

Development and Electronic Characterization of Graphene-Based Hall Effect Devices

by

Camille Lacroix

A thesis
presented to the University of Waterloo
in fulfillment of the
thesis requirement for the degree of
Master of Science
in
Chemistry - Quantum Information

Waterloo, Ontario, Canada, 2024

© Camille Lacroix 2024

Author's Declaration

I hereby declare that I am the sole author of this thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

I understand that my thesis may be made electronically available to the public.

Abstract

Graphene is a two-dimensional carbon material with a unique honeycomb lattice structure and exceptional electronic properties. Its band structure confines carriers to a single plane, allowing them to act like relativistic massless particles at low carrier densities. This has made graphene a focal point in condensed matter physics, particularly following the groundbreaking discovery of the first topological state using a graphene lattice. Research into graphene's potential as a platform for quantum topological computing has surged. In addition to its distinct band interactions, graphene is also being studied as a potential standard for electrical resistance. However, progress in its isolation since its initial synthesis in 2004 has been limited.

This thesis focuses on the synthesis of single-layer graphene (SLG) through low-pressure chemical vapor deposition (LPCVD) on copper films at temperatures above 1000°C . The graphene films are transferred using a wet transfer technique and characterized with atomic force microscopy (AFM) and Raman spectroscopy. Hall devices for electrical transport studies are patterned using maskless alignment photolithography, with palladium as ohmic contacts. Electronic transport measurements are conducted at cryogenic temperatures up to a magnetic field of 5T using 4-terminal measurement techniques.

Moreover, this work explores electronic transport in twisted bilayer graphene (TBG) - tungsten diselenide WSe_2 Hall devices. This structure facilitates the study of strongly correlated electronic states enhanced by spin-orbit coupling induced by WSe_2 . Preliminary experiments to detect unconventional Hall states in similar devices are carried out at millikelvin temperatures and in magnetic fields up to 18 Teslas.

Acknowledgements

I want to express my sincere gratitude to my supervisor, Prof. Jonathan Baugh. You gave me a unique opportunity to flourish in a field that fueled my daily curiosity. Because of you, I realized a dream that I never thought would become possible. Thank you for your support and your time throughout my degree. I sincerely thank Prof. Chandni Usha, our collaborator from the Indian Institute of Science, with whom I had the immense honor to collaborate. With only a few exchanges, every time was enriching; thank you. I want to thank my committee members, Prof. Derek Schipper and Prof. Shirley Tang, for their time and feedback, which complemented this chemistry-physics project. I truly value your expertise in the academic field.

I'm also very grateful to have worked in a cleanroom environment with a staff devoted to their work. Special thanks to Sandra Gibson, Lino Eugene, Greg Holloway, John Nugent, and Taso Alkiviades, who have worked on this project. As part of the staff, I'm grateful to have met Roberto Romero, Alex Mitrovich, and Christine. With you, the environment at the institute is fantastic.

In addition to my supervisor, Dr. François Sfigakis deserves a word of thanks. Your patience with people is exemplary, and I always appreciate working with you. You truly are a gem as a person. Thank you for all the time you spent teaching me and complimenting my understanding.

Finally, I thank the present and previous lab members. It was an absolute pleasure sharing my coursework and research time with you. Your company was always immensely appreciated. I learned so much because of these interactions, professionally and personally.

Dedication

I want to express my gratitude to all the friends I've made along the way, especially those who continue to stand by my side. I also want to thank my parents and family for their unwavering support. Even though only a few of you may read this, please know that your influence has been significant in completing my degree. Your existence has given me the strength to see this through.

Table of Contents

List of Figures	xiii
List of Tables	xvii
List of Abbreviations	xix
1 Introduction	1
1.1 Background	1
1.1.1 Single layer graphene crystalline structure	2
1.1.2 Electronic band structure of Single and Bernal stacking and twisted Bi layer graphene	4
1.1.3 First topological insulator and Chern numbers	13
1.1.4 Quantum hall effect in Single and Bi layer graphene	17
1.2 Motivation	23
1.2.1 Graphene-based Resistance Standard	23
1.2.2 Topological Computing and Chern Insulators	26
2 Chemical Vapor Deposition Synthesis of Graphene	29
2.1 Single-Layer Graphene Synthesis	29
2.2 Material Characterization	34
2.3 Discussion	45
3 Device Fabrication	49
3.1 Hall Bar Pattern	49
3.2 Fabrication Process	52
4 Magnetotransport Measurement of CVD-grown Graphene	55
4.1 Transport Characterization	56
4.2 Discussion	60

5 Twisted Bilayer Graphene-WSe₂	63
5.1 Transport Characterization	65
5.2 Discussion	75
6 Conclusion	77
Letters of Copyright Permission	79
References	89
Appendix A Data Reprocessing	99
Appendix B Optical Microscope Pictures	105
Appendix C Nanofabrication	111

List of Figures

1.1	Graphene's real and reciprocal hexagonal structure.	3
1.2	The band structure of single-layer graphene.	6
1.3	Bloch sphere showing graphene's symmetry.	8
1.4	Crystalline and electronic band structures of Bilayer Graphene.	10
1.5	Berry phase of SLG, BLG, and a conventional 2DEG.	11
1.6	Crystalline structure and electronic band structure of TBG.	12
1.7	Haldane toy's model with the local Berry phase at K and K' valley	15
1.8	Berry curvature of trivial and topological insulator with their respective C	16
1.9	Band inversion	17
1.10	Classical and quantum Hall effect	18
1.11	QHE signature of SLG	21
1.12	Landau quantization	21
1.13	Comparison of BLG and SLG's Hall signature	22
1.14	Quantum Hall Trio	22
1.15	Comparison of Hall quantization in graphene and GaAs/AlGaAs	25
2.1	CVD-graphene synthesis process	31
2.2	Reference growth recipe	31
2.3	High-temperature growth recipe	33
2.4	Dominant Raman active SLG's phonon modes	35
2.5	SLG and BLG double phonon scattering process	35
2.6	SLG Raman spectra	37
2.7	CVDREF Raman mapping	38
2.8	CVDHT Raman mapping	39
2.9	CVDCV Raman mapping	40
2.10	CVDHT AFM images and height profile	42
2.11	CVDCV AFM images and height profile	43
2.12	Graphene growth optical microscope picture	44
2.13	Proposed growth recipes	47

3.1	Graphene based Hall bars devices	50
3.2	Complete device and chip design	51
4.1	4-terminal and 2-terminal measurement setup	56
4.2	Sample sheet resistance as a function of (V_{bg})	58
4.3	Sample sheet resistance as a function of (V_{bg}) at room temperature	58
4.4	Carrier density and carrier mobility as a function of (V_{bg})	59
4.5	Magnetoresistance as a function of magnetic field	59
5.1	TBG- WSe_2 device architecture and its different region	64
5.2	Contact diagram of TBG- WSe_2 device	65
5.3	TBG- WSe_2 sheet resistance as a function of the V_{tg}	67
5.4	TBG- WSe_2 magnetoresistance as a function of V_{tg} at $B=18T$ and $V_{bg} = -5V$	68
5.5	TBG- WSe_2 magnetoresistance as a function of B at fixed $V_{tg} = -2V$ and $V_{bg} = -5V$	69
5.6	TBG- WSe_2 Magnetoresistance and respective carrier density and mobility as function of V_{tg} and fixed $B \pm 1T$ and $V_{bg} = -5V$	71
5.7	TBG- WSe_2 Magnetoresistance and respective carrier density and mobility as function of V_{tg} and fixed $B \pm 3T$ and $V_{bg} = -5V$	72
5.8	TBG- WSe_2 magnetoresistance as a function of V_{tg} and fixed $B \pm 3T$ and $V_{bg} = 0V$	73
5.9	TBG- WSe_2 sample sheet resistance as a function of the V_{tg} and its respective carrier mobility	74
5.10	Proposed setup to measure the AQHE	76
6.1	Reuse and permissions license for Figure 1.4 (a)	80
6.2	Reuse and permissions license for Figure 1.4 (b)	81
6.3	Reuse and permissions license for Figure 1.5	82
6.4	Reuse and permissions license for Figure 1.6	82
6.5	Reuse and permissions license for Figure 1.8 (a)	83
6.6	Reuse and permissions license for Figure 1.8 (b)	83
6.7	Reuse and permissions license for Figure 1.9	84
6.8	Reuse and permissions license for Figure 1.10 and Figure 1.11	84
6.9	Reuse and permissions license for Figure 1.12	85
6.10	Reuse and permissions license for Figure 1.13	86
6.11	Reuse and permissions license for Figure 1.14	87
6.12	Reuse and permissions license for Figure 1.15	87
6.13	Reuse and permissions license for Figure 2.4 and Figure 2.5	88

A.1	Peak fitting	100
A.2	Data reprocessing of high quality graphene	101
A.3	Data reprocessing of low quality graphene	102
A.4	Data reprocessing of low defect density graphene	103
A.5	Data reprocessing of high defect density graphene	104
B.1	CVDREF-01 Microscope picture	106
B.2	CVDREF-02 Microscope picture	107
B.3	CVDHT-01 Microscope picture	108
B.4	CVDCV-01 Microscope picture	109
C.1	Microscope picture of the graphene domains during the fabrication process	115

List of Tables

2.1	Acronyms for different growth recipes.	33
4.1	Ohmic contact resistance as a function of temperature	57
5.1	Ohmic contact resistance as a function of magnetic field	66

List of Abbreviations

2D 2-dimensional

2DEG 2-dimensional electron gas

2DHG 2-dimensional hole gas

3D 3-dimensional

AFM Atomic force microscopy

AQHE Anomalous quantum Hall effect

BLG Bi-layer graphene

C Chern number

CNP Charge neutrality point

CVD Chemical vapor deposition

DI Deionized water

DOS Density of states

FBZ First Brillouin zone

hBN Hexagonal boron nitride

IPA Isopropyl alcohol

LCC Leadless chip carrier

LL Landau level

LPCVD Low pressure chemical vapor deposition

MBZ Main Brillouin zone

PC Poly(Bisphenol A carbonate)

PMMA Poly(methyl methacrylate)

QHE Quantum Hall effect

QNFCF Quantum Nano-Fabrication and Characterization facilities

sccm Standard cubic centimetres per minute

SdH Shubnikov-de Haas

slc standard liter per minute

SLG Single-layer graphene

SOC Spin-orbit coupling

SOI Spin-orbit interaction

TBG Twisted bi-layer graphene

TMD Transition metal dichalcogenide

TR Time reversal

VdW Van der Waals

Chapter 1

Introduction

1.1 Background

Condensed matter physics studies the behavior of condensed phases, focusing on pressure, lattice orientation, and spin ordering to observe unconventional states. Advances in solid-state physics have enhanced our understanding of crystallography, elasticity, metallurgy, and magnetism, predicting intriguing states like superconductors, Bose-Einstein condensates, and magnetic orders such as ferromagnets and antiferromagnets.

The interaction between symmetry and topology has uncovered new electronic structures. Band theory is essential for understanding these structures, leading to the development of materials like quantum Chern insulators, topological insulators, and topological superconductors. Despite considerable theoretical progress, further experimental validation is required to confirm the prediction of these exotic states [1].

Graphene is an ideal system for studying electronic transport in two dimensions, including topological effects associated with edges or boundaries. Although this material does not occur naturally, it is derived from its bulk, graphite. Graphene consists of a single layer of carbon atoms arranged in a flat two-dimensional honeycomb lattice with sp^2 bonding. This sp^2 structure includes three in-plane sigma bonds and one out-of-plane pi bond per carbon atom, enabling high electrical conductivity due to the presence of free-moving electrons in π orbital. By reducing graphite to a single layer, charge carriers become confined to a single plane, forming a 2-dimensional electron or hole gas (2DEG or 2DHG), with enhanced mobility and reduced scattering. This unique configuration makes graphene an excellent platform for exploring quantum phenomena and topological states.

Early theoretical work on graphene's band structure by Wallace, McClure, Slonczewski,

Weiss, Semenoff, and Haldane, to name a few, laid the foundation for understanding its unique electronic properties. These researchers focused on low-energy regimes where charge carriers in graphene behave like massless Dirac particles [2–6]. Among these developments, Kane and Mele’s addition to band theory predicted chiral edge states that are topologically protected and allow for dissipationless transport [7–9].

Novoselov and Geim’s groundbreaking 2004 isolation of single-layer graphene (SLG) using the scotch tape exfoliation method revolutionized the field [10]. This achievement provided a tangible form of graphene for experimental studies and spurred a wave of new theoretical developments to explain its magneto-transport properties[11–14].

Graphene’s unique electronic properties, underscored by theoretical and experimental advancements, have established it as a crucial material for exploring quantum electronic phenomena and topological states. Studying graphene’s band structure is essential for gaining a complete understanding of the potential topological phases that can arise from this material.

In the next chapter, we will examine the detailed band structure of graphene, beginning with its crystallographic structure and focusing on the emergence of Dirac fermions and the Berry phase in the low-energy regime of SLG. We will also explore the band structure of Bernal-stacked bilayer graphene (BLG) and the distinctive structure of twisted-BLG (TBG). Furthermore, the motivation section will investigate graphene’s topological behaviors for various applications. This section will initially cover SLG and its use in metrology, followed by BLG and TBG and their electronic applications and conclude by the defining the specific objectives of this master’s project.

By understanding these aspects comprehensively, we aim to facilitate new technological applications and contribute to the expanding knowledge in the fascinating field of topological materials.

1.1.1 Single layer graphene crystalline structure

Due to its sp^2 configuration, graphene’s lattice is arranged in a honeycomb shape with p_z orbitals perpendicular to chemical bounds. The unit cell of graphene lattice consists of 2 equivalent lattice sites, as shown in Figure 1.1 (a). The primitive vectors are defined as:

$$a_1 = \frac{a}{2} (3, \sqrt{3}), \quad a_2 = \frac{a}{2} (3, -\sqrt{3}) \quad (1.1)$$

Similarly, graphene’s first Brillouin zone (FBZ) adopts a hexagonal shape in reciprocal space characterized by distinct Dirac points. Reciprocal lattice vectors are given by:

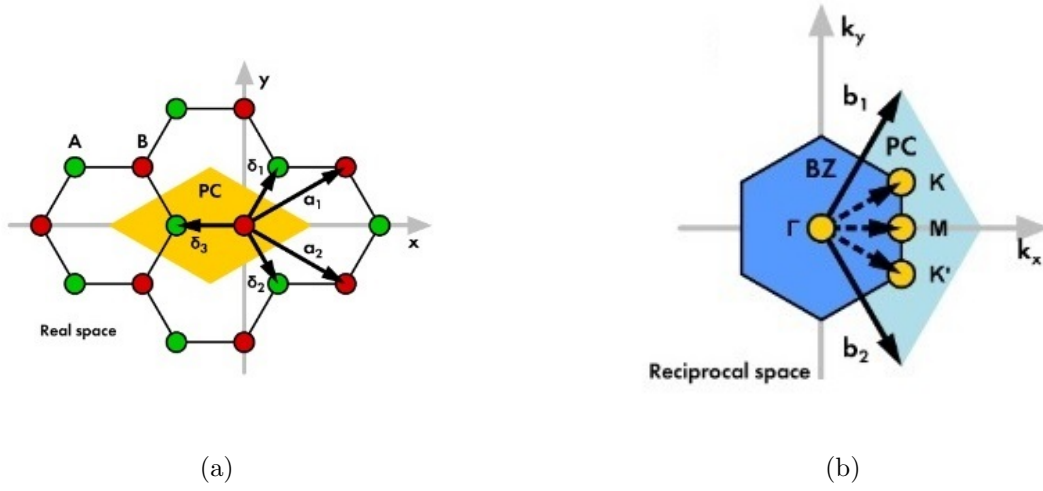


Figure 1.1: **Graphene's real and reciprocal hexagonal structure.** (a) The primitive cell (yellow) is composed of two lattice sites, site A (green) and sites B (red), with primitive vectors a_1 and a_2 . The distance to the nearest neighbor is $\delta = 1.48 \text{ \AA}$ to the second nearest neighbor $\delta = 2.46 \text{ \AA}(\sqrt{3}a_0)$. (b). The first Brillouin zone (FBZ) (blue) is composed of Γ , K, K' and M points of symmetry in momentum space. The reciprocal lattice vectors b_1 and b_2 are superimposed to the primitive cell (light blue) for reference. Adapted from Multidisciplinary Digital Publishing Institute [15]

$$b_1 = \frac{2\pi}{3a} (1, \sqrt{3}), \quad b_2 = \frac{2\pi}{3a} (1, -\sqrt{3}) \quad (1.2)$$

And satisfy the relation $b_1 \cdot a_j = 2\pi \delta_{ij}$, where δ_{ij} is the Kronecker delta. The latter guarantees a constructive interference between the real and reciprocal lattice and its periodicity in terms of lattice translation. This directly maps eigenvalues to eigenvectors of the Bloch Hamiltonian, defined in the next section. Figure 1.1 (b) presents the two nonequivalent corners, K and K', of the hexagonal FBZ. The position in momentum space for these points is given by:

$$K = \frac{2\pi}{3a} \left(1, \frac{1}{\sqrt{3}}\right), \quad K' = \frac{2\pi}{3a} \left(1, \frac{-1}{\sqrt{3}}\right) \quad (1.3)$$

1.1.2 Electronic band structure of Single and Bernal stacking and twisted Bi layer graphene

Single layer graphene electronic band structure

As graphene possesses a free electron in its p_z orbital, the theoretical model that describes a free electron in a periodic potential is a good starting point to capture essential aspects of graphene's electronic structure. This electron wave in a periodic crystal lattice can be predicted using the tight-binding model, which McClure and Slonczewski first used in the case of graphene[3, 4]. This approach assumes a well-approximated linear combination of atomic orbitals to define the solution to the time-independent single electron. The tight-binding Hamiltonian considering only hopping between nearest neighbors is defined as:

$$\hat{H} = -t \sum_{i,j,\sigma} (\hat{a}_i^\dagger \hat{b}_{i+\delta} + H.c.) \quad (1.4)$$

Where t is the hopping amplitude t_1, t_2, t_3 hopping along $\delta_1, \delta_2, \delta_3, \sigma$ bonds and $\hat{a}_i^\dagger$ is the creation and $\hat{b}_j$ the annihilation operator of an atom of sublattice A and B respectively. The operator $\hat{b}_{i+\delta}$ annihilates a fermion at site B with position $R_i + \delta$, R_i being the reference point for unit cell i . The hopping amplitude of the first (t) hopping term is $\approx 2.5eV$ (corresponding to the energy of a π bond) [16]. The distance of the three nearest neighbors, also shown in Figure 1.1, is given by:

$$\delta_1 = \frac{a}{2}(1, \sqrt{3}), \quad \delta_2 = \frac{a}{2}(1, -\sqrt{3}), \quad \delta_3 = a(-1, 0) \quad (1.5)$$

In a periodic system, potential energy needs to satisfy the relation $V(\delta + p) = V(\delta)$. In this form, the Hamiltonian doesn't satisfy the Bloch theorem $b_i \cdot a_1 \neq 2\pi\delta_{ij}$, and a gauge transformation is needed to restore a Bloch form. Therefore, the creation and annihilation operations are rewritten as:

$$c_{\vec{k},A} = \frac{1}{\sqrt{N}} \sum_i e^{i\vec{k} \cdot R_i} c_{i,A}, \quad c_{\vec{k},B} = \frac{1}{\sqrt{N}} \sum_j e^{i\vec{k} \cdot (R_j + \delta)} c_{j,B} \quad (1.6)$$

Where the creation and annihilation operators are redefined in terms of Fourier transformations and sum over all N atomic sites. The two operators are stacked together and rewritten in a vector form such as:

$$c_{\vec{k}} = \begin{pmatrix} C_{\vec{k},A} \\ C_{\vec{k},B} \end{pmatrix} \quad (1.7)$$

Which allows us to rewrite the Hamiltonian in a simple Bloch form :

$$H = \sum_{\vec{k}} c_{\vec{k}}^\dagger H_{\vec{k}} c_{\vec{k}}, \quad H_{\vec{k}} = \begin{pmatrix} 0 & \Delta_{\vec{k}} \\ \Delta_{\vec{k}}^* & 0 \end{pmatrix} \quad (1.8)$$

where $\Delta_k = -t \sum_{j=1,2,3} e^{ik \cdot \delta_j}$. This $H_{\vec{k}}$ is a purely-off diagonal 2x2 matrix. This feature originates from the model used, which doesn't allow direct tunneling between A-A sites. As a result, we only have tunneling with the nearest neighbors from A-B sites.

