preventing detachment of the contacts during electrical wire bonding.

The second step was the deposition of contact metals over the anchors, where a thin film (5 nm Ti/ 120 nm Au) was evaporated directly onto the graphene surface after development of the EBL resist. We found that, due to incomplete removal of the resist by developer on the nanometer level, some polymer resist residuals can remain on the graphene surface before contact deposition. Since this residual layer is present in between the graphene and contacts, it is thought that this may have a detrimental effect on the contact resistance for some devices.

The final patterning step was to define the graphene device edges by oxygen plasma ashing, followed by cleaning with acetone and isopropanol. After completed device fabrication, the SiC/G chips were either encapsulated with a fresh layer of polymer resist or underwent further cleaning. The thick polymer encapsulation layer protects the graphene device from unintended doping from ambient molecules and can also be used as a spacer layer for a top gate.

3.3.1 Resist-Free Metal Evaporation

An alternative fabrication process to avoid contamination of the pristine epitaxial graphene surface involves masked metal deposition of electrical contacts to graphene. This process allows a comparison of the device performance of devices fabricated with polymer-free metal-graphene interfaces to those where some polymer resist residuals are present at this interface (Figure 3.6).

The shadow mask pattern was defined by a deep anisotropic etching of a 50 μ mthick silicon wafer [196]. During metal deposition the mask was suspended in close proximity, ~75 μ m above the pristine epitaxial graphene wafer in high vacuum to reliably achieve 4 μ m metal features on the surface. This technology additionally



Figure 3.6: a) Fabrication of contacts to SiC/G Hall bars by EBL b) Contact deposition through a 50 μ m-thick silicon shadow mask enables an ultra-clean metal-graphene interface. (Not to scale.) AFM topographical images illustrate the contrast in cleanliness between graphene surfaces immediately before metal contact deposition by standard lithography or with a shadow mask, with the RMS roughness equal to 1.8 nm and 0.5 nm respectively. Adapted from Paper D.

allowed the clean deposition of both alignment markers and metal-graphene contact interfaces (Figure 3.4). The inclusion of metal alignment markers for microscopy allowed the later design and placement of Hall bar devices to study the impact of surface inhomogeneities on the transport properties.

Subsequent steps of standard EBL lithography of anchors and graphene etching were still required for the completion of device fabrication. Consequently, other complimentary methods are still required for fully polymer free graphene device fabrication. One approach is to avoid contact between the graphene and polymer with a sacrificial protection layer [197,198], however this technology has not been explored within this Thesis. In Paper D, we show that low contact resistance on the level of one ohm is possible in the quantum Hall regime for both ultra clean metal contacts by polymer free deposition and also by standard electron beam lithography with some amount of polymer residuals remaining at the metal-graphene interface.

3.3.2 Carrier Density Control by Electrostatic Gating

In contrast to graphene on SiO₂/Si, back-gating of SiC/G is technologically challenging to implement [199], since the SiC used for the production of graphene electronic devices is a wide band gap semi-insulator. An alternative route to SiC/G carrier density control is to employ a top gate. Methods for lowering the intrinsic doping of SiC/G material for quantum Hall devices have included photochemical gating [200], molecular doping [201] and corona discharge ionic gating [Paper E].



Figure 3.7: Schematic of the corona discharge effect on PMMA coated SiC/G Hall bar device. Adapted from Paper E.

In corona discharge method, the carrier density of SiC/G can be tuned over a wide range, using an antistatic gun ("Zerostat 3" from Sigma-Aldrich), without the need for a high-voltage setup (Figure 3.7). The gate is contactless, operating through a polymer protection layer (~100 nm of PMMA), and the effects are fully reversible. At room temperature and under atmospheric conditions, the corona charging effect decays with time. However, once cooled below ~200 K, the corona gating effect stabilises, and remains stable for a period of at least several weeks.

3.4 Cleaning the SiC/G Surface

Established microfabrication techniques using lithographic resists result in contamination of the graphene surface by polymer resist residuals. Resist developers and cleaning solvents such as acetone and isopropanol enable the removal of the bulk of resist, however a thin nanometer scale polymer layer typically remains on the graphene surface due to strong van der Waals attraction. In some cases this may lead to poor interfaces between graphene and deposited metal contacts, leading to poor adhesion and high contact resistance. Additionally, the remaining polymer layer may lead to uneven doping, scattering and unstable environmental sensitivity.

In general, the choice of the cleaning method should reflect the nature of the involved bonds or interactions and should be selective in removing unwanted material whilst at the same time preserving the active material or device. A low chemical selectivity between organic polymer residues and graphene poses a substantial challenge to clean the graphene effectively without the introduction of structural damage [202].

Unwanted polymer residuals can be removed from silicon by ozone, generated *in-situ* by deep ultra violet radiation or by oxygen plasma. However, when similar

techniques are applied to graphene, they often result in damage to the graphene lattice, the introduction of defects and even graphene etching [203–207]. This can have a significant detrimental effect on the electronic device properties [208]. For example, this has been shown to cause transitions between metallic to insulating behaviour and from weak to strong localisation [204]. These are unwelcome properties for high performance electronic devices, making alternative graphene cleaning methods highly desirable.

3.4.1 Micron-Scale Device Cleaning by Contact AFM

At the micron scale, individual graphene devices can be cleaned using methods such as current annealing [209] and contact mode AFM sweeping [210]. Current annealing involves passing high currents through fabricated electronic devices. This method is often used in the production of clean suspended graphene devices [84,211,212], although the method is often destructive, leading to a relatively low yield of surviving devices. Another method is to use an atomic force microscope operating in contact mode to sweep clean polymer residuals from the graphene surface (Figure 3.8) [210]. This physical cleaning technique has been found to be very effective at producing nanoscopically clean surfaces [195], [Papers A, D]. However, the technique suffers from numerous drawbacks such as being very slow and rather invasive. As such, the technique is used for micron scale devices and is not readily scalable.



Figure 3.8: Contact mode AFM cleaning of a SiC/G Hall bar device. Device edges are marked blue. Left image shows height and right image shows friction, captured simultaneously. Cleaning is progressing from bottom to top of the image. The bottom half has been cleaned by two contact sweeps whereas the top half is undergoing the first clean sweep. Dark artifacts in the friction show the stepwise cleaning motion of cleaned residuals.