This unitary matrix can be described in terms of Pauli matrices where $H_{\vec{k}} = \vec{d}(\vec{k} \cdot \vec{\sigma}) + d_0(\vec{k} \cdot \sigma_0)$ with $d(\vec{k})$ being the 3-dimensional (3D) space vector and $\vec{\sigma}$ is a vector grouping the Pauli matrices in the x, y and z direction. Therefore, vectors in 3D mapped to this momentum space are found to be :

$$\begin{aligned} d_x(\vec{k}) &= -t \sum_{j=1\dots 3} \cos(\vec{k} \cdot \vec{\delta}_j), & d_y(\vec{k}) &= -t \sum_{j=1\dots 3} \sin(\vec{k} \cdot \vec{\delta}_j) \\ d_z(\vec{k}) &= 0, & d_0(\vec{k}) &= 0 \end{aligned} \quad (1.9)$$

Thus, the energy bands are obtained by diagonalizing the Hamiltonian as follows:

$$\begin{aligned} E_{\pm}(\vec{k}) &= \pm \Delta_{\vec{k}} \\ E_{\pm}(\vec{k}) &= \pm t \sqrt{1 + 4 \cos\left(\frac{3}{2}\kappa_x\right) \cos\left(\frac{\sqrt{3}}{2}\kappa_y\right) + 4 \cos^2\left(\frac{\sqrt{3}}{2}\kappa_y\right)} \end{aligned} \quad (1.10)$$

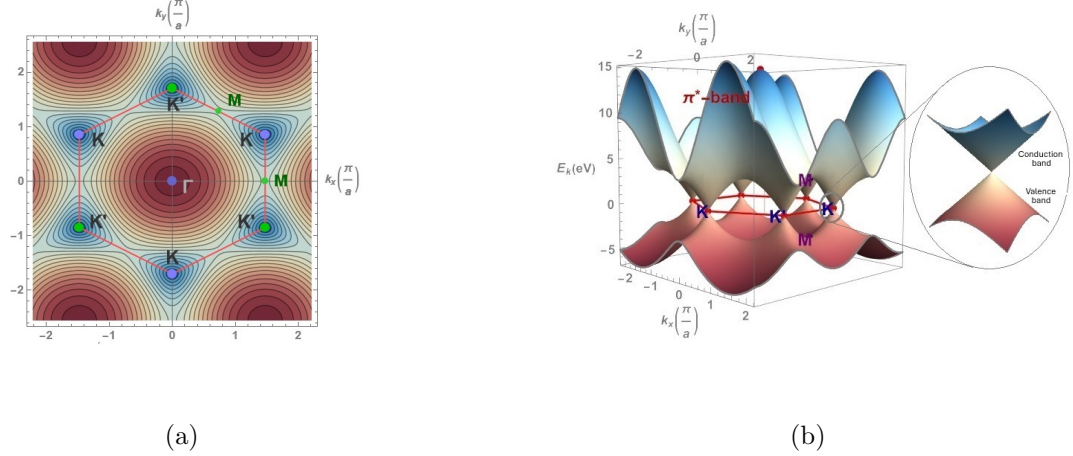


Figure 1.2: **The band structure of single-layer graphene.** (a) 2D picture of the FBZ showing the curvature in the field converging to points K and K'. (b) 3D representation of SLG's FBZ with the additional point of symmetry M, being the middle point between K and K'. A close-up of these points shows the Dirac cones forming in the low-energy regime with the valence band in red and the conduction band in blue.

with $\pm$ representing the conduction and the valence band respectively. Graphene's band structure is presented in Figure 1.2, where we see the conduction and valence band (π and π^*) vanish precisely at the corner of the FBZ, forming the K and K' valleys. Figure 1.2(a) shows the 2D plot of the field curvature converging to singular points in momentum space, better pictured in the 3D plot on the right (Figure 1.2(b)). Now, rewriting the single electron wave function in a structure with relative weight and phase of the wavefunction on each sublattice in spinor form:

$$v_{\vec{k}} = \frac{1}{\sqrt{2(d \pm d_z)}} \begin{pmatrix} d_z \pm d \\ d_x + id_y \end{pmatrix}, \quad v_{\vec{k}} = \frac{1}{\sqrt{2}} \begin{pmatrix} \pm 1 \\ e^{-i\theta_q} \end{pmatrix} \quad (1.11)$$

With $\arctan\theta$ relating the d_x and d_y components and d regrouping the component d_x , d_y and d_z . It is important to note that the magnitude of the 2 components is the same, with the phase being the only degree of freedom remaining for the system.

The Dirac points, where the bands converge to form the K and K' valleys, are the regions that gained interest in the early '50s. As we approach the semi-metal band's junction, charge carriers start behaving differently. Figure 1.2 (b) shows a close-up of the low-energy spectrum of SLG's band structure. The linear dispersion of the low-energy

regime can be approximated up to 1 eV [17, 18], where the band structure adopts a conical shape in that region. Near the Dirac point, where $|\vec{k}| \ll |\vec{K}|$, d_x and d_y can be approximated as $\frac{\sqrt{3}}{2}aR_{\pi/3}$ and the Hamiltonian reduces to a Dirac Hamiltonian:

$$H = \hbar v_f \begin{pmatrix} 0 & k_x \sigma_x + k_y \sigma_y \\ k_x \sigma_x - k_y \sigma_y & 0 \end{pmatrix} = \hbar v_f \sigma \cdot k, \quad (1.12)$$

$$H_K = \hbar v_f (k_x \sigma_x + k_y \sigma_y), \quad H_{K'} = \hbar v_f (k_x \sigma_x - k_y \sigma_y) \quad (1.13)$$

$$H = \hbar v_f (k_x \sigma_x + \tau_z k_y \sigma_y) \quad (1.14)$$

And τ_z introduces a factor that is related to the K (1) and K'(-1) points. This equation is the Dirac Hamiltonian for relativistic massless particles, where the speed of light is replaced by Fermi velocity $v_f = \frac{\sqrt{3}ta}{2\hbar} \approx 10^6 m/s$. The latter equation shows that two degrees of freedom describe the system: the spin degree of freedom(σ) and the valley degree of freedom(k).

Looking at Eq 1.12, we see an opposite behavior for the K and K' valleys. This shows that both sublattices have opposite relations in momentum space and, thus, are considered as time reversal partners. Here, we see that the vorticity of sublattice A is clockwise compared to anti-clockwise for sublattice B. This is an important conclusion of the low-energy regime graphene lattice, stating that the helicity is directly related to the chirality of sublattices A and B. More interestingly, as long as the Dirac points are protected by C_{2z} and TR symmetries, the vortexes and anti-vortexes will never collide and annihilate. This distinctive property can be better understood when looking at the SLG's structure discrete symmetry more precisely for C_{2z} and time-reversal (TR) symmetry.

In the case of a 2D material, the inversion and C_{2z} symmetry are equivalent due to the absence of a 3rd dimension. Looking at the crystalline structure of graphene presented earlier in Figure 1.1(a), we see that it is possible to rotate the structure by 180° around the z-axis to obtain the same lattice back, therefore showing C_{2z} symmetry. Similarly, inversion symmetry implies that all coordinates are mirrored relative to the lattice's center. Figure 1.3 also captures why these symmetries are not equivalent in the 3D case, where realizing the latter operation is impossible. That means, for every $\vec{k}$ we respect the relation of $h(\vec{k}) = \sigma_x h(-\vec{k} \sigma_x)$. TR-symmetry differs because it implies that the system remains unchanged with the inversion of time. For SLG, the opposite vorticity of the K and K' valleys proves the presence of TR-symmetry. In that case, the requirement imposed by this symmetry is that $h(\vec{k}) = h^*(-\vec{k})$ for every $\vec{k}$.

Figure 1.3 presents the case of a system with both Inversion and TR-symmetry. The first highlight is when each symmetry is taken individually. Each symmetry gives us relations

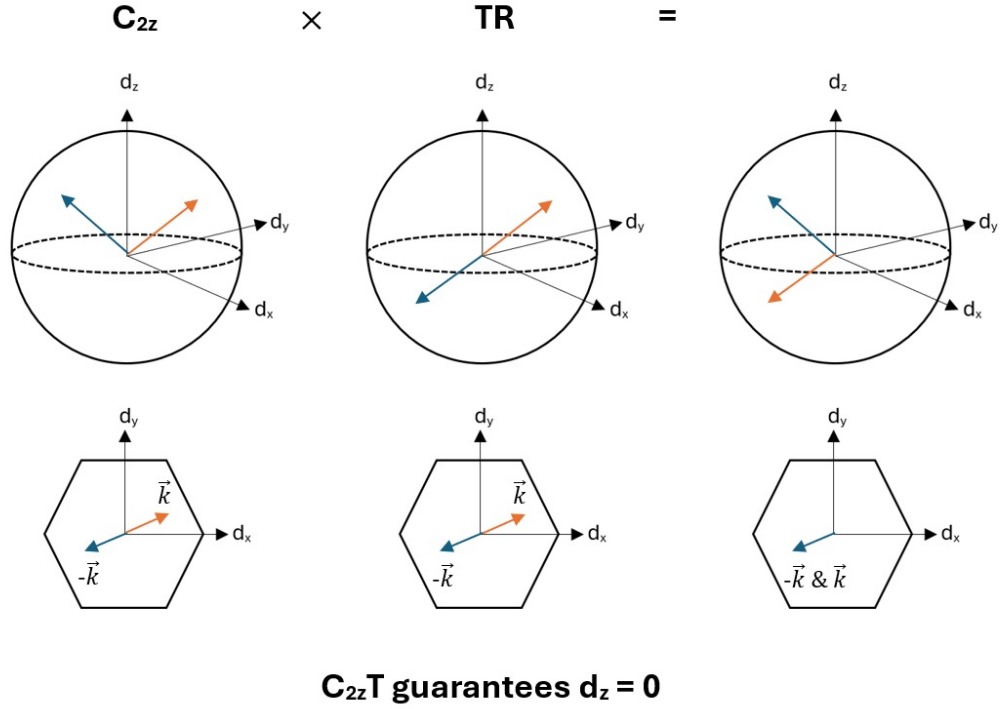


Figure 1.3: **Bloch sphere showing graphene's symmetry.** The leftmost Bloch sphere shows the relations in momentum-space imposed by C_{2z} symmetry. In the center, a Bloch sphere shows the relations in momentum-space imposed by TR symmetry. The rightmost Bloch sphere combines TR and C_{2z} symmetry. This implies that $d_z = 0$ as it is the only solution possible for TR and C_{2z} symmetry to remain unbroken.

in momentum space rather than a constraint. Thus, the symmetries themselves are not strong enough to protect the Dirac points from colliding. When the two symmetries are added, a new constraint appears in the system. The Bloch sphere resulting from the 2 symmetries illustrates the only possible solution to keep TR and Inversion symmetry; this is only possible if there is no third dimension. This is why the Dirac points are protected, and unless one of the symmetries is broken, they will remain stable in space and time [7].

Bilayer graphene electronic band structure

When an additional single layer of graphene is added to the system, Bilayer graphene (BLG) will naturally adopt an AB stacking configuration, also called Bernal stacking. In this configuration, additional interlayer hopping terms are added to the Hamiltonian. Figure 1.4 presents the crystalline structure and band structure of BLG. In this configuration, BLG is still protected by TR and C_{2z} symmetry but not by inversion symmetry. Using the tight-binding model of graphite with additional terms for the nearest neighbor Hamiltonian [19], that gives for BLG:

$$\begin{aligned} \hat{H} = & -\gamma_0 \sum_{i,j} (\hat{a}_{mi}^\dagger \hat{b}_{mj} + H.c.) - \gamma_1 \sum_i (\hat{a}_{2i}^\dagger \hat{b}_{1j} + H.c.) \\ & -\gamma_4 \sum_i (\hat{a}_{2i}^\dagger \hat{b}_{1j} + \hat{a}_{2j}^\dagger \hat{b}_{1i} + H.c.) - \gamma_3 \sum_i (\hat{a}_{2i}^\dagger \hat{b}_{1j} + H.c.) \end{aligned} \quad (1.15)$$

beginaligned Where m represents the 1^{st} the 2^{nd} . In the Bernal configuration, the sites A and B overlap in distinct planes. This adds a strong interlayer hopping term between A and B sites (γ_1) and weaker interlayer A-A and B-B hopping terms. By the convention of notation for graphite, the hopping term used earlier (t) is replaced by γ_n . The extra hopping parameters are presented in Figure 1.4, which are approximately given by $\gamma_1 \approx 0.4\text{eV}$, $\gamma_3 \approx 0.3\text{eV}$, $\gamma_4 \approx 0.04\text{eV}$. The interlayer parameter $\gamma_1 \simeq 0.4 \text{ eV} < \gamma_0 \simeq 2.5 \text{ eV}$ indicates the favorability of the carrier of hopping inter-layers [20]. Rewriting Eq.1.13 in a 4x4 matrix:

$$\hat{H}_k = \begin{pmatrix} V & v_f(q_x + iq_y) & 0 & 0 \\ v_f(q_x - iq_y) & V & \gamma_1 & 0 \\ 0 & \gamma_1 & V & v_f(q_x + iq_y) \\ 0 & 0 & v_f(q_x + iq_y) & V \end{pmatrix} \quad (1.16)$$

With the effective Hamiltonian reducing in the $A_1 - B_2$ subspace to [20]:

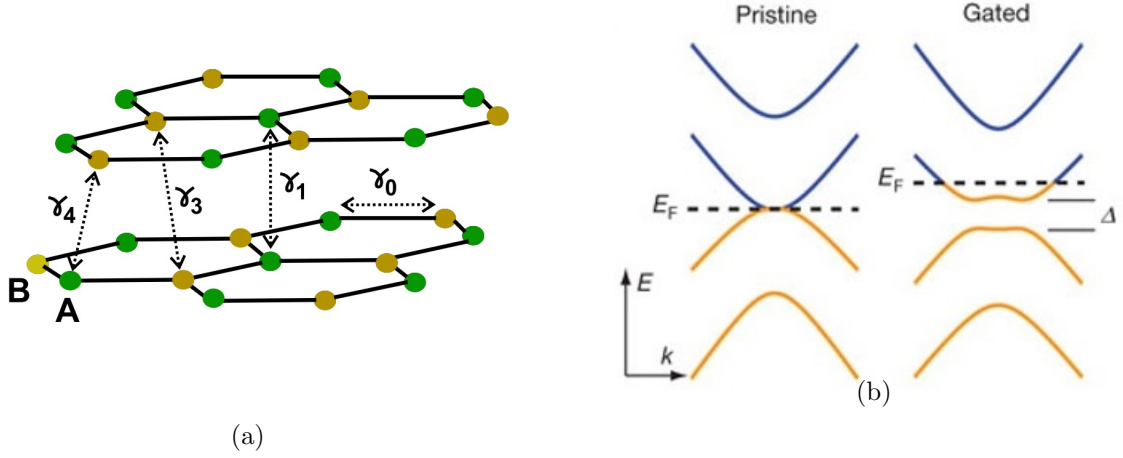


Figure 1.4: **Crystalline and electronic band structures of Bilayer Graphene.** (a) Bernal bilayer graphene (BLG) with the intra-layer hopping term γ_0 , and the additional inter-layer hopping terms γ_1 , γ_3 and γ_4 between the A-A, B-B and A-B respectively. (b) Bernal BLG band's structure with 4 parabolic bands: 2 main and 2 sub. The left picture shows the band structure of pristine BLG compared with that of gated BLG on the right, when an in-plane electric field is applied (e.g., via a top gate electrode). Adapted from American Physical Society [16] and Springer Nature [21].

$$H_{A_1-B_2} = \frac{v_f^2}{\gamma_1} \begin{pmatrix} 0 & (k_x\sigma_x + k_y\sigma_y)^2 \\ (k_x\sigma_x - k_y\sigma_y)^2 & 0 \end{pmatrix} \quad (1.17)$$

The energy spectrum is now given by :

$$E^2 = V^2 v_f^2 \hbar^2 k^2 + \frac{t_1^2}{2} (1 \pm \sqrt{1 + 4v_f^2 \hbar^2 k^2 / t_1^2}) \quad (1.18)$$

Where V is the electrostatic potential difference between the two layers, in its pristine form, no voltage is applied between layers; therefore, $V=0$. When a voltage is applied ($V \neq 0$), it causes the opening of a small bandgap of $\Delta = 2V - 4V^3/\gamma_1^2 \hbar v_f = \sqrt{2}V/\hbar v_f$ [16, 21, 22]. Looking at the low energy spectrum of BLG, Eq 1.16 reduces to :

$$(2E \pm \gamma_1)^2 - 4v_f^2 \hbar^2 q^2 = \gamma_1^2 \quad (1.19)$$

The latter demonstrates the loss of the linear dispersion near $E = 0$, which is replaced by a parabolic relation. Figure 1.4(b) presents the new hyperbolic band structure, featuring two main bands degenerating at points now referred to as Charge Neutrality Points (CNP)

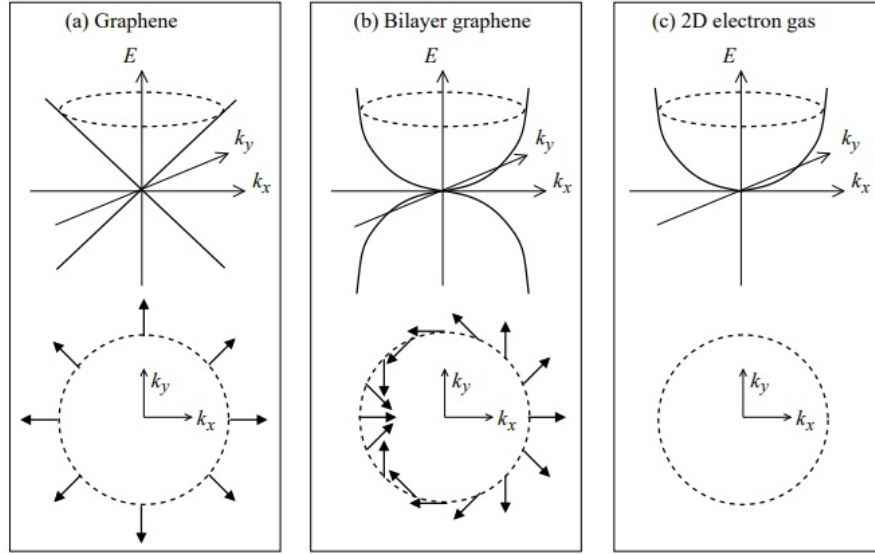


Figure 1.5: **Berry phase of SLG, BLG, and a conventional 2DEG.** A Berry phase of π and 2π is acquired in the case of SLG (a) and BLG graphene (b), respectively. The case of a trivial 2DEG (c). Reproduced from American Physical Society [24]

and the two subbands. Adding this single graphene sheet makes the fermions massive enough to alter the band structure significantly.

Moreover, BLG can be distinguished from SLG by its Berry phase of 2π , where Figure 1.5 compares the Berry phase of SLG, BLG, and a trivial semi-conductor [23]. This Berry phase is defined as the phase acquired when the pseudospin vector completes a full rotation around a singular point. Figure 1.5 shows that SLG has a Berry phase of π , BLG has a Berry phase of 2π , and a conventional 2D semiconductor has no Berry phase. Park et al. proved that this unconventional aspect was related to the Berry phase's winding number [24]; (b) and (c) show the equivalence between a Berry phase with factor 2π and a conventional 2DEG with no winding number.

Twisted bilayer graphene

To briefly discuss the TBG band structure without covering its theory, the weak Van der Waals (VDW) forces allow the separation and also the recombination of graphene layers in ways that are not naturally possible. TBG is a good example of VdW material where the two stacked graphene layers are rotated relative to each other. The addition of a small angle of rotation between the layers gives rise to Moiré patterns. This pattern results from the periodic projection of the relative lattice constant mismatch, which modifies BLG's

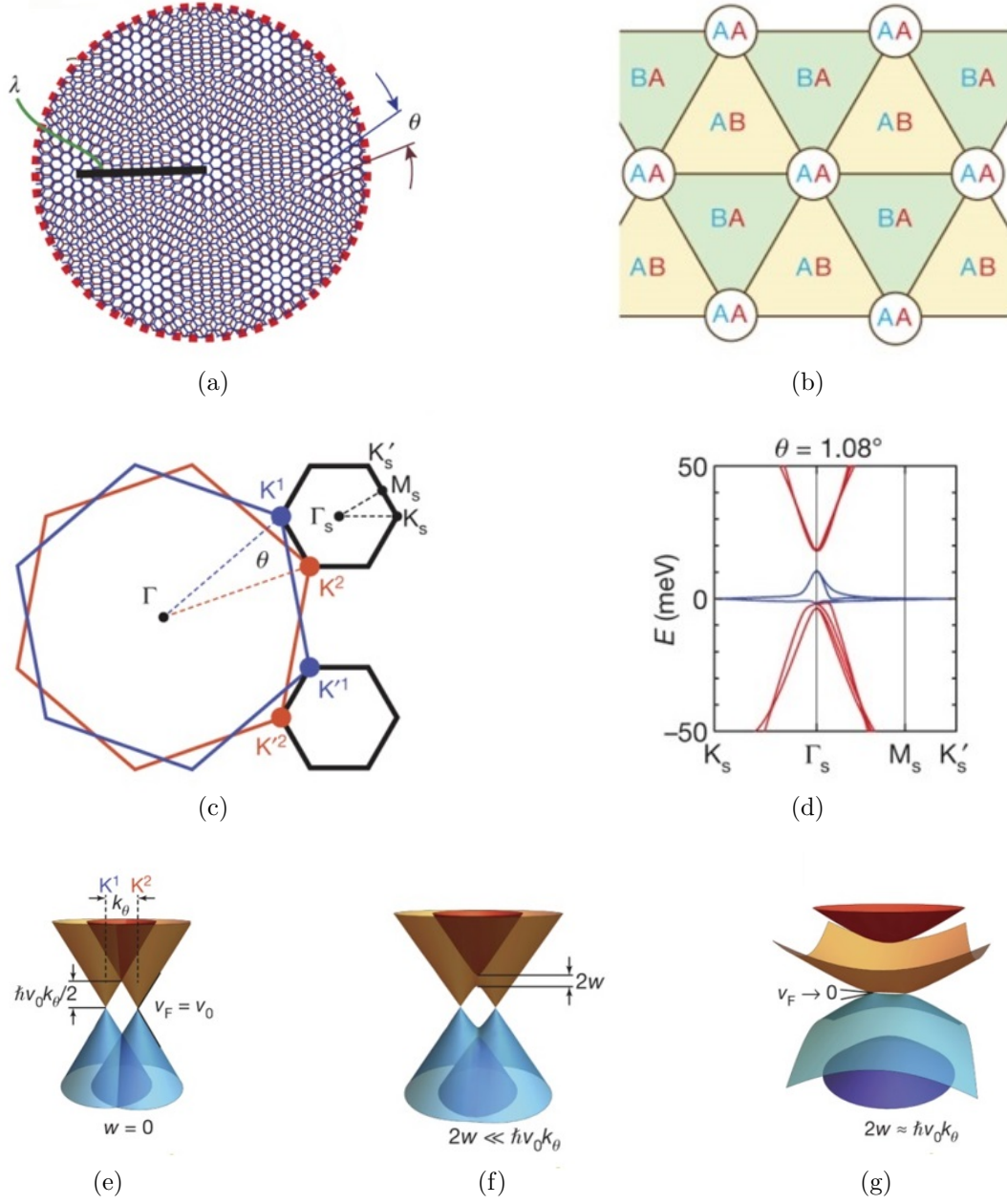


Figure 1.6: Crystalline structure and electronic band structure of TBG. (a) Two sheets of graphene rotated in the plane relative to each other (i.e., "twisted") form a Moiré pattern with Moiré wavelength (λ). (b) The A-A, A-B, and B-A intertwining stacking regions. (c) The main Brillouin zone (MBZ) results from the junction of the FBZs of the first (blue) and second (red) layers, forming the flat band at a "magic"-angle of 1.1° (d). (e) (f) and (g) Interlayer hybridization leading to the formation of a flat band for $w=0$, (f) where $2w \gg \hbar v_0 k_\theta$ and (g) $2w \approx \hbar v_f k_\theta$. Adapted from Springer Nature [25].

band structure. The creation of such a pattern can be seen in Figure 1.6 (a), where the addition of a second layer (blue) to a first layer (red) forms a Main Brillouin zone (MBZ). When the twist angle changes, this MBZ also changes, where a low rotation angle generates a smaller MBZ.

Based on the Haldane model, Allan H. MacDonald and Rafi Bistritzer extended the BLG's tight-binding model for the case of TBG. They predicted the formation of a flat band at a small angle of 1.1° , called the "magic" angle [26]. Po et al. extended this model to accurately describe the flat band while preserving all symmetry in the system [27]. Kang et al. further contributed with a low-energy tight-binding model confirming local symmetry and time reversibility near the flat band [9].

For TBG with a twist angle close to the magic angle, the Moiré pattern generates a superlattice with a unit cell much larger than the crystalline unit cell. In these systems, the distance between the superlattice cell is defined by the Moiré $\lambda = a/2 \sin(\theta/2)$, with $\lambda = 12.8nm$. The new periodic potential introduced by the twisted angle modifies BLG's band structure so that the conduction and valence bands vanish in the A-A regions. These flat bands confine carriers in the low energy regime of less than 10 meV [25] with Moiré hybrid bandgap ranging from 30 to 50 eV [28]. The low kinetic energy allows a stronger electron-electron interaction, which can lead to more exotic physical states [25]. This particular graphene band structure is shown in Figure 1.6. Hybridization of the Dirac point in the A-A regions initiates when the hybridization energy $2w \ll \hbar v_0 k(\theta)$, which pushes the bands toward $E=0$, with k_θ being the momentum displacement of the Dirac cones. For this reason, TBG is distinct from Bernal stacking BLG, where the flat band exhibits very different physics.

1.1.3 First topological insulator and Chern numbers

Berry Phase and Berry Curvature

The Berry phase was first introduced in 1984 to describe the phase accumulated by the wave function that completes a rotation in k-space. This phase is found by taking the integral of the Berry curvature defined in terms of the Berry vector potential $\mathcal{A}$:

$$\Omega(\vec{k}) = \nabla \times \vec{\mathcal{A}} \quad (1.20)$$

With the Berry vector potential that can be obtained directly from the spinor $v_{\vec{k}}$:

$$\vec{\mathcal{A}}(\vec{k}) = i \langle v_{\vec{k}} | \nabla_{\vec{k}} | v_{\vec{k}} \rangle \quad (1.21)$$

Where the Berry phase is defined as:

$$\gamma = \int \Omega(\vec{k}) d^2k \quad (1.22)$$

The Berry vector potential is not observable, whereas the Berry phase is a measurable quantity. This can be thought of as an indicator of the system's electric polarization or "vorticity". Another way to interpret this is to see the Berry phase as reflecting the global properties of the parameter spaces, whereas the Berry vector potential gives a local description.

The Haldane model

The emergence of topological insulating phases can be understood by looking at the respective system's symmetry [1, 29]. First, let's look at when the inversion symmetry is broken. Inversion symmetry breaking can happen with the addition of material, creating lattice mismatch, like in the case of Moiré materials. This introduces a Dirac mass term in the diagonal of the Hamiltonian of Eq. 1.12 with an extra d_z magnitude component Δ . Hence, the eigenenergy is rewritten as: $E_{\pm} = \pm \sqrt{(\hbar v_F k)^2 + \Delta^2}$. This symmetry breaking opens a gap in the graphene band structure (2Δ), changing it into a semiconductor whose carriers behave as massive particles. With hexagonal boron nitride (hBN), the band gap opening is rather weak with $2\Delta = 10\text{-}30 \text{ meV}$ depending on the crystalline alignment[30], and other factors, electric potential, twist angle, etc [21, 31, 32].

The Haldane model is a toy model proposed in 1988 for the 2D honeycomb lattice structure [6]. It is the first model to predict a topological phase transition. For their contribution to topological physics, Haldane, Thouless, and Kosterlitz were awarded the Nobel Prize in Physics in 2016[33]. His contribution is to add a complex next-nearest hopping term in the tight-binding Hamiltonian that breaks TR symmetry. By doing so, a Haldane mass term Δ appears in the diagonal of the 2x2 Hamiltonian in Eq. 1.12, similar to the Dirac mass. Figure 1.7 presents the Haldane toy model, showing tunneling occurring in momentum space. The Haldane Hamiltonian is thus described as:

$$H = -t \sum_{i,j} (c_i^\dagger c_j + H.c) + \Delta \sum_i (\epsilon_i c_i^\dagger c_i + H.c) - t_2 \sum_{i,j} (e^{-i\nu_{ij}\phi} c_i^\dagger c_j + H.c) \quad (1.23)$$

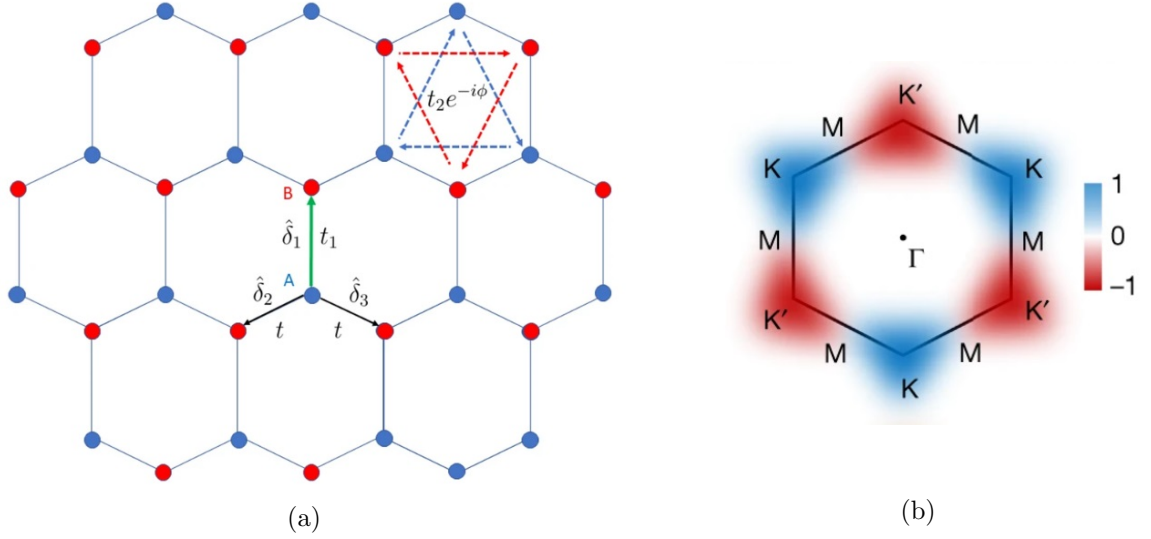


Figure 1.7: **Haldane toy's model with the local Berry phase at K and K' valley**
(a) Haldane toy model with hopping terms evolving clockwise (blue) and anti-clockwise (red) with a global Berry phase located at the FBZ center. (b) local Berry phase (π in blue and $-\pi$ in red) of the K and K' valleys. Adapted from and Springer Nature [34, 35].

where

$$\epsilon_i = \pm 1, \quad \nu_{ij} = \text{sign of } (\vec{u}_1 \times \vec{u}_2)_z \quad (1.24)$$

giving a component in d_z and d_0 :

$$\begin{aligned} d_z(\vec{k}) &= \Delta + 2t_2 \sin(\phi) \sum_{j=1..3} (-1)^j \sin(\vec{k} \vec{a}_j) \\ d_0(\vec{k}) &= -2t_2 \cos(\phi) \sum_{j=1..3} (-1)^j \cos(\vec{k} \vec{a}_j) \end{aligned} \quad (1.25)$$

where, in the K and K' valleys, it reduces to $d_z(\vec{k}) = \pm 3\sqrt{3}t_2 \sin(\phi)$. This ν factor can be understood as the vortices' direction forcing the carriers to rotate in the FBZ, represented by the red and blues arrow in Figure 1.7(a). The figure shows that The full Brillouin zone rotation is completed after 3 valley permutations. The local magnetic flux of each valley $\pm 3\phi$ cancels out when added together, resulting in zero net magnetic flux. When a lap of the FBZ is completed, carriers accumulate a phase called the Berry phase.

Figure 1.8(a) plots the normalized mass flux as a function of the phase of the second hopping term amplitude. When the phases of carriers are changed, TR symmetry no longer applies, and topological bands emerge. The Chern number(C) $= \pm 1$ characterizes this topological transition and calculated as followed:

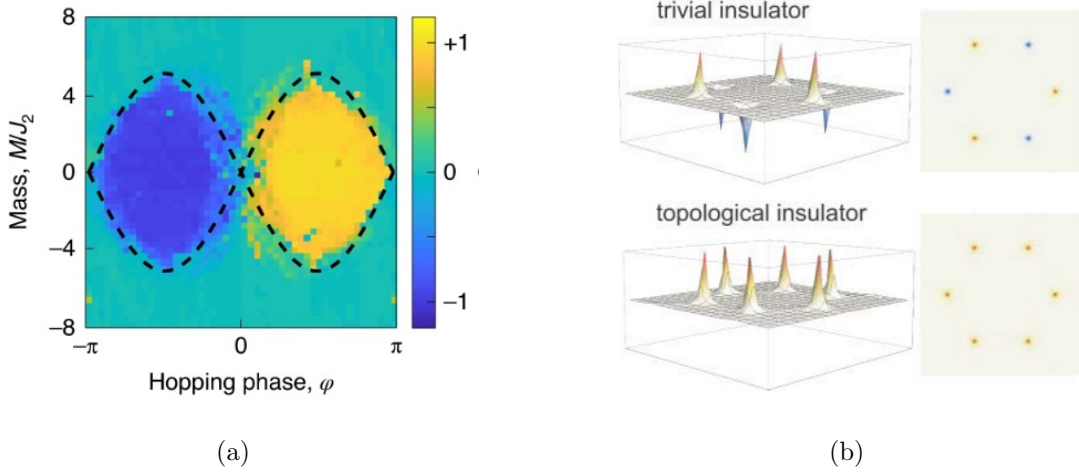


Figure 1.8: **Berry curvature of trivial and topological insulator with their respective C** (a) Plot of the normalized mass flux as a function of the hopping phase of the second hopping parameter leading to topological phase transitions. The topological insulating state is defined with $C = \pm 1$ and a trivial insulator, $C = 0$. (b) Berry curvature with Berry phase (π in blue and $-\pi$ in red) of a trivial $1/3 (3\phi_h - 3\phi_e) = 0 \phi_{Tot}$ (top figure) and a topological insulator $1/3 (3\phi_h + 3\phi_e) = 2\phi_{Tot}$ (bottom figure). Adapted from [36] and Springer Nature [37].

$$C = \frac{1}{2\pi} \int_{BZ} \Omega d^2k \quad (1.26)$$

The latter normalizes the berry curvature over 2π , which represents a circular lap of the FBZ. In the example of a trivial insulator, the integration of the berry curvature results in a net magnetic flux of $1/(3\phi_e - 3\phi_h)$, which corresponds to $C = 0$. In the other case, the integration of the Berry curvature of topological insulator results in a net magnetic flux of $1/3 (6\phi_e)$, which corresponds exactly to a multiple of 2π and therefore results in $C = 1$. This trivial link between the completion of the circular motions and topological states captured by C is very important in topology and serves as an indicator of the presence of topological bands[6].

This topological state can naturally occur in materials like SLG. However, it can also be introduced by adding materials that induce a strong SOC. Kane and Mele were the first to realize that adding spin-orbit interactions (SOI) to the Haldane model could lead to different band interactions. In 2005, they predicted the spin quantum hall state emerging from SLG's band structure in the presence of SOI strong enough to lead to the fusion of conduction and valence, called band inversion [7]. Contrarily of the QHE, Spin QHE is

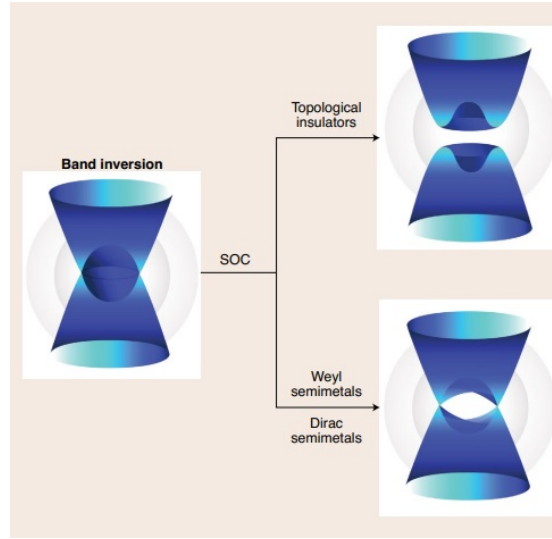


Figure 1.9: **Band inversion** (left) showing tunability of such band structure of becoming topological insulator(top-right) or Weyl-Dirac semi-metal (bottom-right) with spin Hall edges states with control on the SOC strength. Reproduced from Springer Nature [29].

related to the spin current of $\sigma_{xy} = \pm \frac{h}{2\pi}$ without the presence of exterior B and when TR symmetry is preserved. The resulting band interaction opens a gap no longer defined by a unique Dirac point but by a set of points called Weyl nodes. These nodes come in pairs where points act as sources and drains of the berry flux, thus responsible for the split of chiral spin states characterized by $C \pm 1/2$. This addition to the Haldane model extended the understanding of numerous topological phases. Figure 1.9 shows the case of semimetal with band inversion when SOC is induced. Depending on its strength, SOI can fully open a gap and break TR symmetry or partially open a gap, preserving TR symmetry. Overall, Haldane's toy model significantly contributed to the band theory, showing that band structures may have topological properties.

1.1.4 Quantum hall effect in Single and Bi layer graphene

QHE in conventional 2DEG

When an electric current flows through a flat conductive material placed under a perpendicular magnetic field (B), the moving charge carriers will be deflected perpendicularly to their initial direction due to Lorentz's force ($I_{xx} \times B_z$). This causes an accumulation of charges at the edges of the material, leading to the generation of a transverse voltage known as the Hall voltage (V_{xy} or V_{Hall}) (Figure 1.10 (a))[38]. Under these conditions,

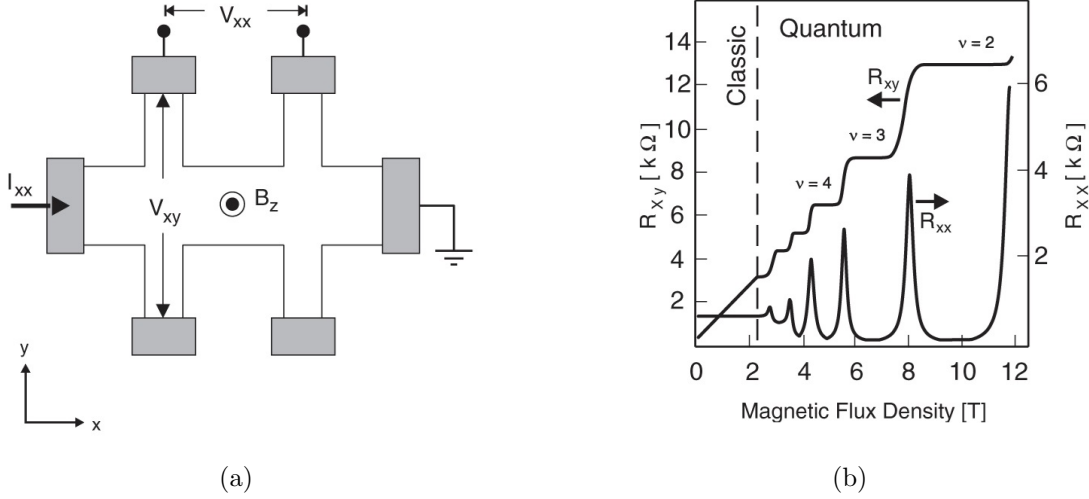


Figure 1.10: **Classical and quantum Hall effect.** (a) Hall bar geometry with charge carriers deviating according to the Lorentz law ($I_{xx} \times B_z$). The Shubnikov de Haas oscillations for the QHE are measured with V_{xx} and the Hall with V_{xy} . (b) Classical Hall and Quantum Hall effects are at low and high fields for conventional 2DEG. Adapted from IOP Publishing [39]

the longitudinal and transverse resistivity are given by ρ_{xx} and ρ_{xy} , respectively, and are described by the following relations:

$$\rho_{xy} = \frac{V_{xy}}{I_{xx}} = \frac{B_z}{n_s e} \quad (1.27)$$

$$\rho_{xx} = \frac{W}{L} \frac{V_{xx}}{I_{xx}} \quad (1.28)$$

With B_z the perpendicular applied magnetic field B , n_s , the density of carriers, and e is the elementary charge. Equation 1.27 shows that the Hall voltage is independent of the sample geometry but proportional to the carrier density at a specific field.

When the system is cooled to cryogenic temperatures, we observe a transition of the classical Hall effect to the quantum Hall effect (QHE). The linearly dependant V_{Hall} evolves into quantized values over a wide range of B , forming Hall plateaus[40]. Shubnikov-de Haas (SdH) oscillations in the longitudinal resistivity accompany the emerging quantum Hall states and confirm the confinement of charge carriers in a two-dimensional electron gas (2DEG). The SdH is characterized by the drop in potential difference to $V_{xx} = 0$ within the range of the plateaus (Figure 1.10 (b)), indicating the suppression of back-scattering.

This is due to the fundamental properties of the bulk that are topologically protected by the Hall bulk states. For back-scattering to occur, charge carriers need to tunnel to the opposite edge, which is strongly suppressed when the sample width is large compared to the cyclotron orbit radius [41, 42].

The formation of these Hall plateaus is understood as Landau levels (LL) being filled with charge carriers undergoing cyclotron motions. This quantization of cyclotron orbits drastically modified the density of states (DOS) by breaking it into discrete levels or LLs. These levels are found by solving the Schrödinger equation of a free electron in the presence of both a magnetic and electric field [43]. The problem reduces to a simple harmonic oscillator with eigenenergies :

$$E_N = \hbar\omega_c(N + 1/2), \quad N \in \mathbb{Z}. \quad (1.29)$$

With the cyclotron frequency defined by $\omega_c = eB/m^*$. By completing the cyclotron orbits, carriers enclose a magnetic flux $\Phi_0 = h/e$, with localized carriers per unit area n_{LL} :

$$n_{LL} = \frac{B}{\Phi_0} = \frac{eB}{h} \quad (1.30)$$

The number of filled LLs, or filling factor, is given by $\nu = \frac{n_s}{n_{LL}}$. When a level is fully filled, the Fermi level of the system lies within the gap between the highest occupied and lowest non-occupied LLs. Plateaus in resistivity appear at the quantized values:

$$\rho_{xy} = \frac{B_z}{n_s e} = \frac{B_z}{e\nu n_{LL}} = \frac{h}{\nu e^2} \quad (1.31)$$

Where h is the Plank constant, e is the elementary charge, and ν is an integer in an ideal sample. LLs are occupied uniformly throughout the sample. In reality, different localized LLs can emerge due to local electric potential differences emerging from the presence of impurities or defects [12]. Experimentally, LLs are observed by varying carrier density and keeping B constant or, by doing the inverse, keeping the Fermi level constant and varying B .

QHE in single and bilayer graphene

Graphene exhibits unique magnetotransport features differing from conventional 2DEGs (Figure 1.11). Solving Eq. 1.12 in an electric and magnetic field, the energy spectrum is no longer modeled by a harmonic oscillator but rather looks like :

$$E_N = \pm \sqrt{2\hbar v_f^2 |N| eB}, \quad N \in \mathbb{Z} \quad (1.32)$$

and LL occurring at filling factors:

$$\nu = 4(N + 1/2), \quad N \in \mathbb{Z} \quad (1.33)$$

Where N is the number of LLs. The glaring difference for graphene is the energy spacing of Landau levels $\delta E_{LL} \propto \sqrt{B}$ compared to $\delta E_{LL} \propto B$ for conventional 2DEG with a distinctive 0^{th} LL, a consequence of graphene's ambipolar behavior (Figure 1.12) [10, 13]. Additionally, Landau levels in graphene are wider and fourfold degenerate due to the extra degree of freedom brought by graphene's K and K' valleys. The emphasis here is the TR relation of the K and K' valleys and the intrinsic relation of the carrier's momentum with the vorticity, not the Berry phase itself. Interestingly, BLG has a different Hall signature than SLG, where Hall plateaus appear at different filling factors (Figure 1.13) [23]. In the case of BLG, the energy spectrum is given by:

$$E_N = \pm \hbar \omega_c \sqrt{|N| (|N| - 1)}, \quad n \in \mathbb{Z} \quad (1.34)$$

and levels appearing at filling factors:

$$\nu = 4N, \quad N \in \mathbb{Z} \quad (1.35)$$

Like SLG, each non-zero LL has four degenerate states except for the 0^{th} LL, where the degeneracy doubles. The 8-fold degeneracy is a special case caused by BLG's energy spectrum degeneracy of $N=0$ and $N=1$ LL. For a long time, the experimental observation of this unconventional QHE was wrongly associated with the absolute value of the Berry phase, which is twice the value of the Berry phase of SLG [24].

Until now, only the case where an exterior B was considered. However, observing Hall conductance without an exterior field being applied is also possible. This phenomenon is called the quantum anomalous hall effect (QAHE), arising from a localized intrinsic or extrinsic magnetic field. Taking the graphene case, previously described by the Haldane model, the AQHE emerges from the valley's vorticity at low carrier density [46–48]. The Hall conductance of the QAHE is characterized by $\sigma_{xy} = Ce^2/h$. The QAHE differs from the QHE in the number of chiral edge states it exhibits (Figure 1.14). Materials exhibiting these states are referred to as Chern insulators. More broadly, these materials fall under the category of topological insulators due to their topological band structure.