3.4.2 High Temperature Annealing

Annealing graphene at high temperatures is a way of removing polymer residues from the surface at the wafer scale. The use of a H_2/Ar annealing atmosphere has been demonstrated [213], however, in the case of SiC/G, this could also lead to intercalation of the graphene buffer layer [116]. For this reason, a controlled atmosphere of argon or ultra high vacuum is desirable. One promising route for optimising this high temperature annealing method is to employ specific polymer resists that appear to be less strongly attracted to graphene than PMMA or ZEP (e.g. LOR) [214]. Nonetheless, it remains a challenge to entirely remove physisorbed polymers from the graphene surface [202].

3.4.3 Wafer scale Aqueous-Ozone Cleaning of SiC/G

Despite the potential for ozone to damage graphene devices, we show evidence in Paper C that under some circumstances ozone and graphene can be made compatible, and can surprisingly even lead to SiC/G devices with desirable electronic properties. The method used consisted of immersing SiC/G chips in a Teflon vessel that contained deionized water into which ozone, generated *ex-situ* in a molecular oxygen gas stream, was bubbled through the reaction vessel for 3 minutes prior to rinsing the devices in deionized water and vacuum-drying at 1 mbar and 60 °C [206]. The samples were then annealed in UHV at 500 °C for 60 minutes (Figure 3.9). For fabricated graphene devices, the annealing temperature is predominantly limited by the metal contacts.

We found that fabricated epitaxial graphene devices that were exposed to this treatment became substantially cleaner from resist residuals on the wafer scale (Figure 3.10). In addition, we found that the ozone and annealing process did not destroy the device properties and resulted in neutrally doped SiC/G ($\sim 10^{10}$ holes cm⁻²) with



Figure 3.9: Aqueous-ozone cleaning (left) and annealing (right) of SiC/G.

relatively high mobility (~10 000 cm² V⁻¹ s⁻¹). This combination of properties for large area graphene devices is desirable for a range of devices from gas sensing [215,216] to quantum metrology [21].

In the case of our SiC/G devices, we found that the cleaning effects of the methods described are inhomogeneous as a result of the existence of distinct material domains. The most prevalent of which were monolayer and bilayer epitaxial graphene domains and areas of bare SiC, where graphene had been selectively removed by oxygen plasma ashing. As could be expected, the amount of residual resist on the surface varied after cleaning and was not equal for the three regions. Perhaps more informatively, the relative cleaning effect for each region was not repeatable for each cleaning method.

For the high temperature annealing method, with and without aqueous ozone, polymer resist residuals were removed most effectively from regions of the bare SiC substrate, followed by bilayer graphene, with the majority of the remaining residuals distributed over monolayer graphene domains. In contrast, contact cleaning AFM removed polymer residuals very effectively from both monolayer and bilayer graphene domains, but rather ineffectively from the bare SiC substrate. This could suggest a higher binding energy of polymer residues on graphene than SiC but with a significantly lower translational barrier due to the smoothness and homogeneity of the graphene crystal. Careful study of these processes may be useful in understanding the physical nature of this bonding and could help in the development of improved processing and cleaning technologies.



Figure 3.10: Atomic force microscope images showing cleaning effect of aqueous ozone and annealing processing on the graphene surface for fabricated devices (a). A breakdown of the effect of each cleaning step is shown in panels (b-d). Adapted from Paper C.

Chapter 4 Achieving Homogeneous Low Doping in SiC/G

For quantum resistance metrology, there is a need to produce electronically homogeneous graphene devices with low charge carrier densities in order to achieve Hall quantisation at experimentally attainable magnetic fields. For instance, with a magnetic field of B = 14 T the carrier concentration should be less than 7×10^{11} electrons cm⁻². The doping of epitaxial graphene on silicon carbide, and the routes to control charge carrier density are more complex compared to exfoliated flakes. As-grown SiC/G is strongly electron doped (~10¹³ electrons cm⁻²) due to interaction with the SiC (0001) substrate [58,119–121]. This SiC-G interaction also leads to Fermi level pinning, making any electrostatic gating of SiC/G rather inefficient [28].

In this Chapter, the intrinsic and extrinsic doping of SiC/G materials are explored using magnetotransport characterisation of epitaxial graphene Hall bar devices. Moreover, careful alignment and patterning of Hall bars with respect to growth features is used to reveal their impact on the electronic transport properties of devices. By understanding and controlling the effects of environmental influence and SiC/G growth features it was possible to reduce the variation of electronic device properties from two orders of magnitude [217–219] down to $\pm 2\%$ [Paper B]. Furthermore, we have developed methods of strong charge carrier density control of SiC/G by chemical adsorbates [Paper C] and ions generated by corona discharge [Paper E]. These methods have enabled not only the development of quantum Hall resistance standards operating under more relaxed experimental conditions [21], but also the study of SiC/G device physics close to the Dirac point [Paper I].

4.1 Overview of Intrinsic and Extrinsic Doping of SiC/G

The electronic doping properties of SiC/G are commonly characterised by angle resolved photoemission spectroscopy (ARPES) or magnetotransport measurements of the Hall effect [22,58,119–121,217–219]. In ARPES, the kinetic energy and angular distribution of photo-emitted electrons is measured to reveal the electronic structure of materials. When the electronic properties of SiC/G (0001) are investigated by ARPES, the measurements routinely reveal strong electron type doping on the order of ~10¹³ electrons cm⁻² (Figure 4.1) [58,119–121]. This is in contrast with magnetotransport characterisation that regularly shows doping on the order of ~10¹² electrons cm⁻² [22]. This discrepancy has previously been attributed to differences in SiC/G material production [28], however, it may also originate from important differences in the processing and measurement conditions.