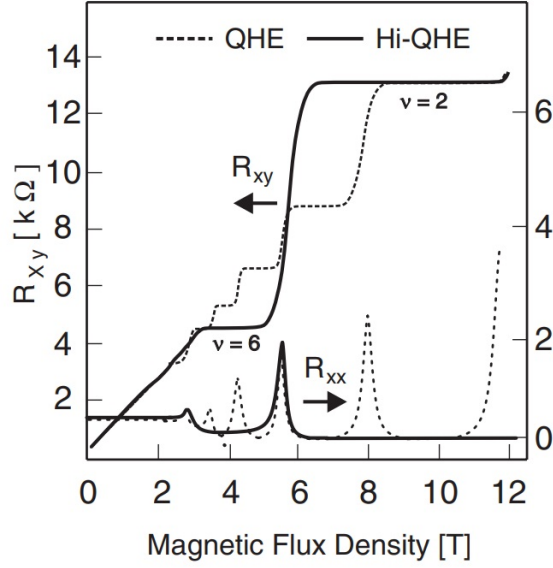


Figure 1.11: **QHE signature of SLG.** Comparison of the QHE in a conventional 2DEG (dashed line) and the case of graphene (solid line). Graphene LLs are fourfold degenerate, but the first LL is observed at $\nu=2$, namely the half-integer QHE. Adapted from IOP Publishing [39]

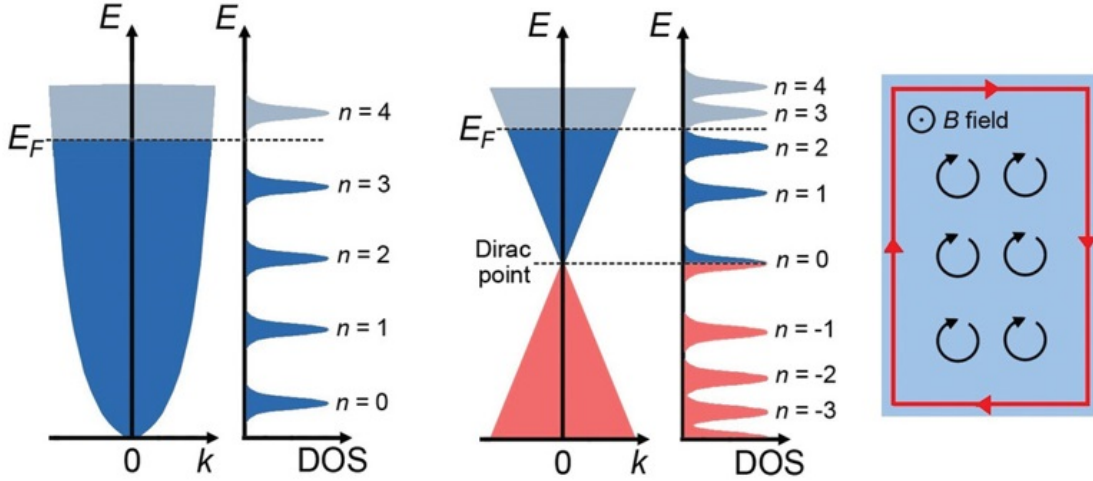


Figure 1.12: **Landau quantization** (a) in the case of a conventional 2DEG and (b) the case of a massless Dirac fermion. The energy spacing between Landau levels (LLs) $\Delta E_{LLs} = \hbar\omega_c$ where $\omega_c = qB/m^*$ for (a) and $\omega_c = \sqrt{2eB/\hbar}$ for (b). (c) A strip of conductive material is placed under a perpendicular magnetic field B . Carriers undergo cyclotron motion in the bulk of the material, with edges propagating unidirectionally. Adapted from John Wiley and Sons [44].

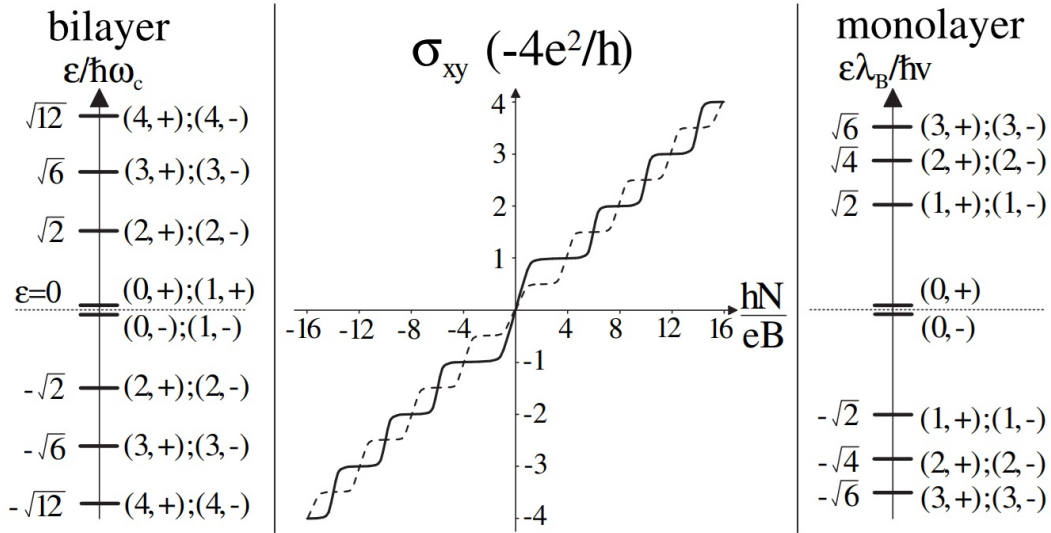


Figure 1.13: **Comparison of BLG and SLG's Hall signature.** LLs separation for BLG (left) and SLG (right), picturing the energy spacing of a 2DEG and a massless Dirac, respectively. Here ϵ correspond to E_N and the brackets (N, τ_z) the LL number N and the valley factor $\tau_z = \pm 1$. At its center, a comparison of the Hall conductivity σ_{xy} as a function of localized carrier density for BLG (solid line) and SLG(dashed line). Adapted from American Physical Society [20].

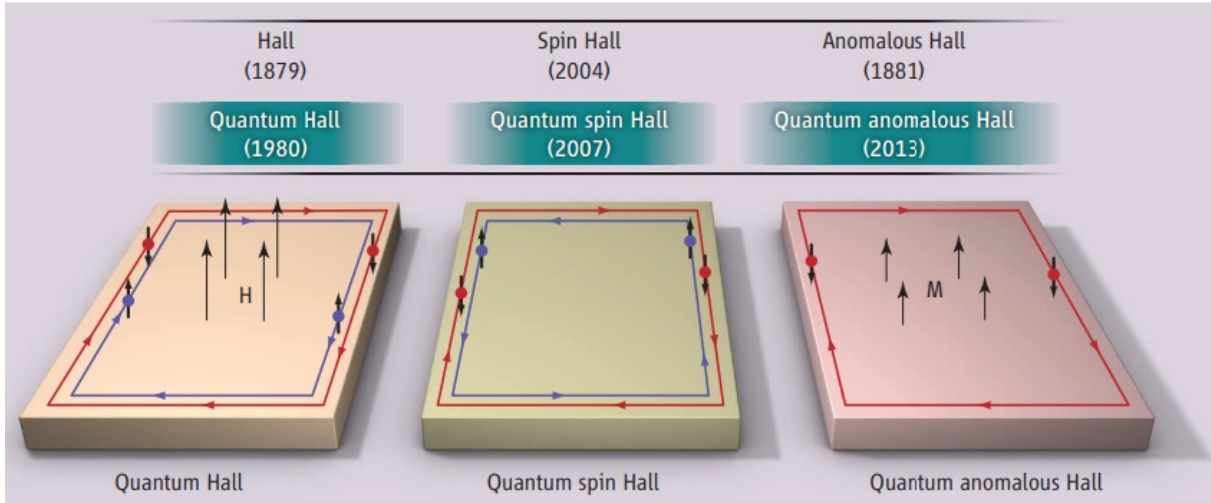


Figure 1.14: **Quantum Hall Trio.** Quantum Hall effect (right), Spin Hall Effect (middle), and Anomalous Hall effect (Left) with their respective discovery date. H and M design the exterior magnetic field B and the sample magnetization, respectively. Reproduced from The American Association for the Advancement of Science [45]

1.2 Motivation

Graphene exhibits a unique Hall signature, making it an ideal platform to study diverse quantum Hall states. However, the material’s quality often limits the study of these phenomena. This limitation arises mainly from the laborious synthesis and nanofabrication process, where graphene is subjected to various stresses and exposed to diverse sources of contamination. For quantum transport, even minor imperfections can affect the sample morphology and limit the carrier’s mobility.

Despite these challenges, the unique properties of graphene make it a promising candidate for applications in metrology, topological computation, and the discovery of exotic insulating phases. Precisely controlling Hall quantization in graphene could lead to significant advancements in these fields. For instance, graphene-based resistance standards in metrology could offer more accessible and cryogenic-free alternatives to the currently used Gallium Arsenide/Aluminium Gallium Arsenide (GaAs/AlGaAs) heterostructure. In topological computation, the unique electronic properties of graphene could enable the development of new device architecture, facilitating the manipulation of quantum dots (QDs). Additionally, exploring graphene’s Chern insulating and other topological phases could deepen our understanding of topological materials and pave the way for new technologies. Graphene’s potential in these areas hinges on overcoming the challenges associated with material purity and reproducibility. Advancements in synthesis techniques, such as CVD, are crucial for producing high-quality graphene.

1.2.1 Graphene-based Resistance Standard

Topological insulators have more robust insulating behavior than “conventional band material” [49]. The Hall resistance $h/e^2 = 25812.807 \, \Omega$, separating the Hall plateaus, is called natural resistance because it is found uniquely with the plank constant (h) and the electron’s charge (e). This phenomenon is interesting for metrology because this QHS is reproducible and stable in any 2DEG (or 2DHG) system as long as the system shows high charge carrier mobility. Based on its robustness, the QHE is now used to define the Ohms with 10^{-9} of uncertainty [50, 51]. Since 1992, Metrology laboratories have calibrated standard resistors using GaAs/GaAs heterostructure devices. Hartland et al. were the first to report a large calibration procedure based on the Hall plateau at $\nu = 2$ of GaAs/AlGaAs, the material currently used as resistance standard [52].

Due to its exceptional electronic properties, graphene has emerged as a promising candidate for developing next-generation quantum resistance standards. Traditional resistance

standards based on GaAs/AlGaAs heterostructures require stringent conditions to achieve high measurement accuracy [53]. However, graphene has the potential to provide more accessible and cryogenic-free resistance standards, assuming that high-quality SLG can be produced with large-scale homogeneity and reproducibility [39, 53, 54].

Metrological institutes use cryogenic current comparator (CCC) bridges to calibrate standard resistances with high accuracy, down to parts per billion (ppb) [39]. The CCC bridges utilize a superconducting quantum interference device (SQUID) to compare magnetic flux, where the magnetic field is proportional to the current, with exceptional precision. For graphene to be used effectively as a resistance standard, specific sample requirements must be met. Larger channels are needed to apply a larger critical current, which is necessary for accurate CCC measurements. Typically, large coverage of around 6000 μm with ohmic contact resistance lower than 10 ohms is desirable [55].

In 2015, Ribeiro Paulo et al. observed Hall quantization with an accuracy of 1×10^{-9} under more relaxed experimental conditions. This achievement was made at a temperature of 10 K and a magnetic field of 3.5 T, and the observation was sustained over a range of 10 T with currents up to 0.5 mA [53]. For comparison, GaAs/AlGaAs requires 10 T, 1.3 K, and 0.05 mA to achieve the same level of accuracy [56]. This significant improvement demonstrates graphene’s potential to operate under less stringent conditions while maintaining high precision.

Graphene demonstrates the Quantum Hall Effect (QHE) with exceptional precision. Nevertheless, several experimental challenges must be addressed to establish graphene as a reliable resistance standard. Achieving Hall quantization in graphene requires addressing several issues. First, substrate inhomogeneities, lattice defects, and contaminants must be minimized. Enhancements in the size and quality of graphene films are crucial for their use in metrology. A promising method to address this issue is encapsulating graphene with hexagonal boron nitride (hBN) [57].

In 2004, Novoselov and Geim first used mechanical exfoliation, known as the ”scotch-tape technique,” to isolate graphene layers from highly oriented pyrolytic graphite (HOPG) [10]. This method relies on weak interlayer Van der Waals forces compared to strong intralayer covalent bonding, allowing the separation of a single layer of the VdW material. The thin flakes are transferred onto the desirable substrate using dry transfer techniques. The graphene obtained by exfoliation is cleaner and has fewer impurities or defects, resulting in fewer scattering events. Using this method, researchers have achieved ultra-clean graphene with carrier mobility above $1,800,000 \text{ cm}^2/\text{Vs}$, encapsulated in hBN [58]. However, the scalability of mechanical exfoliations is limited, as flake sizes rarely exceed 1 mm^2 [59]. In its early discovery, graphene’s mobility was reported to be around $15,000 \text{ cm}^2 \text{ V}^{-1}$

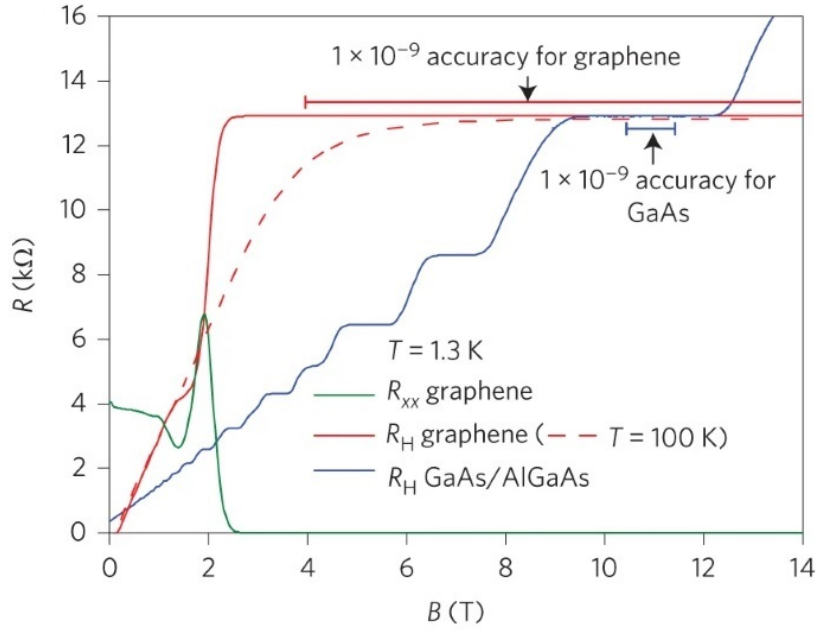


Figure 1.15: **Comparison of Hall quantization in graphene and GaAs/AlGaAs.** Hall plateau of GaAs/AlGaAs (Blue) at $T = 1.3$ K compared and, 100 K graphene (red) and associates SdH oscillations (green). Adapted from Springer Nature [53].

s^{-1} on a bare Si/SiO₂ substrate [60]. The highest mobility reported for exfoliated graphene is now above $350,000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at room temperature [61]. In the latter experiment, the SLG was encapsulated with WSe₂, a TMD, and hBN.

Since Novoselov’s advancements, researchers have explored other ways to isolate graphene. In 2009, Park S. and Ruoff R. S. reported the first high-quality graphene growth using CVD [62]. CVD-grown graphene offers extensive coverage, making it attractive for industrial applications. However, the material’s polycrystallinity is almost unavoidable. The grain boundaries, formed by merging graphene domains, create energetic barriers and increase the risk of scattering charge carriers [54]. Consequently, mobility in CVD-grown graphene is typically $5,000$ to $12,000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ when used on a bare substrate [63, 64]. Another disadvantage of CVD synthesis is the wet-transfer processes needed to transfer large graphene films. These techniques require the use of photoresists and strong oxidizing agents, compromising the material’s quality [63].

Higher mobility is usually observed in SLG single crystals, free of grain boundaries. For example, when SLG is encapsulated with hBN, the substrate inhomogeneities are reduced, and the carrier mobility can go as high as $37,000 \text{ cm}^2/\text{Vs}$ [57]. The highest reported mobility for single-crystal SLG is $150,000 \text{ cm}^2/\text{Vs}$ [57], achieved using a wet-

transfer technique. However, CVD techniques lack reliability in controlling nucleation sites and developing scalable. As a result, CVD-grown graphene requires greater reproducibility and uniformity before it can replace the current resistance standard [54, 63].

Nevertheless, graphene holds significant potential as the next-generation resistance standard. Its capability to operate at higher temperatures and potentially in cryogenic-free setups makes it an appealing candidate for future metrological applications. However, further progress in fabrication techniques and control over material contamination is essential for its widespread adoption in national metrology institutes (NMIs).

This master’s project aims to produce high-quality, low-defect (SLG) through chemical vapor deposition (CVD). As a high mobility carrier is required for observing quantized Hall plateaus, we aimed to synthesize SLG with mobility higher than $5000 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$. The project’s initial phase focuses on synthesizing SLG using low-pressure CVD (LPCVD) and thoroughly characterizing the material. Preliminary results from atomic force microscopy and Raman mappings are promising, demonstrating our ability to grow high-quality SLG. Following its synthesis, Hall devices were patterned and then characterized at low temperatures. We have not yet observed the QHE in our samples, but the transport characterization of these Hall devices remains in the early stages. The thesis is structured to reflect the project’s progression: Chapter 2 explains the LPCVD growth and characterization of the graphene films, Chapter 3 focuses on the fabrication of Hall devices, and Chapter 4 centers on their magnetotransport measurements.

1.2.2 Topological Computing and Chern Insulators

Topological quantum computation uses the robust topologically protected Hall state to protect the qubits, physical units storing quantum information, from local disturbances. This qubit is created by confining the 2DEG (or 2DHG) in 1D to form a QD. Carriers can be loaded and unloaded onto the QD to perform quantum manipulation. The spin-up and down of an electron are used as an analog to bits 1 and 0 of a classical computer. Another key element of these QD devices is the confinement charge carriers required to initiate, manipulate, and read out quantum states.

Due to the impossibility of confining carriers in SLG, BLG is generally considered for this application. BLG has long been considered a promising candidate for hosting spin qubits due to its high natural abundance and lightweight atoms. As a result, two primary decoherence mechanisms, spin-orbit coupling (SOC) and hyperfine coupling, are mitigated in graphene-based qubits [65].

Considerable advancements have been made regarding the controllability and the read-out of BLG single QD [42, 66–70]. Graphene QDs promise, in particular, to facilitate the device scalability by taking advantage of the graphene’s ambipolar nature to form p-n junctions as natural barriers between QDs. The case of a double and triple QD system has already been explored theoretically and shows promising results in terms of scalability [66, 71, 72]. Graphene QDs, in particular, hold the potential to enhance device scalability by utilizing graphene’s ambipolar nature to form natural p-n junction barriers between QDs. The theoretical exploration of a double and a triple graphene QD shows already promising results regarding its scalability [66, 71, 72].

Graphene valleys can be lifted when an external magnetic field is applied, unlike the valleys found in silicon. L. Banszerus et al. demonstrated that applying a perpendicular magnetic field ($B_{\perp}$) causes the loss of spin degeneracy, while an in-plane magnetic field $B_{\parallel}$ affects valley degeneracy, offering a wide variety of qubit manipulation techniques [71]. Using this distinctive aspect, a high-fidelity charge detection, above 99%, and spin T_1 relaxation times, with valley states relaxation times up to 500 ms, was achieved. These advancements and the development of models simulating tunneling and spin-orbit interaction (SOI) provide a solid foundation for the larger-scale implementation of BLG QD devices.

Pablo Jarillo-Herrero and his research team at MIT were the first to isolate magic-angle-TBG. They demonstrated the possibility of tuning its flat band and its superconducting states [25]. The study of TBG’s potential for hosting superconducting qubits is currently at the preliminary stage but ongoing.

Recently, researchers have focused on the fractional quantum anomalous Hall (FQAH) states in Moiré materials, which are predicted to host anyons: quasi-particles with topologically protected edge states, obeying non-Abelian statistics at zero magnetic fields. These non-Abelian anyons, such as Majorana fermions, have a unique property where the sequence of their exchange affects the system’s quantum state. This property is promising for quantum computation because it enables qubit manipulation that is inherently robust against errors, offering a pathway to fault-tolerant quantum computing [73]. In early 2024, Long Ju et al. were the first to report a fractional quantum anomalous Hall state in rhombohedral pentalayer graphene–hBN Moiré superlattice, proving possible to realize such states in graphene systems [74]

Our collaboration with Professor Usha’s group from the Indian Institute of Science has given us an opportunity to observe and characterize these states in graphene. They provided us with a TBG stack-WSe₂ Hall bar device to perform magnetotransport characterization in high magnetic fields. This unique architecture combines the strongly correlated

systems found in Moiré superlattices and the SOC induced by the TMD, thus increasing the likelihood of forming Chern insulating phases. While this study did not reveal these topological phases, the characterization of this device is an important component of this master's research project, and therefore, chapter 5 of this thesis will cover a comprehensive analysis of its magnetotransport properties.

Chapter 2

Chemical Vapor Deposition Synthesis of Graphene

2.1 Single-Layer Graphene Synthesis

The Quantum Nano-Fabrication Center (QNFCF) has an LPCVD system capable of growing large-area SLG. The Angstrom Engineering LPCVD system consists of an 8" diameter quartz chamber designed for a 6" diameter wafer and can be modified for smaller samples. In such cases, an inner quartz tube of 2" diameter partially covered with molybdenum foil is placed inside the main chamber. The sample is usually positioned inside a quartz boat in this inner tube. Gases such as argon (Ar), methane (CH_4), and hydrogen (H_2) are introduced using mass flow controllers (MFCs). These gases are mixed before being injected into the chamber and pumped out of the system with a mechanical pump, which also serves to control the chamber's pressure. The growth chamber is surrounded by heating and cooling components, allowing temperature control up to 1100°C and rapid cooling. Finally, growth recipes are created and managed using the Aeries Angstrom software.

LPCVD provides a low-pressure environment known to obtain cleaner materials with low impurities. Additionally, the low-pressure environment promotes uniform SLG coverage, whereas other CVD techniques, such as atmospheric pressure chemical vapor deposition, generally result in few-layer graphene [75]. Parameters such as grain size, morphology, and the number of layers must be controlled to obtain high-quality graphene. Controlling the reaction is the critical element in obtaining large SLG crystal domains. The primary reaction mechanism responsible for graphene growth on a metallic substrate at high temperatures includes surface-mediated growth, which dominates for metallic substrates with low carbon solubility like Copper (Cu), and the segregation and precipitation of carbon

species, which dominates for metals with high solubility [76]. We use Cu as a metallic substrate for its low carbon solubility. The process of synthesizing graphene involves five key steps:

1. Dehydrogenation of carbon species, mainly through gas-phase reactions
2. Absorption and dehydrogenation on a metal surface
3. Diffusion of active species on or in the metal surface
4. Nucleation on the metal surface
5. Lateral growth of graphene grains

The first two steps are competing mechanisms for the dehydrogenation of carbohydrates, with gas reactions being further promoted when a metallic substrate with low carbon solubility is used. Nucleation of the crystals begins when carbon species near the substrate surface reach a sufficient size and possess enough energy to overcome the substrate's energy barrier. The reaction continues as long as carbon species are available or the graphene edges are dehydrogenated [76].

The QNFCF has a standard operational procedure for growing SLG on a Cu substrate. We use Cu foil 25 microns thick 99.98 % trace metal basis bought from Sigma-Aldrich. Before loading the substrate for growth, the oxide layer is etched using a glacial acid acetic purchased from Fisher Scientific. The foils are cut in pieces of 1" by $\frac{1}{3}$ ", cleaned, and sealed in a bag for their transportation. This step is realized a few hours before starting the growth as the Cu surface will re-oxidize over time.

Copper foils are placed at the bottom of the quartz boat and then loaded in the growth chamber. The growth recipe proposed by the QNFCF is structured in 6 steps:

1. Initial flush of the chamber
2. Ramp-up to the annealing temperature
3. Annealing of the metallic substrate
4. Ramp-up to growth temperature
5. Growth
6. Cooling to room temperature.

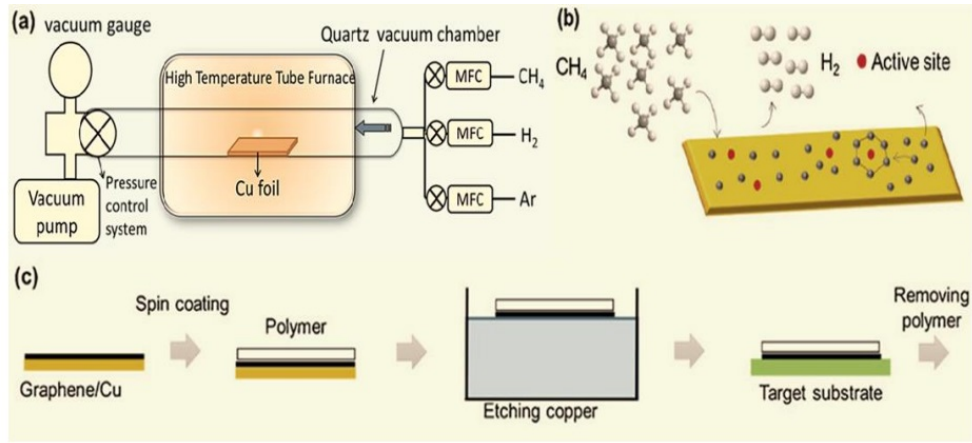


Figure 2.1: **CVD-graphene synthesis process.** (a) The CVD reaction chamber shows the injection of gases using MFCs, their travel to the chamber, and their subsequent pumping out of the system. (b) The growth mechanism on a metallic substrate reveals the metal's active site in red, with hydrogen and carbon atoms pictured in white and gray, respectively. (c) Description of wet-transfer process. First, PMMA-A4 is spin-coated on graphene, and the Cu layer is then etched with ammonium persulfate (0.5M). Following this, the graphene is transferred onto the Si/SiO₂ substrate, and the polymer is removed using Remover PG. Reproduced from Multidisciplinary Digital Publishing Institute [77]

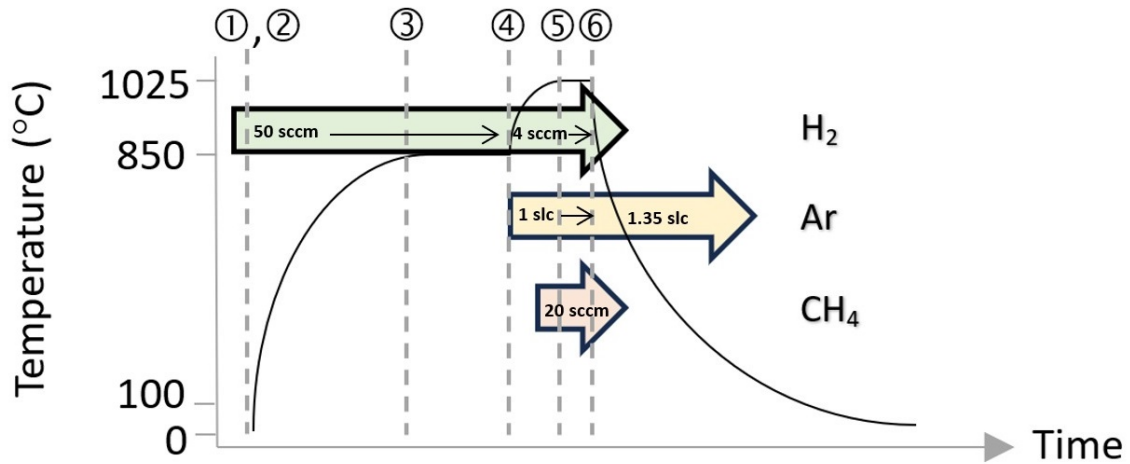


Figure 2.2: **Reference growth recipe.** Step (1) and (2) flushing step and then ramp-up to the annealing temperature of 850°C with an H_2 flow is kept at 50 sccm. Step (3) annealing, where the same parameters are maintained for 30 minutes. Step (4) ramp-up to the growth temperature of 1025°C with an Ar flow of 1 slc and the H_2 flow reduced to 4 sccm. Step (5) growth, begins by introducing 20 sccm of CH_4 and lasts 10 minutes. Step (6) Cool down. Shut down the CH_4 and H_2 flow but increasing the Ar flow to 1.35 slc.

First, particles that may have entered during boat loading (Figure 2.1) must be eliminated. The following step is to ramp up the temperature to 850°C using 50 sccm of H_2 . This temperature and gas settings are maintained for 30 minutes during the annealing step to eliminate volatilized residues [78, 79]. This lower-temperature annealing phase cleans the copper surface and segregates it from unwanted compounds before the growth stage. Then, the temperature is increased to 1025°C under 4 sccm of H_2 and 1 slc of Ar. These conditions are sustained for approximately 2 hours before introducing any carbon source into the reactive chamber. This higher-temperature annealing step encourages Cu surface recrystallization and promotes the (111) crystallographic orientation necessary to reduce defects within the Cu lattice [80]. The growth phase begins with the introduction of 20 sccm of CH_4 and 4 sccm of H_2 (25 mTorr and 5 mTorr respectively). These conditions are maintained for 10 minutes without altering the flow of Ar. Once the growth is complete, the system is rapidly cooled to 600°C , with the argon flow increasing to 1.35 slc. The most time-consuming step is gradually cooling to room temperature, which can take up to 24 hours. Ar flow is finally halted as the chamber reaches room temperature.

The first growth using the QNFCF reference recipe was performed to assess graphene quality. It was observed that graphene’s domains were separated from each other, which is unsuitable for our intended application, where uniform coverage is essential. Consequently, improvement regarding the growth recipe was needed to enhance graphene coverage and uniformity. New growth recipes were, therefore, developed with modified parameters such as growth temperature and partial pressure of reactive gases.

An initial growth was conducted without any modifications to the established process and serves as a reference for subsequent trials. The second growth was carried out at an elevated growth temperature, transitioning from 1025°C to 1070°C , to enhance carbon solubility and reduce the nucleation density, resulting in bigger grain size [75, 79, 81] (Figure 2.2). However, due to an instrument offset, the growth temperature was actually 1100°C , exceeding Cu’s melting point (Figure 2.3). This growth was thus realized using a metallic substrate in a liquid phase. For the last trial, the Cu foils were curved in the quartz boat to see if the disposition would impact the crystal structure. All other parameters of this growth were kept similar to the reference growth presented in Figure 2.2. To facilitate the understanding, graphene resulting from the different growth recipes will be presented in Table 2.1.

The Cu foil is removed from the growth chamber and etched using a wet transfer technique. First, a poly-methylmethacrylate-A4 (PMMA) layer is spin-coated onto the grown graphene and allowed to dry overnight. The PMMA supports the graphene film during the transfer. A 0.5M solution of ammonium persulfate (98%, Sigma-Aldrich) is

Table 2.1: Acronyms for different growth recipes.

CVDREF	CVDHT	CVDCV
Reference growth	Growth completed on a liquid substrate	Growth completed on a curved substrate

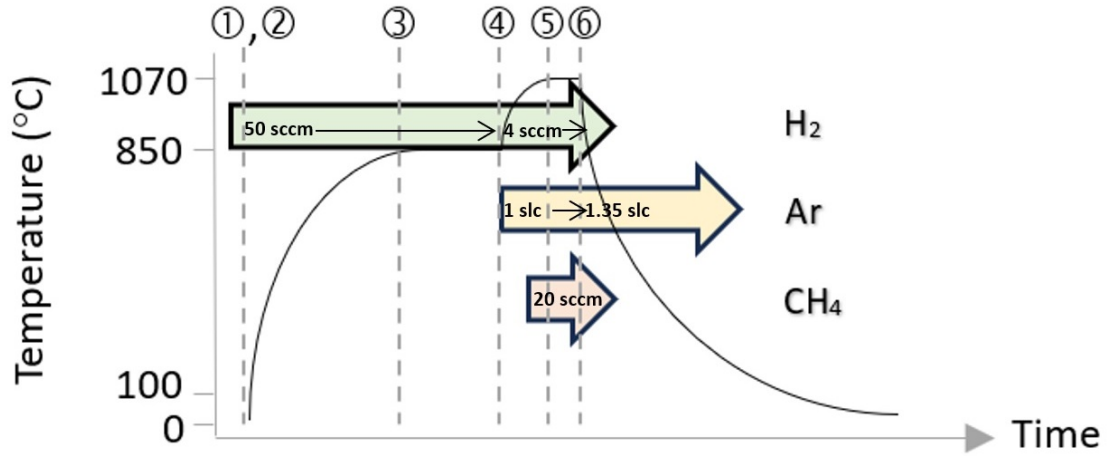


Figure 2.3: **High-temperature growth recipe.** Step (1) and (2): flushing step and then ramp-up to the annealing temperature of 850°C with an H_2 flow is kept at 50 sccm. Step (3): annealing, where the same parameters are maintained for 30 minutes. Step (4): ramp-up to the growth temperature of 1070°C with an Ar flow of 1 slc and the H_2 flow reduced to 4 sccm. Step (5): growth begins by introducing 20 sccm of CH_4 and lasts 10 minutes. Step (6) Cool down. Shut down of the CH_4 and H_2 flow but increase the Ar flow to 1.35 slc.

prepared to etch the Cu foil. The graphene is put with the PMMA side up and left with the Cu side until the metallic substrate was barely or no longer visible. The film is rinsed and then transferred onto a Si/SiO_2 substrate of approximately 1 cm^2 . The sample is dried vertically, and the polymer is washed with acetone, rinsed in isopropyl alcohol (IPA), and deionized water (DI). The substrate is selected to have a thick oxide layer of $\approx 300\text{nm}$ and low resistivity, in our case $0.001\text{-}0.005\Omega \cdot \text{cm}$, to be usable as a back gate in the future device architecture. The Si/SiO_2 wafer is dice into pieces measuring $1.2\text{ cm} \times 1.2\text{ cm}$ and cleaned before transferring the graphene film.

2.2 Material Characterization

The SLG characterization involves several methods: atomic force microscopy (AFM) to measure the material's thickness, Raman spectroscopy to assess its electrical properties, and optical microscope pictures for visual examination.

The samples were first characterized using Raman spectroscopy. Graphene's Raman spectrum exhibits three prominent bands: the D band ($\approx 1350\text{cm}^{-1}$), the G band ($\approx 1580\text{cm}^{-1}$) (Figure 2.4(a)), and the 2D band ($\approx 2700\text{cm}^{-1}$). The G band corresponds to the in-plane vibration of the carbon ring. In contrast, the 2D band corresponds to the breathing of the carbon ring, both providing valuable insights into the graphene's transport properties. The 2D peak is associated with the E_{2g} Raman active phonon mode at the center of the FBZ. This is a first-order Raman process involving the scattering of a single phonon. The D peak is associated with the a_{1g} vibrational mode at the K point of the FBZ. This is a second-order Raman process involving two-phonon scattering, which leads to more complex spectral features (Figure 1.3(b)). The ratio of the intensity of the 2D band compared to the G band ($I(2D)/I(G)$) can be used to determine the number of graphene layers and provide information about the material's electrical properties (Figure 2.5). Similarly, the presence and the intensity of the D band ($I(D)/I(G)$) offer insights into the material's defect density. This peak is also associated with the A_{1g} vibrational mode but requires the activation of a defect. Therefore, this band is absent from the pristine graphene sample. The G and D bands' intensity ratio indicates the material's quality.

A Renishaw Raman Spectrometer equipped with a 532nm wavelength laser and a 2400l/mm grating was used for the analysis. The samples were mapped over an area ranging from 60 to $150\text{ }\mu\text{m}^2$ at 900 points, with specific instrument settings including a 10% laser intensity, 2 seconds of exposure time, and 2 acquisitions, using a $50\times$ objective. Raman spectra were acquired within two ranges: 1300 to 1800 cm^{-1} covering the D and G

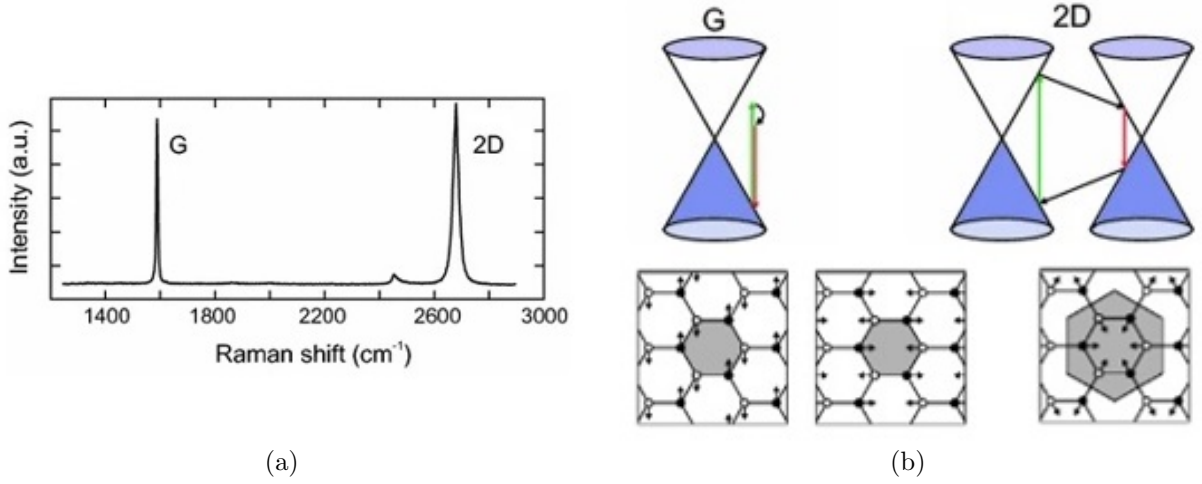


Figure 2.4: **Dominant Raman active SLG phonon modes.** (a) SLG Raman spectra (b) Raman processes responsible for the G and the 2D band. The green arrow represents the excitation process, and the red arrow, the relaxation process. The G peak corresponds to 2 A_{1g} vibrational modes and the 2D band to the E_{2g} vibrational mode. Adapted from Springer Nature [82] and Multidisciplinary Digital Publishing Institute [15].

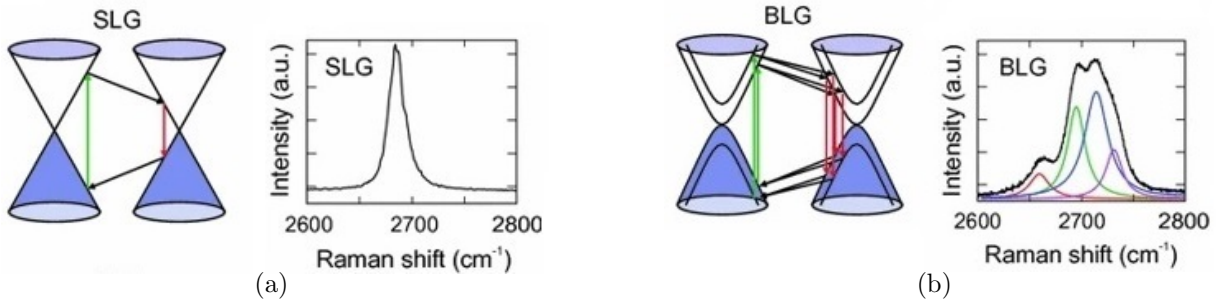


Figure 2.5: **SLG and BLG double phonon scattering process.** (a) SLG 2D band structure is characterized by its narrowness (b) Deconvolution of BLG 2D band reveals 4 sub-bands due to the additional antisymmetric process, resulting in the broadening of the 2D band. Adapted from Springer Nature [82]. excitation process and the red arrow, the relaxation process.

bands, and 2400 to 2800 cm^{-1} covering the 2D band. The acquired data are reprocessed to remove cosmic rays and perform baseline correction using the acquisition software WiRE.

Criteria were implemented to assess graphene’s quality based on the Raman mapping of the samples. It is well-established in the community that high-quality single-layer graphene (SLG) presents a $I(2D)/I(G)$ band ratio of > 2 with 2D band full-width-half-maximum (FWHM) $< 35cm^{-1}$ and is therefore used as the first indication of high-quality graphene cm^{-1} [79, 83]. The third criterion concerns the defect density, determined using the intensity ratio of D/G peaks. A threshold value of $I(D)/I(G) > 0.1$ considers the material to have low defect density.

Figure 2.6 shows the Raman spectra of CVD-grown graphene and displays the three characteristic bands of graphene. The top spectrum exhibits a sharp 2D band with 2D band FWHM = 31.8 cm^{-1} and is 2.2 times smaller than the G band. In this specific region, an intensity ratio of 0.7 for the D/G band indicates the presence of defects. The bottom spectra display a wider 2D band, with 2D band FWHM = 41.7 and an $I(2D)/I(G)$ band ratio of 1. A minor defect peak is detected with an $I(G)/I(D)$ band ratio of 0.1. The fitting of the peaks was realized using Python, which was used to map the $I(2D)/I(G)$, 2D band FWHM, and the $I(G)/I(D)$ band intensity ratio across the sample. Appendix A covers the data reprocessing more extensively.

These spectra introduce the color scale used following mapping to characterize the sample’s quality. The color purple is used with smaller ratios or 2D band FWHM values and higher values to yellow. For example, the maximum value for the $I(2D)/I(G)$ band ratio is 4, and 1 for the $I(G)/I(D)$ band ratio will appear yellow on the mapping.

The CVDREF mapping is illustrated in Figure 2.7. The graphene crystals are barely visible, with only 13% with $I(2D)/I(G)$ ratio greater than 2, and with FWHM under 35 cm^{-1} . The central regions with the highest quality also exhibit a low-defect area with an $I(D)/I(G)$ ratio of less than 0.1. These graphene domains have an irregular shape with random coverage.

The CVDHT mapping is shown in Figure 2.8. The characteristic dendritic shape of the crystal domains contrasts with the substrate and is discernable from in $I(2D)/I(G)$ mapping. About 83% of the spectra show an $I(2D)/I(G)$ band ratio above 2, with the majority above 3.5. The center of the crystals shows a different profile with an $I(2D)/I(G)$ ratio under 2. The FWHM mapping reveals that a majority of graphene coverage has FWHM under 36 cm^{-1} , with the center of the crystal showing a wider 2D band at approximately 70 cm^{-1} . The graphene isn’t pristine based on the $I(G)/I(D)$ band ratio mapping.