Prior to magnetotransport characterisation, graphene Hall bar devices must first be fabricated on SiC/G. This process is likely to result in some modification of the SiC/G doping characteristics due to exposure to various polymers, chemicals and solvents. In contrast, ARPES measurements do not share the requirement of device fabrication and are typically performed on pristine grown SiC/G. Furthermore, whilst ARPES requires UHV conditions, magnetotransport measurements can be performed in a variety of different atmospheric or vacuum conditions. The result is that the final SiC/G devices are likely to be chemically influenced by external dopants, to a greater extent than as-grown SiC/G characterised by ARPES.



Figure 4.1: ARPES spectra for clean graphene grown on the silicon face of SiC, measured in UHV. The Fermi energy offset is a signature of intrinsic electron doping. Adapted from [121].



Figure 4.2: SiC/G doping effect for different surface coverage of polymer and environmental dopants. Adapted from Paper C.

In fact, it is well known that graphene materials can be extremely sensitive to chemical adsorbates at their surface [216,220,221]. The adsorption of even single molecules on the surface of clean graphene surfaces can lead to a measurable change in charge carrier density for neutral devices assessed by magnetotransport [215]. Similar adsorbates are also present in ambient conditions, leading to reports of a hole-type doping effect for clean, exposed materials [222].

In practice, graphene devices can sometimes suffer from unstable doping between measurements. We have observed this effect for exposed SiC/G devices that have been subjected to basic cleaning procedures by solvent and it is largely attributable to the effect of ambient dopants [22]. For this reason SiC/G devices can be encapsulated in a layer of polymer resist [200] to improve the homogeneity and reproducibility of device doping measured to be a few $\sim 10^{12}$ electrons cm⁻² [Paper B].

of doping reproducibility, Despite the challenges magnetotransport characterisation retains some key advantages in comparison to ARPES. For ARPES, only the material properties are characterised, whereas magnetotransport provides characterisation of the full device properties, highly relevant for technological applications. Furthermore, electronic devices can be fabricated and aligned with respect to the substrate with high accuracy, allowing the electronic characterisation of individual surface features that may be below the measurement spot size in ARPES. In addition, magnetotransport allows characterisation of not only charge carrier density but also the carrier mobility. For these reasons the two characterisation tools can be considered as complementary, but not directly interchangeable.

4.2 Variability in the Electronic Properties of SiC/G

Single crystal monolayer graphene can be reliably grown epitaxially over large areas on SiC (0001) [18,105–108]. However, when the electronic properties of these materials are characterised by magnetotransport measurements, the charge carrier density and mobility have been previously reported to vary by up to ~2 orders of magnitude, even between devices fabricated on the same chip [217–219]. Prior to developing methods to decrease carrier concentration in SiC/G, we investigated the underlying causes of these electronic variations towards the achievement of wafer scale electronic homogeneity for SiC/G devices. There are several possible causes to consider for the variations of SiC/G device properties. The main defects on the device scale are known to be an uneven surface morphology [126,127] and layer inhomogeneity [136,137]. In this section we explore the consequences of these material defects on the electronic properties of micron scale devices.

4.2.1 Correlating Microscopy and Transport

When a nominal monolayer of graphene is grown on SiC, this usually contains some proportion of micron scale bilayer graphene inclusions [136,137]. Bilayer graphene nucleates and grows preferentially along the length of SiC steps on the reconstructed substrate. Consequently, these two features, steps and bilayer patches, are closely inter-related. In our studies we observe that whilst bilayer graphene nucleates only in the vicinity of SiC steps, not all steps seed the formation of bilayer graphene patches.

In order to correctly understand the significance of these growth defects on the electron transport properties, it is very important to distinguish between them. This is challenging on a practical level since it usually requires two complimentary microscopy techniques. The challenges and methods for microscopy of SiC/G were discussed in detail in Chapter 3. To reiterate the main conclusions, we can study SiC steps by height AFM and DIC optical imaging, whilst identifying layer inhomogeneities by optical absorption, phase AFM and Kelvin probe microscopy.

We combined microscopy techniques to map the SiC/G substrate prior to device fabrication. Optical and scanning probe microscopy were used to identify substrate steps and layer inhomogeneities. Electron microscopy techniques were avoided since they are fundamentally invasive and can modify the electronic properties by introducing defects and doping. In order for scanning probe microscopy to be most accurate and effective, it is advantageous to perform it on a pristine clean surface. For fabricated graphene devices, SPM is not straightforward since graphene is usually contaminated by the introduction of polymer resists during device processing. In spite of some promising demonstrations, non-invasive cleaning of the graphene surface remains challenging. Our solution was to use clean, polymer-free, metal evaporation



Figure 4.3: Optical images of 24 devices fabricated varying step orientation, layers on a Siface SiC/G wafer. Devices were designed to be purely monolayer, purely bilayer, parallel to steps, perpendicular to steps, containing a bilayer patch, containing two bilayer patches, containing trilayer patch etc. Image dimensions are $120 \ \mu m \times 100 \ \mu m$.

through a shadow mask to produce alignment markers on the pristine clean SiC/G substrate, followed by large area ($80 \ \mu m \times 80 \ \mu m$) high resolution height and phase AFM mapping. This enabled sub-micrometer alignment accuracy of the fabricated devices that were subsequently designed to study individual growth features of the SiC/G in terms of their charge transport properties (Figure 4.3).

We investigated the relationship between SiC/G morphology and electronic properties by correlating SiC/G surface microscopy with magnetotransport measurements. The method involved a combination of different technologies and techniques including clean marker deposition, microscopy analysis, design and fabrication with careful alignment followed by polymer encapsulation and finally the magnetotransport characterisation of devices. In order to test the large-scale uniformity of growth, 28 Hall bar devices were aligned and fabricated spanning the surface of a single SiC/G chip (7 x 7 mm²). All devices were patterned during the same fabrication process to investigate and compare the resulting electronic properties under controlled experimental conditions.