In the case of CVDCV, the mapping is shown in Figure 2.9. The crystal features of the

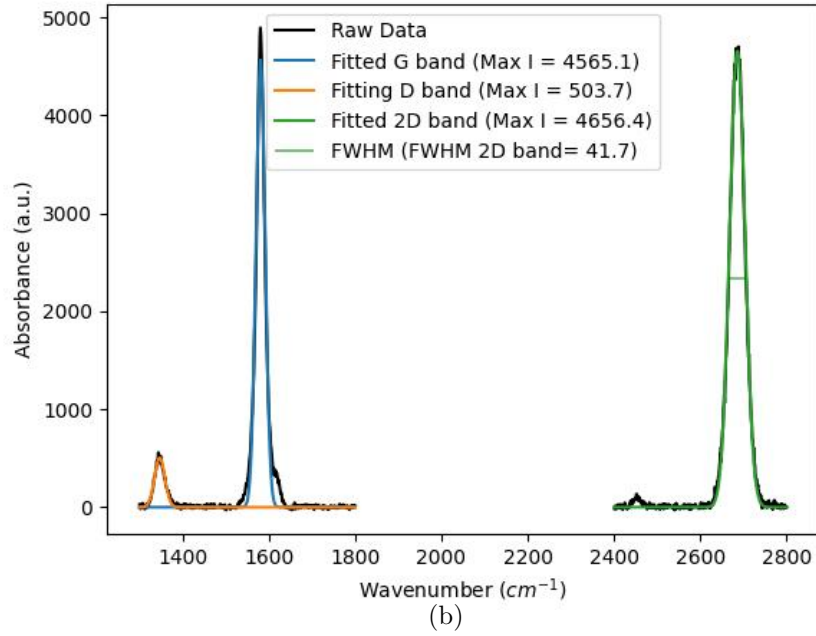
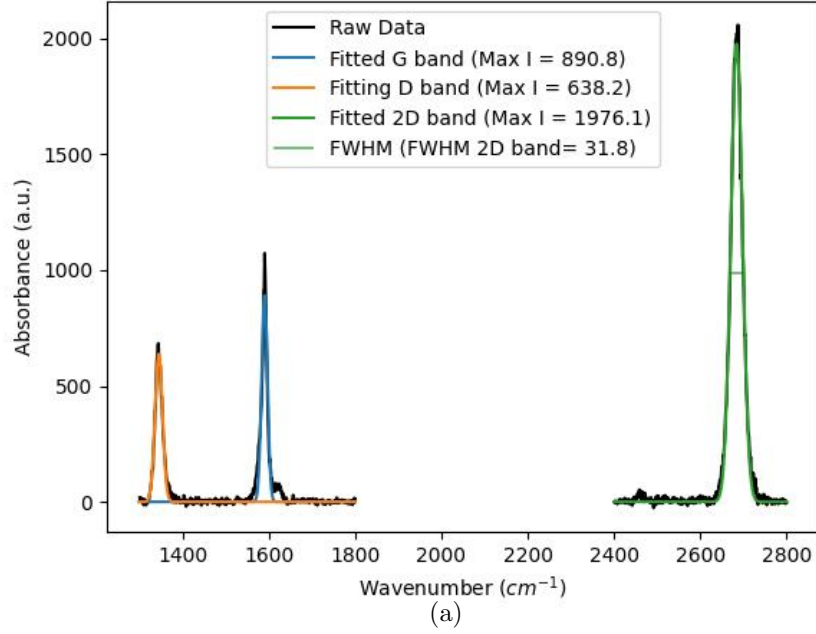
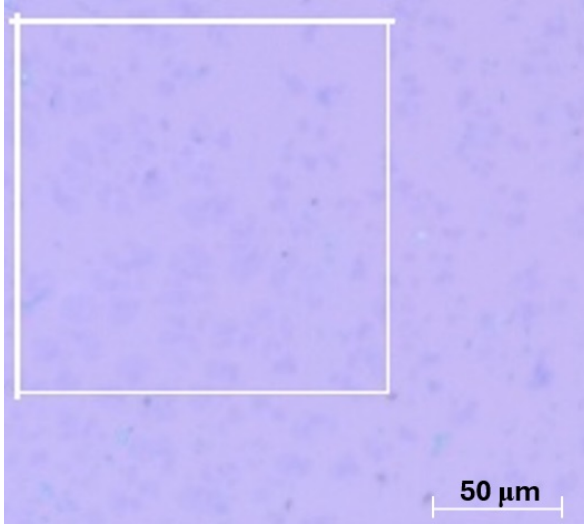
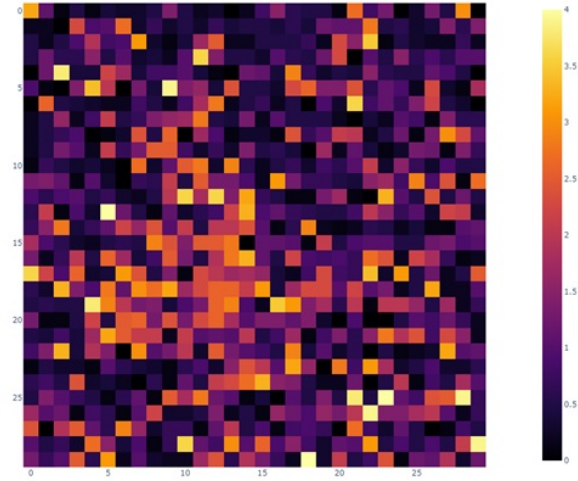


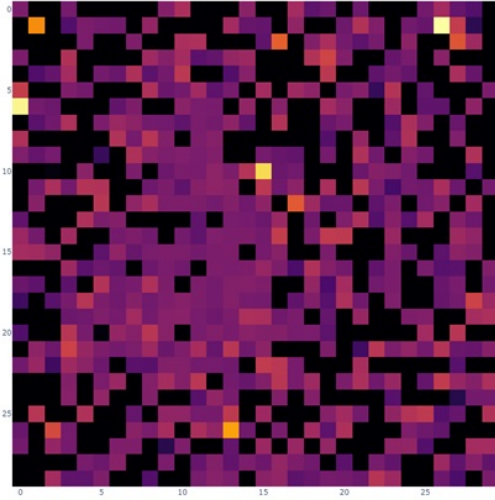
Figure 2.6: **SLG Raman spectra.** (a) From CVDCV sample - $I(2D)/I(G)$ band ratio of 2.2 with 2D band FWHM of 31.8. The $I(D)/I(G)$ band ratio of 0.7. (b) From CVDHT sample - $I(2D)/I(G)$ band ratio of 1.0 with 2D band FWHM of 41.7. The $I(D)/I(G)$ band ratio of 0.1. All spectra are acquired with 10% laser intensity, 2 seconds of exposure time, and 2 acquisitions.



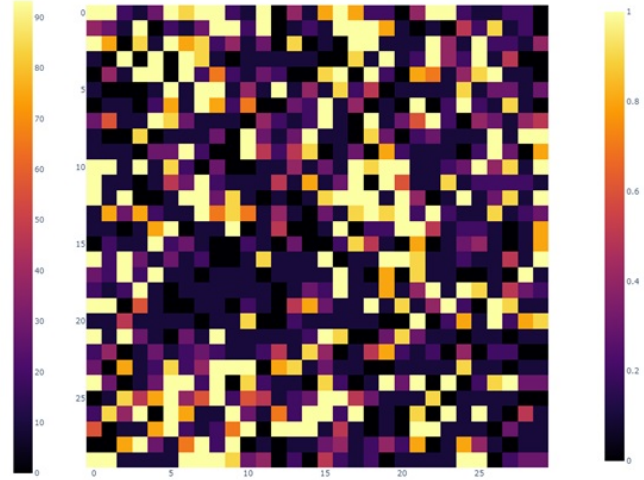
(a) Picture of the mapped region



(b) $I(2D)/I(G)$ band ratio

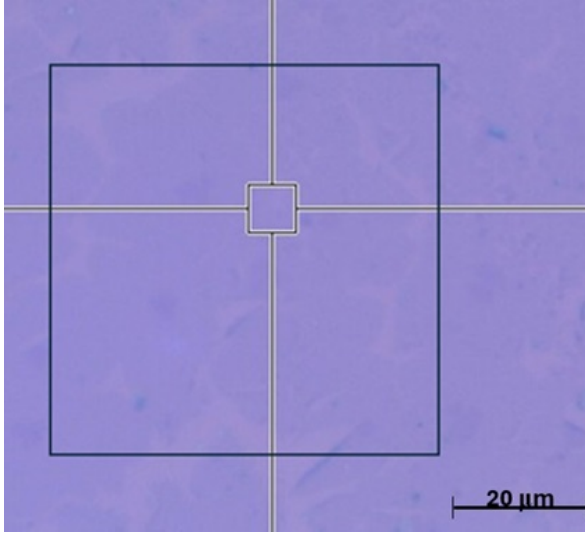


(c) FWHM

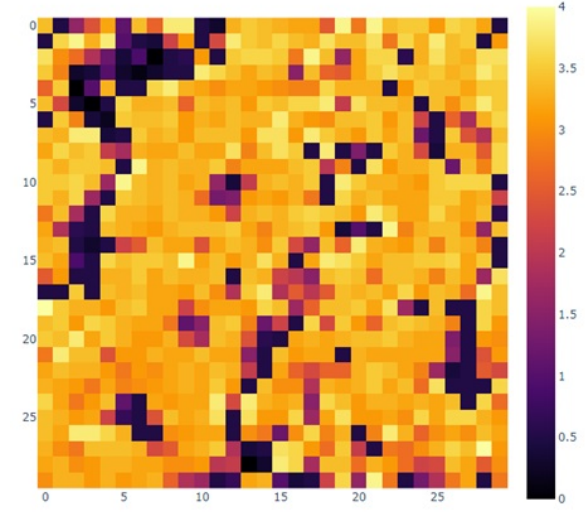


(d) $I(D)/I(G)$ band ratio

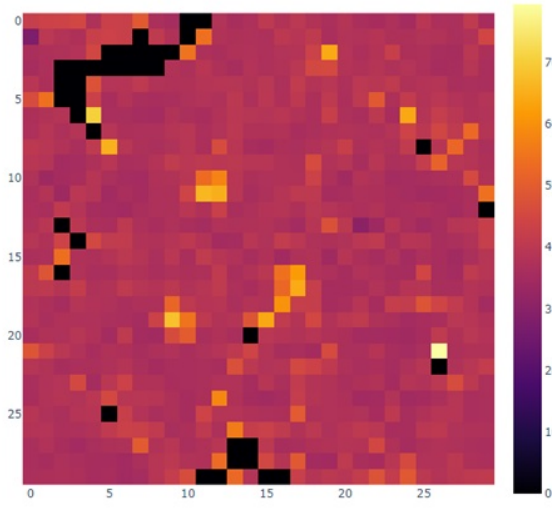
Figure 2.7: **CVDREF Raman mapping.** (a) Picture of the mapped region. (b) $I(2D)/I(G)$ band ratio. (c) FWHM. (d) $I(G)/I(D)$ band ratio. 900 (30×30) spectra are acquired over $150 \mu m^2$.



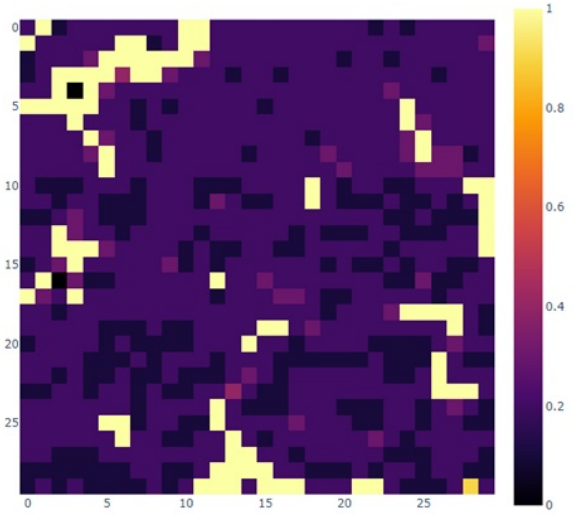
(a) Picture of the mapped region



(b) $I(2D)/I(G)$ band ratio

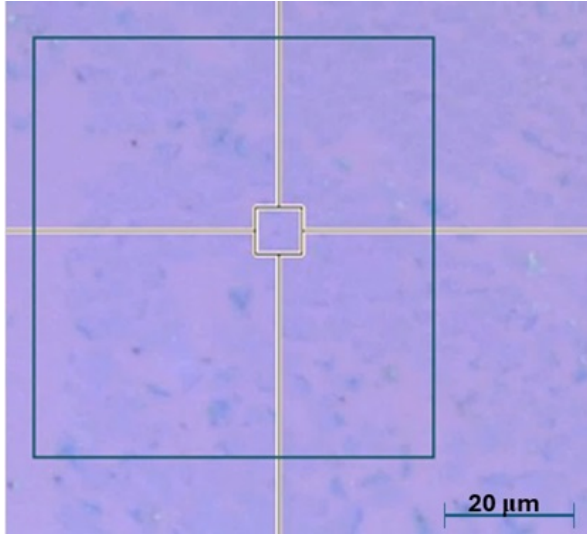


(c) FWHM

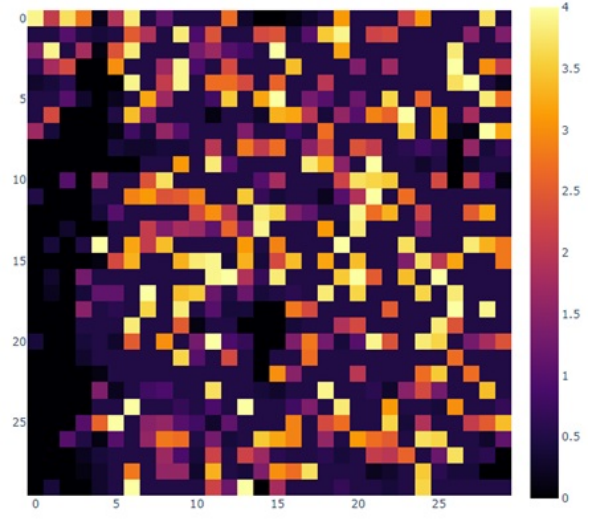


(d) $I(D)/I(G)$ band ratio

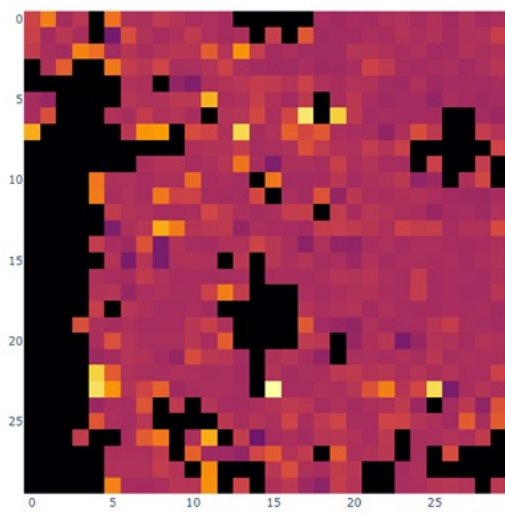
Figure 2.8: **CVDHT Raman mapping.** (a) Picture of the mapped region. (b) $I(2D)/I(G)$ band ratio. (c) FWHM. (d) $I(G)/I(D)$ band ratio. 900 (30×30) spectra are acquired over $60 \mu m^2$.



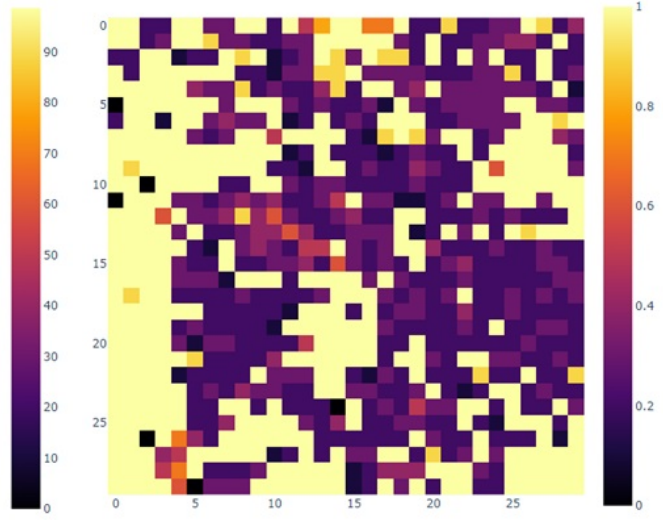
(a) Picture of the mapped region



(b) $I(2D)/I(G)$ band ratio



(c) FWHM



(d) $I(D)/I(G)$ band ratio

Figure 2.9: **CVDCV Raman mapping.** (a) Picture of the mapped region (b) $I(2D)/I(G)$ band ratio (c) FWHM (d) $I(G)/I(D)$ band ratio. 900 (30×30) spectra are acquired over $60 \mu m^2$.

graphene are less recognizable than in the previous growth, with a considerably varying $I(2D)/I(G)$ band ratio, where 29% of the spectra have a graphitization ratio above 2. The FWHM profile of the 2D band is similar to the previous mapping at around 36 cm^{-1} , with regions on the edge sometimes showing FWHM approximately 75 cm^{-1} . Looking at the graphene domain, the $I(G)/I(D)$ band ratio is overall more significant than in the previous sample, with the D band, on average, three times smaller than the G band.

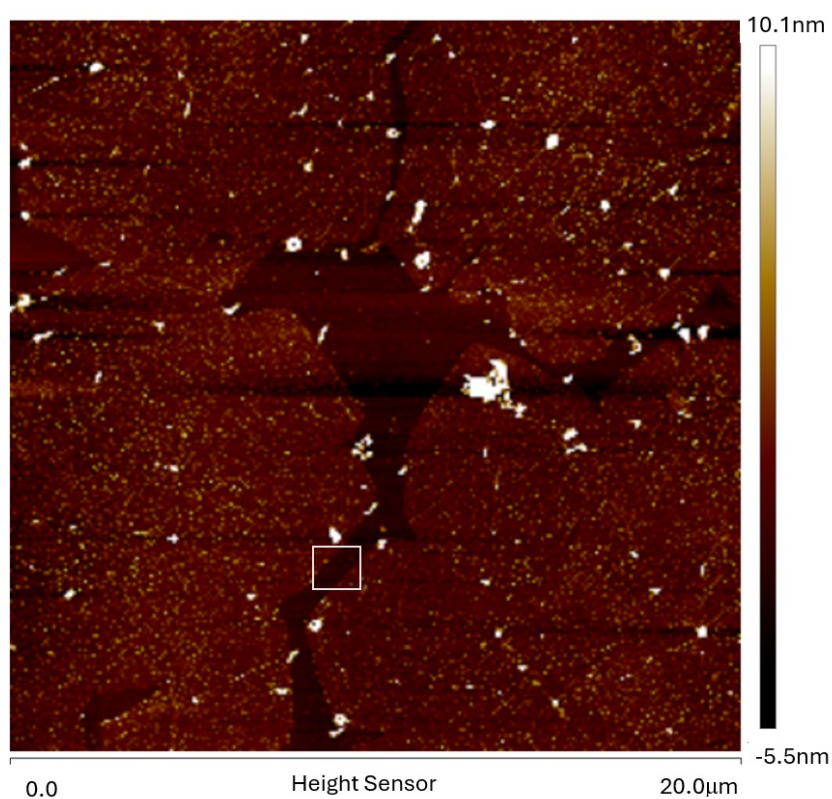
Atomic force microscopy (AFM) can measure features as small as the angstrom range. This instrument operates by bringing a cantilever close to the substrate, enabling it to sense any interactions between the tip and the surface, such as van der Waals forces. A laser is used to calibrate the initial position of the cantilever, allowing the photodetector to detect any deviations from this position. As the stage scans the material's surface, the AFM tip deflects when encountering any height variation, and this information is used to create a high-resolution topographical map of the sample surface.

The Bruker Icon Atomic Force Microscope in ScanAsyst-air mode is used to analyze the properties of grown graphene. This model is derived from tapping mode, with a retroactive loop adjusting the tapping parameters during scanning to enhance sensitivity. A more extensive section of $\approx 20\mu\text{m}^2$ of 251 lines with a rate of 0.5Hz is initially selected, followed by a smaller section of about $1\text{-}4\mu\text{m}^2$, where the scan is averaged over three times. The data are then reprocessed in the NanoScope Analysis software, where the surface is first flattened before using the section tool to analyze and measure specific features.

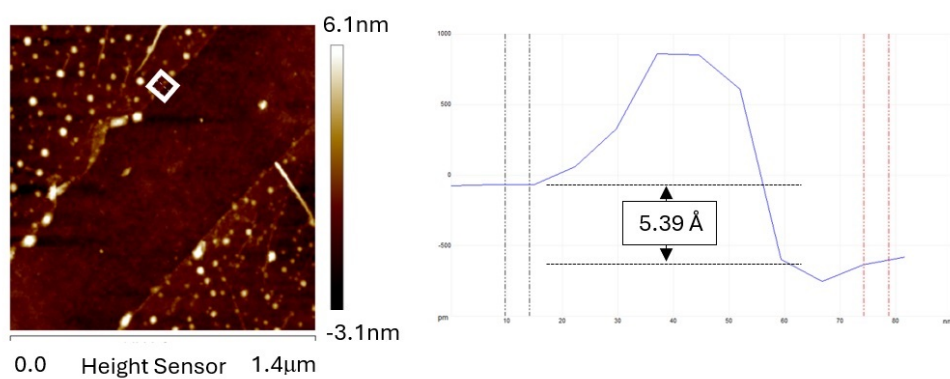
The theoretical thickness of SLG is approximately $3.4\text{ \AA}$, equivalent to twice the carbon-carbon bond length or the interlayer spacing in graphite (0.335 nm) [84]. However, experimentally measured thicknesses typically range from 0.5 nm to 1 nm [10, 84]. These discrepancies arise due to the unavoidable interactions between the graphene, substrate, and AFM tip, which can introduce an additional height offset of around 0.4 nm [84]. For BLG, the expected theoretical thickness is $\approx 6.7\text{ \AA}$, but reported measurements generally range from 1 nm to 1.6 nm [10].

Figure 2.10 shows the AFM height profile scan of CVDHT, where a height of $5.39\text{ \AA}$ is measured at the crystal's edge. No discernible step is detected in the nucleation centers, which are identified as multilayer regions through Raman spectroscopy. This observation was consistent across multiple crystals. Figure 2.11 presents the AFM height profile of CVDCV, showing a step height of $7.77\text{ \AA}$. Both samples exhibit a significant presence of contaminants on the graphene surface.