Magnetotransport measurements were first performed on micrometer sized Hall bars selectively fabricated on purely monolayer graphene. We found excellent uniformity of the resulting electronic properties for all monolayer graphene devices, distributed sparsely over the entire SiC/G chip. The electron carrier densities and device mobilities were found to be $n = 2.7 \times 10^{12}$ cm⁻² and $\mu = 1350$ cm² V⁻¹ s⁻¹, respectively. Standard deviations of both the density and mobility were found to be ± 2 %. This included Hall bars selectively oriented either perpendicular or parallel to



Figure 4.4: Variations in electronic properties across a SiC/G wafer depend predominantly on the coverage of bilayer graphene. Purely monolayer graphene devices display excellent uniformity (inset). Hall bar channels were fabricated perpendicular (green) and parallel (white) to SiC steps. The red outlier shows a device fabricated with monolayer Hall crosses and a bilayer Hall channel, to demonstrate the uncertainty of Hall mobility for inhomogeneous material. Adapted from Paper B.

the few nanometre high SiC substrate steps, demonstrating that unit cell high steps do not affect electronic properties.

The exceptional device uniformity displayed is in strong contrast to previous reports where device carrier densities and mobilities were found to vary over orders of magnitude [217–219]. This demonstrates that monolayer graphene can be grown with good electronic uniformity and that SiC substrate steps up to at least 2 nanometres in height do not play an important role in these electronic device properties for SiC/G grown under suitable conditions. The result is also a demonstration of good uniformity of carrier density control throughout device processing and measurements, after polymer encapsulation.

4.2.2 The Source of Variability in SiC/G: Bilayer graphene domains

After establishing the wafer scale electronic uniformity of monolayer SiC/G, we continued this material correlation study to investigate devices containing bilayer graphene patches. This alignment and fabrication process was found to be more challenging than for monolayer graphene since bilayer patches on the predominantly monolayer graphene surface were relatively small (approximately ~ 1.5 μ m × 6 μ m). These bilayer devices were fabricated on the same wafer as the monolayer devices described and also processed and characterised either at the same time or under identical conditions.



Figure 4.5: (a) Phase-contrast AFM of SiC/G surface enabling alignment (b) and micro-fabrication of bilayer graphene Hall bar devices. Bilayer domains appear as dark areas. Adapted from Paper B.

In contrast to the homogeneity between purely monolayer graphene devices, bilayer graphene was found to exhibit substantially different electronic properties. The bilayer graphene electron carrier density was significantly higher $(n \approx 8 \times 10^{12} \text{ cm}^{-2})$ and the mobility was lower $(\mu \approx 900 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1})$ than for monolayer graphene under the same experimental conditions. For the case of inhomogeneous devices, comprising of both monolayer and bilayer graphene, the electronic properties were found to vary depending on the proportion of the contained layers (Figure 4.4). The relative proportion of monolayer and bilayer graphene was geometrically estimated, based on high-resolution phase AFM images. A linear interpolation between the electronic properties of purely monolayer and purely bilayer devices was sufficient to describe the properties of devices containing a mixed geometry of the two layers to first approximation.

One can readily see that if these same devices were measured without prior knowledge of the monolayer and bilayer graphene content, the electronic properties of Hall devices would appear to be rather inhomogeneous on the wafer scale, similar to previous reports. In fact, the initial SiC/G material studied in this investigation was relatively uniform. In other cases, material grown with a greater variation of layer thickness and for higher steps (10 - 30 nm) are likely to lead to even greater variations in the electronic properties. This highlights the importance of eliminating layer inhomogeneities in SiC/G growth in order to achieve homogeneity of electronic material properties for wafer-scale applications. Until this goal is achieved, it is important to be aware of the existence of surface defects and their geometry for the accurate and informative characterisation of SiC/G materials by magnetotransport measurements.

4.2.3 Confirming the Identification of Monolayer and Bilayer Graphene

The corona discharge method was used to gate graphene layers towards neutrality for the study of SiC/G quantum Hall effect within the limits of available magnetic fields (B = 14 T). The observation of quantum Hall effect with the expected resistance quantisation plateaus [14,17,71] confirmed the identification of monolayer and bilayer graphene domains originally identified by optical and scanning probe microscopy (Figure 4.6).

The observation of bilayer quantum Hall effect on SiC/G is a significant challenge. Firstly, due to the self-limiting growth process of graphene on SiC (0001), bilayer growth occurs predominantly in the form of micron scale patches along the length of reconstructed SiC substrate steps. These have not been trivial to identify by microscopy in a non-invasive way (Chapter 3). The production of precise alignment markers required for alignment of sparsely occurring small scale features usually leads to the contamination of the graphene surface by polymer residuals, further hampering microscopy.

Once identified and patterned, we found bilayer SiC/G to have strong electron doping ($n \approx 8 \times 10^{12}$ cm⁻²). At this high doping the previously established photochemical gating method [200] to reduce the charge carrier density was insufficient for the observation of quantum Hall behaviour. Corona gating of such a bilayer Hall bar device allowed the observation of partial but imperfect resistance quantisation at T = 2 K and at magnetic fields up to B = 9 T. This may arise from the structural inhomogeneity of bilayer the bilayer device, hinted at by high resolution phase AFM [53,223] and the opening of a transport gap in bilayer graphene under high perpendicular electric fields [45,58,60].



Figure 4.6: Quantum Hall effect measured for monolayer and bilayer SiC/G Hall bars, identified by phase AFM imaging. Bilayer devices were measured at two measured for two different charge carrier densities, gated by corona discharge. Adapted from Paper B.

4.3 SiC/G Electronic Properties Near Charge Neutrality

Having identified bilayer graphene as source of electronic variability, we explored the properties of SiC/G devices in the low doping regime. At low doping, the Fermi energy of graphene naturally occurs at the charge neutrality point between electrons and holes. Close to this neutrality point, charge carriers can be described as relativistic Dirac fermions, resulting in exotic physical behaviour of interest both fundamentally and for the development of new graphene based technologies [5,13,33,34]. Whilst in principle intrinsic graphene can be charge neutral, it has not proved possible to reach perfect neutrality point of graphene, any inhomogeneity of the doping profile will lead to the formation of so-called electron-hole puddles [225–229]. The transport properties of SiC/G devices are explored by corona discharge gating [Paper E] and via aqueous ozone and annealing [Paper C], introduced in Chapter 3.