The $2D/G$ and FWHM mapping confirms the presence of regions of single-layer graphene (SLG) with high quality ($I(2D)/I(G) > 2$) for all growths. What sets them apart is the

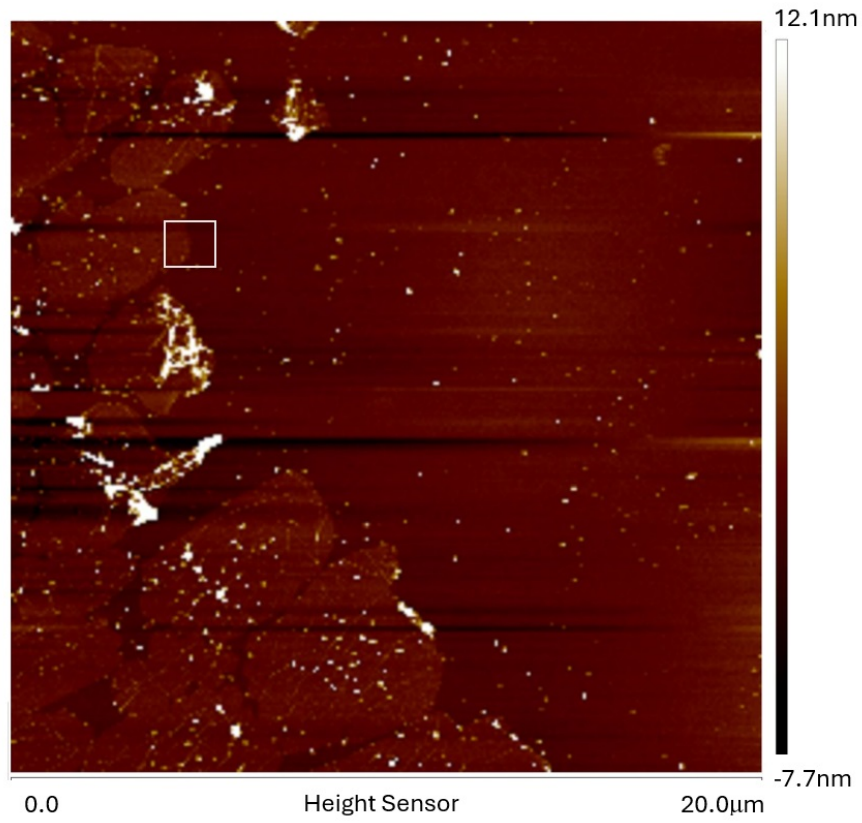


(a)

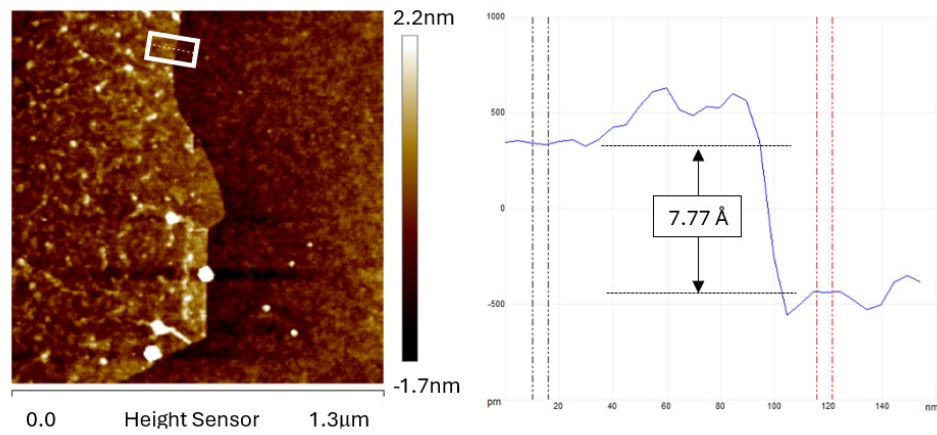


(b)

Figure 2.10: **CVDHT AFM images and height profile.** (a) AFM image of $20\mu m^2$. (b) AFM image of crystal edges of $1.4\mu m^2$. Height profile of the region delimited by the white square.



(a)



(b)

Figure 2.11: **CVDCV AFM images and height profile.** (a) AFM image of $20\mu m^2$ (b) AFM image of crystal edges of $1.3\mu m^2$. Height profile of the region represented by the white square.

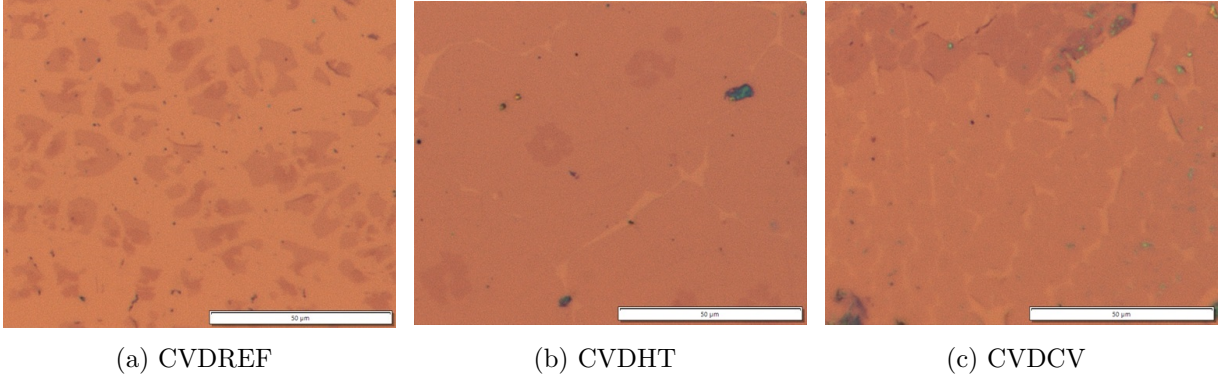


Figure 2.12: **Graphene growth microscope picture.** (a) CVDREF. The graphene crystals have an irregular shape, as if they were damaged during the process. (b) CVDHT. The crystal domains are large ($> 25\mu m^2$) with a dendritic shape. (c) CVDCV. The crystal domains are small ($< 10\mu m^2$) with shape resembling hexagons. All picture where taken at 100x magnification.

crystal domains' coverage and uniformity differences. Some mappings show almost no defects compared to others, where the defect band dominates the spectrum, even if the graphene comes from identical growth sequences. These defects could result from the chemical doping caused by PMMA but are essential for the wet transfer of graphene. Since SLG is one of the thinnest materials, measuring values in the Å with high accuracy is challenging [84]. Both graphene films exhibit AFM height profiles that fall within the reported thickness range for SLG, confirming the presence of SLG regions suitable for our application.

Figure 2.12 compares each growth at a magnification of 100x. At low magnification, PMMA residues with numerous cracks and ripples from the wet transfer are visible in all growths. The crystal domains lack grain boundaries, have an area of ≈ 7.5 to $10 \mu m^2$, and spacing of ≈ 2 to $10 \mu m^2$. The crystals appear irregular and appear to have been etched. Some growths show nearly absent or uneven graphene. The second growth, completed with Cu in a liquid phase, exhibits a different dendrite shape and large crystals of ≈ 25 to $30 \mu m^2$, forming several polycrystalline domains. A darker color at the crystal's nucleation center indicates a multi-layer region, as less light passes through the material [85]. The last growth resulted in crystal shapes resembling hexagons with crystal domains of approximately 1 square micrometer and sometimes forming polycrystalline domains. These crystals are ≈ 5 to $10 \mu m^2$ in size. Due to insufficient coverage, no graphene resulting from the reference growth was used for further characterization. Appendix B contains additional optical microscope pictures with 2.5x, 10x, 20x, and 50x magnifications for all growth completed.

2.3 Discussion

When observing a picture of the reference growth, most of the crystals appear randomly on the substrate and seem to have been etched. Interestingly, these features are absent in other growth, which denotes an inconsistency between growths. According to Le Chatelier’s principle, it is possible that the edges of graphene crystals are being etched in a hydrogen-rich environment to reform methane [86]. Another probable cause is the presence of impurities, like oxides, in the gases [76]. Considering the poor hydrogen environment used in our process, these results suggest contamination of the growth chamber with oxides. As none of the gas flow changes, further investigation is needed to understand the sources of contamination or other possible causes responsible for the material’s etching.

The catalytic decomposition of Cu is enhanced at high temperatures $\approx 1000^{\circ}\text{C}$ but remains endothermic for complete dehydrogenation. As a result, this reaction is unfavorable and leads to an increase in gas-phase reactions. When there is a high ratio of $\text{CH}_4 : \text{H}_2$, methane dehydrogenation becomes the preferred reaction, resulting in the formation of high concentrations of carbon species with a greater potential for forming multilayer graphene [76]. This was observed during the second growth on a liquid substrate. The darker shade at the crystal’s center exhibits the characteristics of BLG with $I(2\text{D})/I(\text{G}) < 2$ and FWHM double SLG’s FWHM. The AFM height profile did not capture any steps at the crystal center. Increased concentrations of carbon species generally lead to bottom-up graphene layer formation. Alternatively, the inverted case can occur, where the second layer is grown from the top down, but usually involves the absorption and diffusion of carbon species underneath the layer, which is feasible when the graphene coverage is high [76]. The absence of detected steps here suggests the latter mechanism. Graphene crystals grown on liquid substrates are known for their uniform nucleation density with large nucleation sizes, up to $10000\mu\text{m}^2$, and the particular absence of grain boundary formation [87–89]. The mapping reflects this particularity with an $I(2\text{D})/I(\text{G})$ ratio exceeding 3.5. This homogeneity extends over large areas of the crystal. These crystals exhibit a dendritic shape, which is more pronounced compared to other single-layer graphene (SLG) crystals but is nevertheless expected under reactive conditions with a high ratio of $\text{CH}_4 : \text{H}_2$.

There is a need for improvement regarding crystal shape, size, and, particularly, the repeatability of the process. One critical point that requires attention is the contamination of oxides, which is crucial for achieving reproducible growth [90]. Starting with the system, the inner quartz tube and the boat should remain inside the LPCVD chamber and only be brought to room temperature when loading or unloading Cu foil [90]. Turning our focus to the manipulations, the preparation of Cu foil should also be approached differently.

Amontree J et al. demonstrated that the foil used by industrial presses to prepare Cu foil adds carbon to the material's surface. As only the oxide layer has been removed, an etching step is recommended to be added in the Cu foil preparation following the oxide layer removal. To this end, dipping the Cu in an ammonium persulfate solution for a few minutes should be sufficient, ideally removing $> 5\mu m$ on each side. In summary, this approach grants better control over the potential sources of contamination of the LPCVD system.

Additional steps are needed during Cu foil preparation to improve the graphene quality further. For example, a thin layer of Cu foil must be removed to reduce the substrate's surface roughness and the presence of impurities limiting the latter. To this end, the substrate must be polished chemically or mechanically, removing $\approx 5\mu m$ on each side of the material and smoothing its surface [90].

The growth parameters for the recipes have been completely changed, as none of the crystals showed a hexagonal shape. First, we need to assess the oxygen contamination of the chamber. Two recipes are proposed and presented in Figure 2.13 to assess this. For both recipes, the annealing temperature is changed from $850^{\circ}C$ to $1000^{\circ}C$ using 1 slc of Ar flow with the chamber pressure set to a maximum pressure of 1 Torr, this for 20 minutes. The temperature is maintained for the growth step to reduce the gas-phase reaction while trying to keep a low crystal density, replicating the process conducted by Amontree J et al. A flushing step is also added to purge the gas lines before the growth step. In both cases, the ratio of reactive gases becomes 1:10 $CH_4:H_2$ with a flow rate of 5 sccm and 50 sccm, respectively, with the pressure of the chamber set at 1 Tor. A lower $CH_4:H_2$ ratio leads to the formation of hexagonal crystal domains [76]. The only difference between the two recipes lies in the composition of gases used during the annealing step. Annealing at higher temperatures reduces Cu ripples, reducing the chances of graphene defects. An inert environment is also more suitable for this step as it promotes a poor Cu surface in hydrogen and catalyzes Cu's catalytic reaction. The first recipe proposed only uses argon during the annealing step compared to the second recipe, which uses a mix Ar: H_2 of 50:5. The small addition of hydrogen during this step is used to reduce oxide contamination as the presence of hydrogen can balance the presence of O_2 in the system [76, 90]. Comparing these two recipes will help us better understand the growth environment and better orient the parameters needed to achieve large-area defect high-quality SLG for subsequent growth trials.

For the characterization of SLG, a laser intensity of 1% with an increase in accumulated spectrum should be realized. High-power lasers can generate thermal damage and create pictures using the D bands. Even if some spectra didn't present any D band, reducing

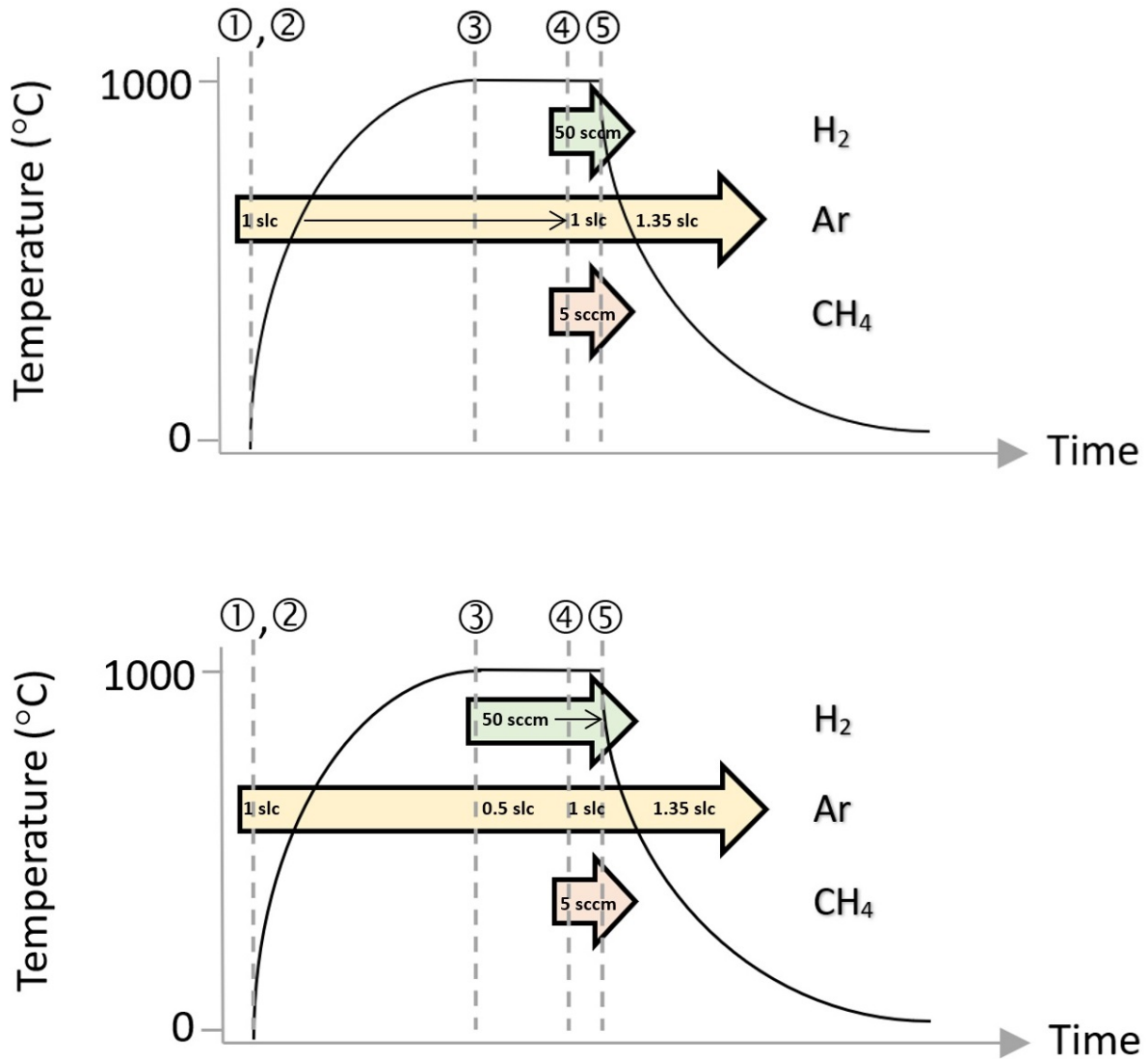


Figure 2.13: **Proposed growth recipes** (a) Step (1) and (2) flushing step and then ramp-up to the annealing temperature of 1000°C with an Ar flow kept at 1 slc. Step (3) annealing, where the same parameters are maintained for 20 minutes. Step (4) growth, introducing 50 sccm of H_2 and 5 sccm of CH_4 for 10 minutes. Step (5) Cool down, shut down of the CH_4 and H_2 flow and increase of the Ar flow to 1.35 slc. (b) same as (a) with only difference in Step (3) annealing with 0.5 slc of Ar and 50 sccm of H_2 .

laser power eliminates this error source and helps judge the material's quality. A defect band can also be linked to the wet transfer, requiring the use of chemicals known to dope graphene.

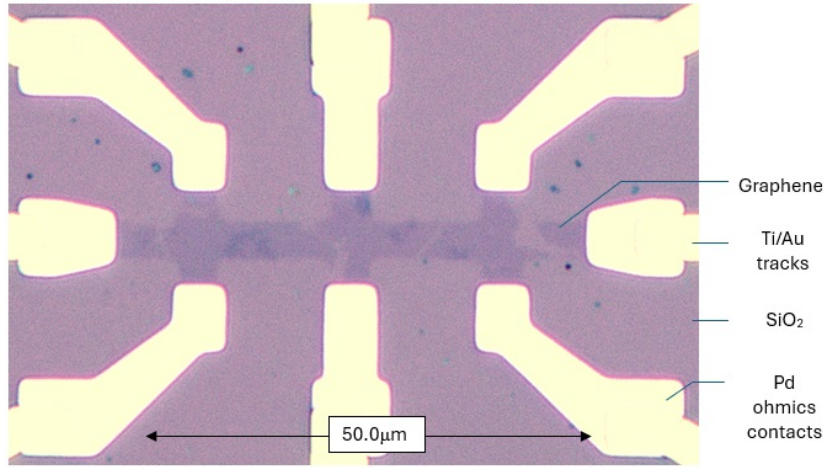
This research's operation mode strategically changes focus to single crystal rather than polycrystalline SLG growth. This shift is significant as it allows us to gain control of crystal domains before extending the process further. First, focus on crystal shape and then on crystal size and optimize both to obtain high quality and uniform graphene coverage. When large-area graphene is desired, the growth time can be increased. It's a characteristic of the Cu substrate to be self-limiting, meaning that the formation of multi-layer graphene is usually highly unfavorable. When the desired crystal with a hexagonal shape and large domain size can be obtained reproducibly, we can focus on the transfer of SLG single crystal from the Cu-substrate using a polymeric stamp.

Chapter 3

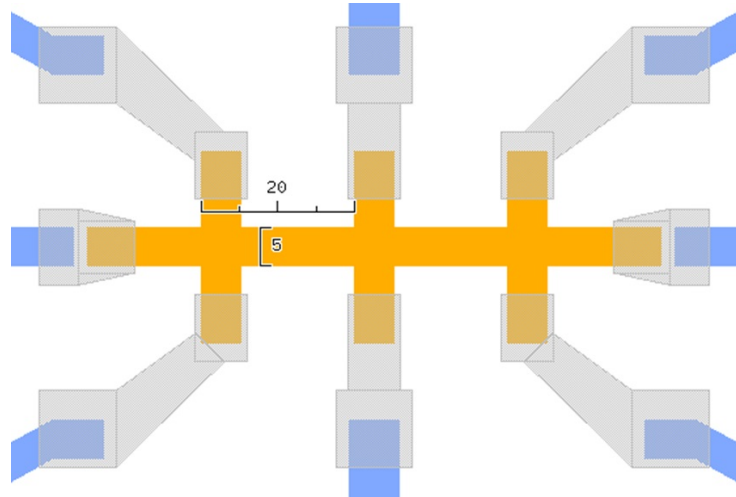
Device Fabrication

3.1 Hall Bar Pattern

Figure 3.1 presents an optical micrograph of a CVD-grown graphene Hall bar. The figure displays the substrate and the ohmic contacts connecting the graphene channels to the metallic tracks. The device fabrication process remains consistent with the previous project [91]. The only change is the provenance of the graphene, which is now transferred in our laboratories. Both the large and small Hall bars have remained their original sizes, with dimensions of $20\ \mu\text{m}$ by $8\ \mu\text{m}$ and $5\ \mu\text{m}$ by $2\ \mu\text{m}$ respectively. Both Hall bars have a length-to-width ratio of 4. A larger Ti/Au pad at the bottom of the device is used to connect the back gate. Figure 3.2 shows the design of the entire chip, which includes 80 graphene-based Hall bar devices. The figure's color scheme represents different fabrication steps. The first step, shown in blue, involves patterning the tracks and pads (light blue), alignment marks, and back gate (darker blue). This first step is used to align the pattern of the successive steps. The second step is illustrated in orange, while the last is depicted in gray.



(a)



(b)

Figure 3.1: **Graphene based Hall bars devices.** (a) Optical micrograph of a large Hall bar of CVD-grown SLG (Device CVDHT-01-H07-5) - Eight Pd Ohmics contacts (50nm) contact the graphene channel to the Ti/Au (20/80nm) tracks. The graphene Hall bar appears in a darker pink, and the SiO₂ layer appears in a lighter shade. (b) Hall bar design ($L \times W : 20$ showing the first nanofabrication step (blue), the second (orange), and the thirds (orange), where PD covers both the graphene and the Ti/Au contacts

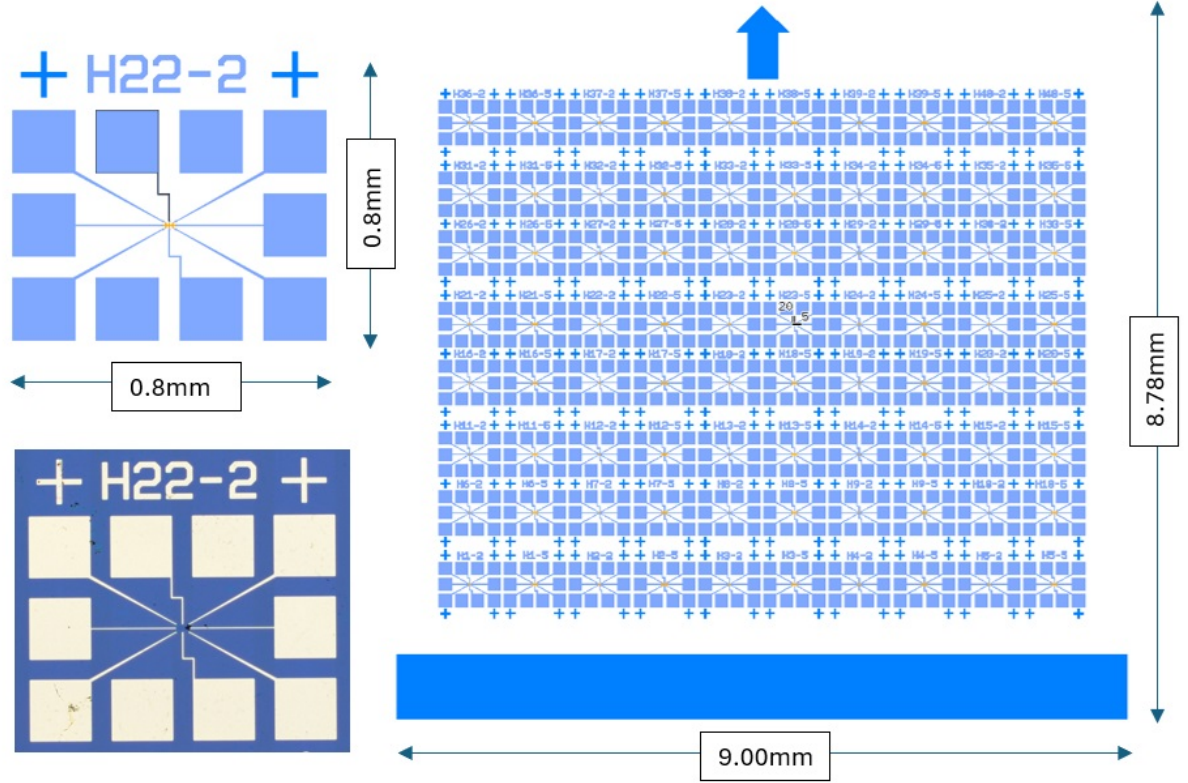


Figure 3.2: **Complete device and chip design.** Chip design of 80 Hall bar devices (Right). The alignment marks and track patterning (blues), Hall bar (orange), and the ohmic contacts (gray) patterning are completed using photolithography. Close-up of one Hall device pattern and finished device (Left).