4.3.1 Low Charge Density via Aqueous Ozone and Annealing

In addition to electrostatic gating, a complementary route towards low-doped SiC/G devices is via aqueous ozone and annealing processing [Paper C]. The role of surface polymer resist residuals and atmospheric adsorbates on the electronic properties of monolayer SiC/G devices were investigated by surface cleaning. Fabricated devices were thoroughly cleaned of polymer resist residuals by aqueous ozone processing and high temperature annealing, enabling surface access to atmospheric dopants. SiC/G devices exposed to this processing procedure subsequently displayed extremely low effective hole-type carrier densities from magnetotransport measurements, on the order of ~10¹⁰ holes cm⁻², close to the charge neutrality point. This is in stark contrast to high intrinsic electron type doping on the order of ~10¹³ electrons cm⁻² for as-grown samples measured by ARPES [58,119–121].

In this study, in contrast to other comparable reports employing ozone processing and wet chemical methods [203–207], the electronic integrity and mobility of the graphene devices were preserved. This was revealed by a high SiC/G Hall mobility of over 10 000 cm² V⁻¹ s⁻¹ (Figure 4.7) Additionally it was confirmed that the graphene device was still dominated by monolayer graphene through the observation of half integer quantum Hall effect with plateaus observed at $R_{xy} = \pm h/(2e^2)$, ruling out intercalation of the buffer layer during the chemical processing [116]. We concluded that the p-type doping effect observed in these samples after processing was caused by the presence of ambient dopants at the surface of the graphene device, enabled by the removal of polymer resist. This chemical method led to charge neutral SiC/G, with very low charge density disorder, without



Figure 4.7: (a) Monolayer graphene quantum Hall effect, observed at magnetic fields below 2 T, reveals extremely low p-type doping and high mobility after processing. (b) Temperature dependent Hall mobility and p-type carrier density of the processed graphene device. Lines are a guide to the eye. Adapted from Paper C.

the requirement for active electrostatic gating and potential scalability to wafer dimensions.

4.3.2 Neutrality and Charge Disorder in Graphene Devices

Experimentally it has not been possible to reach perfect charge neutrality in any graphene system. When the Fermi energy of graphene approaches the charge neutrality point then the properties become dominated by disorder [228, Paper I]. Local sample variations in graphene doping or strain lead inevitably to non-uniform charge distributions for real devices of finite size [36,229]. At vanishingly low charge carrier densities, close to charge neutrality, this leads to the formation of electron-hole puddles [193,226,231–233]. The origins and level of this charge disorder for neutral graphene on SiC are discussed in Papers C, I.

Close to neutrality in graphene, both electrons and holes may contribute to charge transport. In this regime, calculation of the Hall coefficient becomes

$$R_{H} = -\frac{1}{e} \frac{n_{e} \mu_{e}^{2} - n_{h} \mu_{h}^{2}}{(n_{e} \mu_{e} - n_{h} \mu_{h})^{2}},$$
(40)

where $n_e(n_h)$ and $\mu_e(\mu_e)$ are the electron (hole) density and mobility respectively. The Hall resistance at low charge density leads to an estimation of the effective carrier density as follows:

$$n_{eff} = \frac{(n_e \mu_e - n_h \mu_h)^2}{n_e \mu_e^2 - n_h \mu_h^2}.$$
 (41)

The experimentally relevant case of disordered graphene near charge neutrality has been theoretically modeled [234]. In this model the charge inhomogeneity can be quantified by the standard deviation of the energy fluctuations of electron-hole puddles. It is assumed that the potential landscape follows a Gaussian distribution, where the root-mean-square of potential variations around its average value can be described by a disorder parameter, *s*. For graphene, a smaller disorder parameter represents smaller energy fluctuations of this potential landscape, leading to shallower electron-hole puddles and a more uniform charge homogeneity. It is this potential disorder that experimentally sets the limit for the minimum measurable carrier density for a graphene device, according to:

$$n_0 = D \frac{s^2}{4},$$
 (42)

where D is the graphene density of states:

$$D = \frac{g_s g_v}{2\pi (\hbar v_f)^2}.$$
(43)

The disorder parameter can be experimentally extracted from the temperature dependence of the charge carrier density [234] by fitting to the following equation:

$$n_e(T) = n_0 \times \left[1 + \frac{\pi^2}{3} \left(\frac{k_B T}{s} \right)^2 \right].$$
 (44)



Figure 4.8: Temperature dependence of effective charge carrier density extracted from the Hall effect. Fit to theory (dashed line) suggested in [234] allows a quantitative estimation of the disorder parameter, *s*. For this aqueous ozone and annealing processed sample, $s = 15\pm1$ meV.

Assessment of the disorder parameter allows quantitative comparison between the electronic homogeneity of different graphene materials and devices. The extraction of this charge disorder parameter enables the assessment and comparison of the low-density charge disorder for different graphene devices. This can include differences originating from material properties, processing methodologies and gating techniques.

In Papers C and I, the transport properties of graphene devices were studied close to the charge neutrality point by corona discharge gating and by aqueous ozone processing and annealing. The low-density charge disorder was extracted from the temperature dependence of charge carrier density (Figure 4.8). It was demonstrated that epitaxial graphene devices on SiC show a favourably low charge disorder (~10 - 15 meV), surpassing exfoliated graphene on SiO₂ (~50 meV) and being comparable to high quality boron-nitride encapsulated graphene flakes (~5 meV).

In further experiments, we have investigated the low-density mobility of SiC/G close to charge neutrality. Four nominally monolayer SiC/G devices were individually gated by liquid ionic gating [235]. At room temperature, a voltage can be applied to sweep the gate, however as the temperature is reduced, the ionic solution freezes leading to a stable doping effect at helium temperatures. Preliminary results show the charge mobility to be strongly non-linear as a function of charge carrier density, increasing sharply close to the charge neutrality point, similar to other graphene systems [14].



Figure 4.9: Hall mobility of SiC/G bar devices gated to low charge carrier densities, characterised at 2 K. Each data point represents a different gating and cool-down cycle for four measured devices on a single chip. The lower limit of measurable carrier density of the devices was set by the charge carrier disorder prevented the measurement of carrier densities below 2×10^{11} cm⁻² (shaded region). The dashed line is a polynomial fit.

Chapter 5 Understanding Quantum Hall Irreproducibility

Hall bar devices patterned from epitaxial graphene on SiC can show very precisely quantised resistance in the quantum Hall effect, suitable for metrology. However, the device requirements for metrologically precise measurements are stringent, while the technology of SiC/G material and devices are still at an early stage of development. For this reason, the reproducible production of such devices remains a challenge. The issues surrounding SiC/G material inhomogeneities and doping control were explored in Chapter 4.

In this Chapter these investigations are extended to understand the origins of device irreproducibility in the quantum Hall regime. The role of surface morphology and graphene layer inhomogeneity are examined, followed by an investigation of contact resistance variations for quantum Hall devices. Understanding these two major sources of irreproducibility are an important step towards the production of reproducible, metrologically precise devices for wafer scale quantum Hall arrays [30] and for the widespread distribution of these primary resistance standards beyond national metrological institutions.

Quantum Hall Inhomogeneity due to SiC/G Steps and Patches

The quantum Hall effect is signified by a quantisation of the transverse resistance accompanied by a vanishing of the longitudinal resistance for a Hall bar device (see Chapter 2 for details). In practice, such perfect quantisation is not always observed. For some devices, either the longitudinal resistance of the device remains finite in the available magnetic field or the transverse resistance does not tend to the precisely quantised value. Such devices are unsuitable for quantum resistance metrology, where precise quantisation is an essential pre-requisite. In the simplest case, this incomplete quantisation can be the result of excessively high charge carrier density for the experimentally available magnetic field (see Chapter 4). Alternatively this can also originate from the electronic properties of the initial material or from device imperfections related to fabrication, contacting or gating of the material.

For epitaxial graphene quantum Hall devices, the problem of finite residual longitudinal resistance has been observed by several independent groups. The two main material related candidates for these observations are the presence of local graphene layer inhomogeneity [53] and the existence of SiC surface steps that may in some cases lead to discontinuities or strain of the graphene material [236]. In Paper A, these hypotheses were investigated using the microscopy and correlation methods previously discussed. Monolayer graphene Hall bars were deliberately patterned to



Figure 5.1: Schematic diagram showing four terminal longitudinal resistance measurements under quantum Hall conditions. The monolayer graphene device is designed perpendicular to terrace steps with a single bilayer patch interrupting one of the two Hall channels.



Figure 5.2: Optical microscopy images and corresponding quantum Hall measurements for a purely monolayer graphene Hall bar (a) and a monolayer Hall bar containing a bilayer patch (b). Both devices are oriented with their channels perpendicular to unit cell high SiC steps. [Paper A]

contain bilayer graphene domains between two pairs of voltage probes in order to distinguish between the effects of SiC steps and bilayer graphene patches (Figure 5.1).

Devices were gated to low charge carrier densities ($\sim 10^{11}$ electron cm⁻²), cooled to liquid helium temperatures (4 K) and characterised by magnetotransport in magnetic fields up to 14 T. Under these conditions, inhomogeneous quantum Hall behaviour was observed in the devices. For the purely monolayer regions of the devices, the longitudinal resistance reduced to $R_{xx} = 0$. This behaviour was observed even in cases where the Hall bar device crossed many SiC steps of unit cell heights ($\sim 1-2$ nm). However, for the device regions where bilayer graphene patches connected the opposing edges of the device, it was found that $R_{xx} \neq 0$, under the same measurement conditions (Figure 5.2).

Moreover, the transverse resistivities of the devices were found to tend to the characteristic quantised resistance values for monolayer graphene. The remaining R_{xx} within regions of the devices (~k Ω) was attributed to a metallic short between the device edges, caused by the presence of the bilayer graphene patch inhomogeneity.

As was demonstrated in Chapter 4, monolayer and bilayer graphene have very different quantisation conditions due to both fundamentally different quantisation filling factors and in terms of their different charge carrier densities for SiC/G devices. The stark difference in device performance, even within a single Hall bar, demonstrates the importance of achieving homogeneous monolayer graphene material growth and the need to fabricate devices that are not vulnerable to the specific imperfections that may occur within any given material for observation of the quantum Hall effect.

5.1 Low Contact Resistance for Quantum Hall Metrology

Even in the case that the longitudinal resistance of a device reduces to zero, it still may not be suitable for quantum metrology due to restrictively high contact resistances. In the quantum Hall regime, high contacts resistances can lead to the thermal excitation of electrons to higher Landau levels, reducing the accuracy of the transverse resistance quantisation. The minimisation of device contact resistances has previously been demonstrated to improve the measurement accuracy in GaAs quantum Hall resistors, with a useful benchmark being that contacts below 100 Ω can lead to an accuracy of up to one part per billion [237].



Figure 5.3: Left: SiC/G wafer containing 28 Hall bar devices. Right: Histogram of measured contact resistances by three-terminal measurements in the quantum Hall regime. Adapted from Paper D.



Figure 5.4: Measured contact resistance variation for 8 micrometer wide SiC/G Hall bar devices, fabricated with ultra-clean metal-graphene interferences. Contact resistances were often very low, suitable for metrology (blue). However, some contacts exhibit disruptively high contact resistance (red).

High contact resistances, on the order of $\sim k\Omega$ are arguably one of the main reasons that accurate resistance measurements were not achievable on initial measurements of exfoliated graphene devices [27]. For epitaxial graphene devices the fabricated by standard e-beam lithography with Ti/Au contacts, the quantum Hall contact resistances have in some case been reported to be below 10 Ω [18]. However a serious reproducibility issue for the fabrication of these low resistance contacts presents a major challenge. In Paper D the issue with irreproducible contact resistance in the quantum Hall regime was investigated for SiC/G Hall bar devices (Figure 5.3).

The established method of three-terminal quantum Hall contact resistance measurement [238] was used to assess over 100 Ti/Au contacts. Each device was photochemically gated to low doping [200], measured at liquid helium temperature of 2 K and at high magnetic field up to 9 T. Whilst the majority of contacts showed low resistances (< 100 Ω), suitable for metrology with the lowest achieved being 0.6 Ω , a significant proportion also displayed prohibitively high resistance (> 1 k Ω). This level of reproducibility of low contact resistances has allowed the production of small quantities of highly precise quantum Hall devices. However, extensive characterisation and quality control assessments were required between growth, fabrication and application for the production of each useful device. For these reasons, the realisation of so-called quantum Hall arrays of 100-1000 series and parallel quantum Hall bar devices remains a substantial technological challenge [30]. In order to improve the reproducibility and performance of quantum Hall devices on SiC/G, it is essential to first understand the underlying causes of this irreproducibility and to eliminate them. Several causes of the spread in contact resistances were considered. In Chapter 3 it was shown that standard electron beam lithography fabrication leaves unremoved polymer resist residuals at the contact interfaces. The role of such residuals, and the likely imperfect graphene-metal contact interfaces that result were investigated by fabricating, measuring and comparing ultra-clean graphene-metal contacts with those fabricated by standard lift-off. The spread of measured contact resistance values persisted even in the case of ultra-clean interfaces (Figure 5.4). Furthermore, the distribution of high and low resistance contacts displayed an unusual geometric dependence, with a wide spread of values observed even within single micron scale devices. Following from these considerations leads logically into a re-examination of the role of material inhomogeneity on the contact resistance irreproducibility.

5.1.1 Understanding SiC/G Contact Resistance Irreproducibility

In addition to the graphene-metal interface, the 'legs' of the graphene Hall bar are also included in standard three-terminal resistance measurements. In the quantum Hall regime, this leg resistance reduces to zero and does not contribute to the measured contact resistance. However, in the presence of local material or device inhomogeneities, such as bilayer graphene interruptions, this assumption may no longer be valid. This can be the case even when the measured longitudinal resistance within the device reduces to zero and the transverse resistance is quantised.

In order to investigate the role of bilayer graphene imperfections as the source of high resistance contacts in the quantum Hall regime, we performed careful analysis of the characterised devices by optical microscopy and high resolution Kelvin probe microscopy [189,194]. The results showed that in the vicinity of high measured contact resistances, bilayer graphene patches were found to connect the edges of the Hall bar legs (Figure 5.5). In contrast, measured low resistance contacts were found to contain continuous percolation paths of monolayer graphene for edge mode current flow throughout the contact legs, even in the presence of substantial bilayer graphene patch inclusions (> 15%). Elimination of these bilayer graphene discontinuities should allow for more reproducible, high precision quantum Hall effect for SiC/G devices. In the meantime, optical microscopy can be used for rapid quality control and device alignment and alternative Hall bar geometries can be explored that may offer greater tolerance to the specific geometry of the material defects (Figure 5.6).



Figure 5.5: Surface potential image of sections of a graphene Hall bar obtained by Kelvin probe force microscopy (1LG graphene bright color, 2LG dark contrast). The left leg contains 2LG interruptions, correlated with higher measured contact resistance (5.1 k Ω) The lower schematic illustrates the resistance contributions in an epitaxial graphene Hall device as measured in the three-terminal geometry. The presence of bilayer graphene patches results in a geometrically dependant resistance additionally to the monolayer graphene component. Adapted from Paper D.



Figure 5.6: Rectangular Hall bar design fabricated on a pre-screened SiC/G material with few bilayer graphene inclusions. The resulting quantum Hall contact resistances were all measured below 10 Ω . Adapted from Paper D.

5.1.2 Increasing Device Sizes for Metrology

One route to reducing the detrimental impact of micron scale device inhomogeneities in the quantum Hall regime is to produce devices with sufficiently large size. This can also lead to the varied benefits of less demanding fabrication, lower device contact resistances and higher quantum Hall breakdown currents. In fact, for these reasons, large Hall devices (several millimeters) are already in use for GaAs resistance standards [239]. Whilst larger Hall bar devices are straightforward to fabricate, the challenge stems from the ability to produce large areas of electronically homogeneous and continuous material, with low charge carrier density suitable for quantum Hall measurements in experimentally attainable magnetic fields.

These requirements have proven challenging to achieve due to the early stage of technological development for SiC/G, leading to typical device geometries on the tens of micron scale, vulnerable to the influence of bilayer patch inhomogeneities. In Paper E it was demonstrated that quantisation is in fact possible on this scale for SiC/G with rectangular 2.5 mm × 1.25 mm device geometries (Figure 5.7). This acts as a further demonstration of the high electronic uniformity and homogeneous low electron doping achievable for SiC/G that allow Hall quantisation at magnetic fields below 5 T at liquid helium temperature (4 K).



Figure 5.7: Large scale monolayer graphene device homogeneity demonstrated by quantum Hall effect measurements on a 2.5 mm \times 1.25 mm Hall bar. Adapted from Paper E.

Chapter 6 Summary

Epitaxial graphene on silicon carbide has found an important niche in quantum resistance metrology. However, there is a need for quality control of this material due to the uncontrollable surface reconstruction of SiC during high-temperature annealing, leading to the appearance of stepped terraces and the nucleation of multilayer graphene domains. The impact of these features on electron transport and quantum Hall devices has previously not been well understood. Furthermore, the quantum Hall effect is not readily observable in 'as-grown' SiC/G (0001) materials due to the restrictively high intrinsic doping from the substrate. The effect of Fermi level pinning from large charge reservoirs in the substrate further reduces the effectiveness of conventional electrostatic top gates.

We developed two complimentary routes towards charge neutrality in SiC/G (0001), allowing the study of charge transport properties in the low charge density limit. These techniques also enable measurements of the quantum Hall effect at lower and more easily attainable magnetic fields, useful for metrology (~2-5 T). The disparate methods developed to reduce the intrinsic SiC/G were strong electrostatic gating by corona discharge and aqueous-ozone and annealing cleaning, leading to surface access of ambient acceptors. For both methods the high charge carrier mobility and excellent electronic homogeneity of the material were preserved.

We also found that single and multilayer graphene domains of epitaxial graphene on silicon carbide can be accurately identified by inspection with an optical microscope. Additionally, the nanoscopic details of the reconstructed SiC surface can be studied independently by utilising optical interference, making this an ideal method for rapid and non-invasive quality control. By correlating these nanoscopic growth features with electron transport, we were able to reveal the wafer scale homogeneity of monolayer graphene on SiC. Unit-cell high SiC substrate steps are found not to have an impact on these transport properties, even for devices spanning many

terraces. In contrast, the device properties are strongly influenced by the inclusion of bilayer graphene patches, leading to a substantial increase and variability of electron doping.

Whilst the unique electronic properties of SiC/G allow exceptional measurement precision in quantum resistance metrology, there remains a significant challenge in the reproducibility of these high performance devices. We demonstrated that the irreproducibility of SiC/G quantum Hall devices can originate from the existence of bilayer graphene imperfections. This can manifest either as incomplete Hall quantisation or restrictively high contact resistances in the quantum Hall regime. Each of these factors can limit the measurement precision for quantum resistance metrology.

Taken together, our findings highlight the importance of achieving electronically homogeneous monolayer graphene over the full surface of SiC wafers by focussing on the elimination of bilayer graphene material imperfections. Additionally, we suggest simple but effective methods for improving the reproducibility of SiC/G device properties by non-invasive optical quality control followed by suitable design and alignment of graphene devices. We believe our results will help the advancement of epitaxial graphene research and technology on the way towards large-scale device integration for applications in quantum resistance metrology and beyond.

Appendix

A1 Device Fabrication Recipe

Standard fabrication of graphene Hall bars by electron beam lithography consisted of the following three steps:

1) Deposition of Substrate Anchors

- Spin-coat 350 nm of copolymer resist, diluted 10% in ethyl lactate (MicroChem Corp.) onto the pristine SiC/G chip, followed by baking on a hotplate for 5 min at 160° C.
- Repeat for 300 nm ZEP520A (Nippon Zeon Co., Ltd).
- EBL exposure. Acc. Voltage = 50 KeV, i = 10 nA, $Dose = 250 \ \mu\text{C/cm}^{-2}$ (JEOL JBX-5DII).
- Develop ZEP520A (top layer) in o-Xylene for 60 seconds, rinse in Isopropanol (IPA), and blow dry with N₂.
- Repeat for bottom layer in IPA/H₂O (93%: 7%) for 1 minute 30 seconds (deionized water).
- Remove graphene with oxygen plasma for 1 min; 50 W of RF power, 250 mbar and 10 sccm of O2 Plasma Therm BatchTop PE/RIE m/95.
- Evaporate titanium, 5 nm, with rate Å/s followed by gold, 70 150 nm, with rate 2 Å/s (Lesker PVD225).
- • Lift-off in acetone, rinse in isopropanol and blow-dry with N_2 .

2) Deposition of Ohmic Contacts

• Repeat all fabrication process described above with the exception of the oxygen plasma step (*Important*: do not remove graphene under contacts).

3) Defining Graphene Edges

- Spin-coat 100 nm of copolymer resist, diluted 10% in ethyl lactate, then bake on a hotplate for 5 min at 160° C.
- Repeat for 300 nm ZEP520A.
- EBL exposure. Acc. Voltage = 50 KeV, i = 1-10 nA, $Dose = 250 \mu C/cm^{-2}$.
- Develop ZEP520A (top layer) in o-Xylene for 60 seconds, rinse in Isopropanol (IPA), and blow dry with N_2 .
- Repeat for bottom layer in IPA/H₂O (93%: 7%) for 1 minute 30 seconds.
- • Remove graphene with oxygen plasma for 1 min; 50 W of RF power, 250 mbar and 10 sccm of O2 Plasma Therm BatchTop PE/RIE m/95.
- • Lift-off in acetone, rinse in isopropanol and blow-dry with N_2 .

A2 Magnetotransport Measurement Systems

Magnetotransport measurements were performed in an Oxford Instruments Maglab cryostat. Superconducting magnets allowed fields up to $B = \pm 9$ T and the variable temperature insert (VTI) was controllable between T = 2 - 360 K, by helium flow and resistive heaters. The atmosphere within the VTI was helium gas or vacuum pumped. Alternatively, higher magnetic fields, up to $B = \pm 14$ T, were accessed in a Quantum Design Physical Property Measurement System (PPMS), with a temperature range of T = 2 - 400 K.

A3 Optical Microscopy Setup

Optical images presented in this Thesis were obtained with an Olympus MX50 microscope, equipped with infinity corrected objectives (100x/0.90), (50x/0.80 20x/0.46), (10x/0.30), (5x/0.15) as wells as a digital camera (Infinity-1, CMOS sensor, 2.0 Megapixel). For phase imaging (Nomarski Differential Interference Contrast) we used a polarizing filter (U-POTP), a tunable half wave plate (U-DIC) and a filter to eyepiece/camera (U-AN), all from Olympus.

Olympus Infinity 1 Camera: U-TV0.5XC-2 Output: Infinity 1-2CB Lamp: MX-LSH

Optics: MPlan Apo 100x/0,90 BD ∞/0 UMPlan FI 50x/0,80 BD ∞/0 UMPlan FI 20x/0,46 BD ∞/0

UMPlan FI 10x/0,30 BD ∞/-UMPlan FI 5x/0,15 BD ∞/-

Differential Interference Contrast: Polarizing Filter 1: U-POTP Tunable Half-wave Plate: U-DICR Polarizing Filter 2: U-AN
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Paper Contributions

The contribution by the author of this Thesis, Tom Yager, to these papers is as follows.

Appended Papers

A: TY designed, fabricated and measured the devices. TY and SM discovered the optical analysis method. TY developed the method. TY and SL co-wrote the manuscript.

B: TY designed, fabricated and measured the devices. TY analysed the data. TY and SL co-wrote the manuscript.

C: TY measured the devices, analysed the data and co-wrote the manuscript. MW developed applied the ozone process.

D: TY fabricated and measured the devices, analysed the data and co-wrote the manuscript.

Other Contributions

E: TY designed and fabricated devices. SL, AL and TY developed the method.

- F: TY fabricated the devices.
- G: TY designed, fabricated and measured devices.
- H: TY fabricated the devices.
- I: TY measured devices and contributed to the analysis.

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