3.2 Fabrication Process

Graphene Hall bars are created using maskless photolithography, O₂ plasma etching, and Ti/Au (20/80) and Pd(50) for the metallization of the alignment marks and the ohmic contacts, respectively. The photoresists used in this process are copolymer poly(methyl-methacrylate) (8.5) 10% in ethyl lactate (MMA), Shipley 1805, and Shipley 1811, which are both positive photoresists. The process involves spin-coating MMA onto graphene, followed by the Shipley, which never comes into contact with the graphene. Due to this, an additional step of reflowing the photoresist has been added so that both polymers can adhere together. Supplementary details about the nanofabrication process can be found in Appendix C.

1. Alignment marks and tracks patterning

- (a) Pre-process Backing
- (b) Photolithography
- (c) Graphene's etching
- (d) Metallization
- (e) Liftoff

2. Graphene Hall bars patterning

- (a) Pre-process backing
- (b) Photolithography with inverted exposure
- (c) Graphene's etching
- (d) Photoresist removal

3. Ohmic contacts patterning

- (a) Pre-process Backing
- (b) Photolithography
- (c) Metallization
- (d) Liftoff
- (e) Post-process Backing

It's important to note that graphene is very sensitive to the nanofabrication process, including the presence of water molecules beneath the graphene crystals. During the spin-coating of the photoresist, the torch can cause damage to the graphene film or remove any remaining water molecules [91]. However, in our case, the most limiting problem was the nucleation size of the crystals, which needed to be closer to form continuous domains. Out of the 80 Hall bars patterned, only a few survived the process and were suitable for further measurement. These are precisely the Hall bars with the smallest features. The latter is also discussed in Appendix C.

Chapter 4

Magnetotransport Measurement of CVD-grown Graphene

A Hall bar *CVDHT* – 01 – *H21* – 2 was used to measure the transport properties of CVD graphene on a liquid substrate. The Hall bar has small dimensions, with a length and width of $8\mu\text{m}$, respectively. Out of the 8 original contacts, only 5 are usable for measurements. The selected Hall bars undergo a visual inspection to ensure they have fewer defects, imperfections, and residues.

The back gate is connected in the same manner as before. The chip is scratched at the bottom of the design, the dark blue bottom pad, as shown in Figure 3.2. Silver epoxy, Epo-Tek H20E, is applied to the scratch to connect the Ti/Au pad to the underlying Si substrate. Before its application, the silver epoxy is left at ambient conditions for several hours to allow the solvent to evaporate and make the epoxy more viscous.

The chip is then glued onto a chip carrier before wire-bonding the desired device to the pins of the chip carrier. Wire-bonding is carried out using the Westbond 7476E Manual Wirebonder with aluminum wires, using the default settings. Subsequently, the chip is cooled using a Janis 1.5K Cryostat to characterize transport at a temperature close to $\approx 1.6\text{K}$. Magnetotransport measurements are performed using standard AC lock-in 2-terminal and 4-terminal measurement techniques. With this cryostat, magnetic fields up to 6T are reachable. The lock-in amplifier used in this setup is the Stanford Research Systems Model SR830DSP, coupled with a pre-amplifier model SR560 from the same manufacturer. The voltage source used to manipulate the back gate is a Keithley model 230, which ranges from $\pm 100\text{V}$.

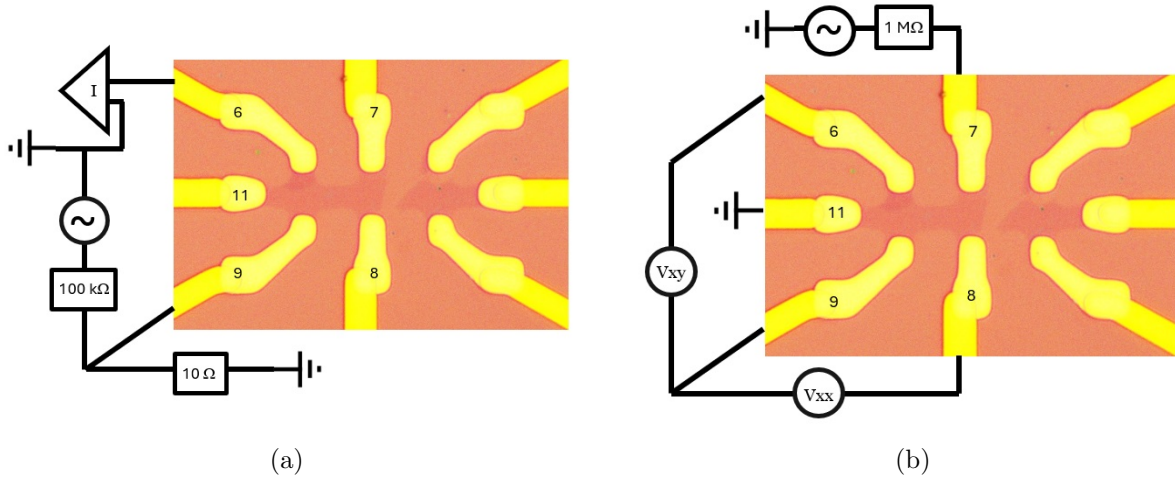


Figure 4.1: **4-terminal and 2-terminal measurement setup.** (a) 2-terminal measurement setup with 100 μ V applied to measure the total current of the circuit. (b) 4-terminal measurement setup where 100 nA of constant current is applied to the sample to measure V_{xx} and V_{xy} .

4.1 Transport Characterization

Figure 4.1 illustrates the 2-terminal and 4-terminal setups used to evaluate the ohmic contact resistance and perform the Hall measurements. On the right, the 2-terminal setup employs a voltage divider of 10 for 10000 V. By setting the Lock-in to a current input of 10^6 V/A gain, 1V is applied to the sample and determining its resistance using $\Delta V = RI$. This measure includes the resistance of the lock-in, both the input and the output line, and the device's resistance, which typically totals around 2 $k\Omega$. The 4-terminal setup is shown on the left, where 1 M Ω resistor is utilized for the $\pm I$ contacts. $\pm V_{xx}$ and $\pm V_{xy}$ signal are pre-amplified with a gain of 100 and measured with lock-in set to the voltage input of 10^6 V/A gain. In that case, the 100 nA is applied to the sample. The resistance of the sample is determined by measuring V_{xx} , and the ohmic contact resistance is obtained by subtracting the resistance measured with the 4-terminal from the 2-terminal measurement. Other than assessing the ohmic contact resistance, a 4-terminal measurement is always used.

Table 4.1 presents the device's ohmic contact resistance at room temperature (RT) and cryogenic temperature. The best contact to measure the Hall voltage is I_{6-9} and I_{8-9} for the longitudinal voltage. The ohmic resistance ranges from 1.6 $K\Omega$ to 7.9 $K\Omega$ at RT and from 2.9 $K\Omega$ to 12.5 $K\Omega$ at T 1.42K. The ohmic contact resistance is in the same range as the sample sheet resistance, which is expected for graphene-Pd metal contacts [92].

	RT	$T = 1.42K$
$I_{7-8}(k\Omega)$	6.5	11.5
$I_{6-9}(k\Omega)$	1.6	2.9
$I_{7-6}(k\Omega)$	7.9	12.5
$I_{8-9}(k\Omega)$	3.1	4.5
$I_{8-11}(k\Omega)$	3.1	4.6
Sheet resistance ($\Omega/\square$)	357	397
Peak Mobility ($cm^2 V^{-1} s^{-1}$)	3036	

Table 4.1: **Ohmic contact resistance as a function of temperature.** Hall voltage contact (contact I_{6-9}), and the longitudinal voltage contacts (contacts I_{7-6} and I_{8-9} . Sample sheet resistance and peak mobility measured chronologically in time following events that may change the sample's behavior

Figure 4.2 and Figure 4.3 present the charge neutrality point (CNP) at $1.423K$ and $T = 160K$, respectively. The CNP at $160K$ occurs at a back-gate voltage (V_{bg}) of $49V$, with a corresponding resistance (R_{sheet}) of 985Ω . There are two other noticeable inflection points, a characteristic of multilayer graphene, appearing between V_{bg} values of $60 V$ to $67 V$ and. At these points, the sheet resistance (R_{sheet}) is approximately 1154Ω . The CNP at $T = 1.423K$ is shifted to (V_{bg}) of $43V$ with resistance (R_{sheet}) of 1258Ω . The sheet sample sheet resistance at ($V_{bg} = 0$) is measured at $160K$ and $1.423K$ to be 357 and $397 \Omega/\square$ respectively.

The carrier's density is calculated using the formula $n = \frac{IV}{eV_{Hall}}$, where V_{Hall} is the anti-symmetrized V_{xy} for both $\pm B$ ($V_{xy,+B} - V_{xy,-B}/2$). Anti-symmetrization is necessary because the offset is significantly larger than the Hall voltage for graphene samples. The reduction in carrier density should be understood as electron and hole carriers pairing up rather than disappearing altogether. The carrier's mobility is found using the formula $\mu = \frac{I(L/W)}{enV_{xx}}$, with V_{xx} being symmetrized ($V_{xx,+B} + V_{xx,-B}/2$). Maximum mobility is expected at the lowest carrier density, and mobility is zero at the charge neutrality point (CNP).

Figure 4.4. illustrates the carrier's density and mobility as a function of gate voltage at a fixed magnetic field of $2T$. The highest mobility measured for the sample occurs at $V_{bg} = 26$ with a carrier mobility of $3036 cm^2 V^{-1} s^{-1}$ and a carrier density of $39.71 \cdot 10^{15} m^{-2}$. The carrier's mobility dip and density peak at $V_{bg} = 49V$ exactly at one of the CNPs. Other inflection points are expected to be observed at $V_{bg} \approx 60V$, but measurements near these regions become almost irrelevant due to the charge-density fluctuation created by the electron-hole puddles [93]. As the voltage source reaches its limit of $100V$, the sample density entirely transitions to the electron carrier side.

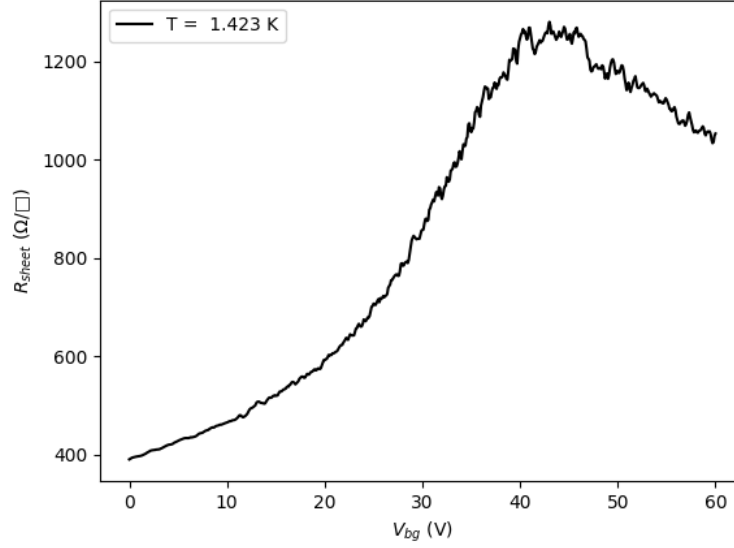


Figure 4.2: **Sample sheet resistance as a function of (V_{bg}).** CVDHT-01-H21-2 device sheet resistance as a function of back-gate voltage taken at $T=1.423\text{K}$. The CNPs is found at $V_{bg} = 43$.

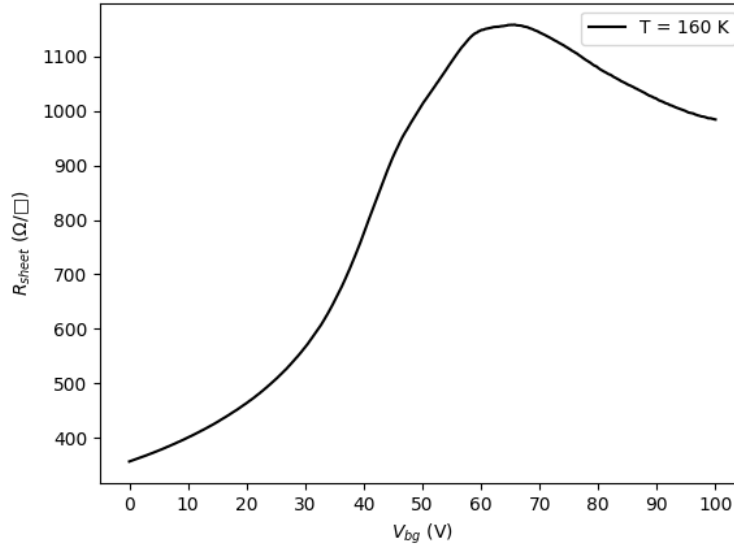


Figure 4.3: **Sample sheet resistance as a function of (V_{bg}) at room temperature.** CVDHT-01-H21-2 device sheet resistance as a function of back-gate voltage taken at $T=160\text{K}$. The CNPs are found at $V_{bg} = 49$, $V_{bg} \approx 60$ and $V_{bg} \approx 66.9$.

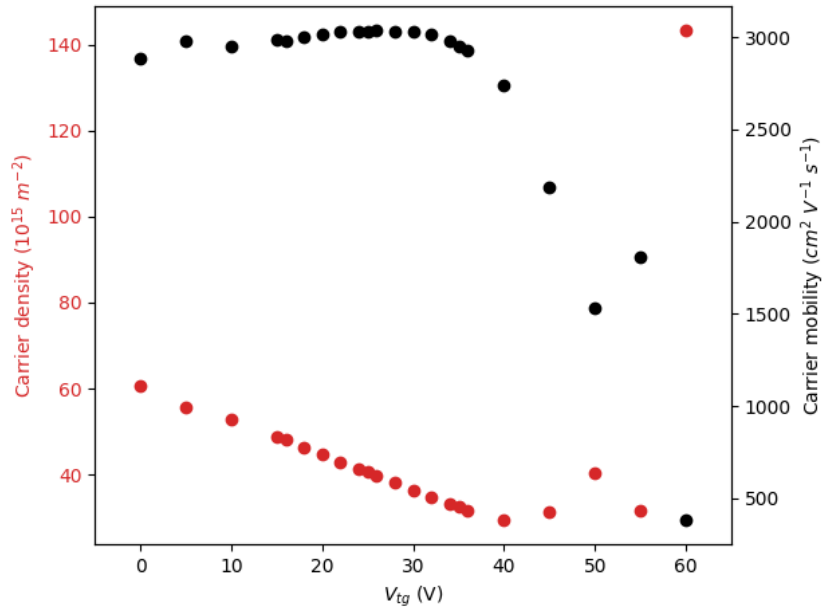


Figure 4.4: **Carrier density and carrier mobility as a function of (V_{bg}).** The carrier density (left axis) and the carrier mobility (right axis) as a function of the back gate voltage normalized and anti-normalized at $B \pm 2\text{T}$. Device CVDHT-01-H21-2 measured at $T = 160\text{K}$.

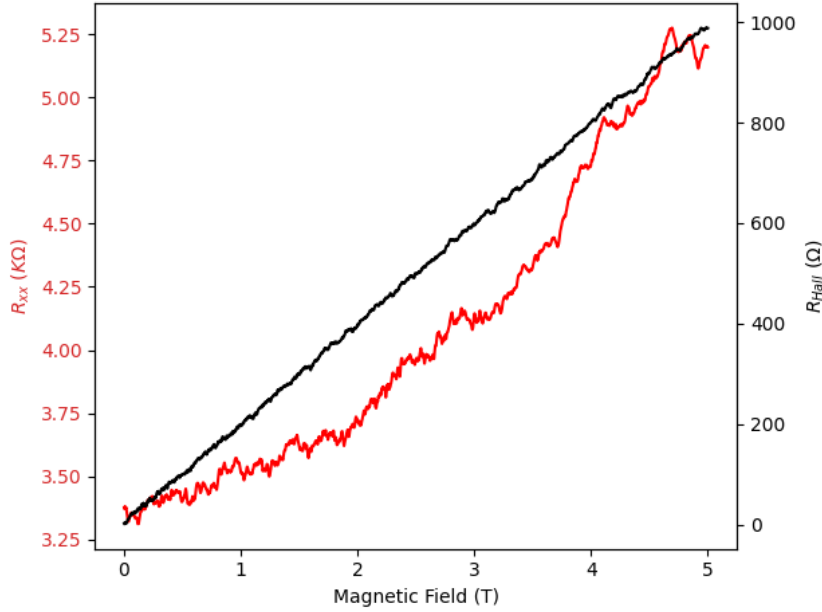


Figure 4.5: **Magnetoresistance as a function of magnetic field.** The Hall (right axis) and the longitudinal resistance (left axis) as a function of a magnetic field at fixed density $40.58^{11} \text{ cm}^{-2} (V_{bg} = -25\text{V})$. Device CVDHT-01-H21-2 measured at $T = 1.833\text{K}$.

In Figure 4.5, magnetoresistance is plotted as a function of the magnetic field from 0T to 5T at a fixed back gate voltage of $V_{bg} = 25V$. No Hall plateaus or SdH oscillations are observed, even when the density was set to the highest mobility. The R_{xx} dependency in the field is parabolic, as expected for multilayer graphene [94]. All the devices exhibit multilayer regions, as confirmed by the microscope and Raman spectroscopy, indicating characteristics consistent with multilayer graphene.

4.2 Discussion

The transport characteristics of the graphene used in this project show improvement compared to the previously SLG-hBN (.6nm on a $1\text{cm} \times 1\text{cm}$ Si/SiO₂ substrate) purchased from Grolltex. Using this material, Sakuragi achieved a carrier mobility $3327\text{ cm}^2V^{-1}s^{-1}$ for a density of 7.16^{11} cm^{-2} after in-situ current annealing of the sample [91]. In our case, we didn't use this procedure to improve the material's quality and still observed a close to the above value. The highest mobility measured in our sample is slightly lower at $3036\text{ cm}^2V^{-1}s^{-1}$, at a density of $39.7110^{11}\text{ cm}^{-2}$. Overall, our samples generally exhibit a higher carrier density and a lower sheet resistance.

This initial characterization of graphene confirms the doping of the material. This issue has been previously reported in experiments where the Dirac point was also p-doped [91]. However, the exact step leading to the source of contamination has yet to be identified. The nanofabrication process, which involves spin-coating photoresists like MMA, is known to dope graphene and can only be avoided if the graphene layer is protected with materials such as hBN [63].

Further investigation into the observation of low carrier mobility, $\approx 3000\text{ cm}^2V^{-1}s^{-1}$ is also needed. This low mobility is related to electron-phonon scattering processes intrinsic to the material rather than the material's doping. As pre-fabrication Raman mapping indicates high-quality graphene, Raman mapping after nanofabrication could aid in understanding whether the fabrication process has caused any structural changes.

Lastly, placing the material on a bare Si/SiO₂ substrate reduces graphene's intrinsic mobility. The roughness of the oxide layer and the presence of charge impurities increase the possibility of scattering events. A device with suspended graphene or encapsulated hBN-graphene-hBN is needed to reduce the substrate scattering centers. Damage might also have occurred during the graphene transfer. Imaging our graphene by scanning tunneling microscopy will better indicate the sample's intrinsic defects and how they might have

formed. The energy-dispersive X-ray spectroscopy will also confirm that no more copper particles will remain after the transfer.

Chapter 5

Twisted Bilayer Graphene-WSe₂

In 2023, a collaboration began with Prof. Usha's group from the India Institute of Science, bringing expertise in quantum transport in graphene to our spintronic group. The main goal of the collaboration is to design and develop magic-angle TBG-based quantum-dot devices. We aim to use TMD, such as WSe_2 , stacked on top of graphene to induce the spin-orbit coupling (SOC) by proximity [95, 96]. This architecture allows the study of unique electronic phases of magic angle TBG. The two VDW materials are encapsulated with hBN to ensure the quality of the sample. A secondary objective of this project, as the quantum-dot devices are still in fabrication and optimization, is to explore the various new Quantum Hall phases and their topological signatures emerging at low temperatures. This objective was achieved using facilities available through the Quantum Colab, allowing the exploration of regimes at millikelvin temperatures and magnetic fields up to 20 T.

Usha's group fabricated a TBG device with a twisting angle of $\approx 2^\circ$ and sent it to Waterloo to perform magnetotransport measurements. The device architecture is shown in Figure 5.1, depicting the top and side views of the device design. The heterostructure was assembled using the "tear and stack method" employing a polymeric stamp made of Poly-(Biphenol-A-carbonate) (PC) film and a polydimethylsiloxane (PDMS) block. The graphene is torn apart, and the existing flake stack picks up half of it. The stage is then rotated to the desired angle, and the second half is picked up. The TBG-TMD stack is encapsulated with hBN of approximately 25 nm for the bottom gate and approximately 16 nm for the top gate. The sample was then released on a Si/SiO₂ substrate with ≈ 285 nm of oxide. The device has a SLG and a TBG region. Figure 5.2 presents a more detailed device architecture. The Hall bar shape was patterned using E-beam lithography and etched with Reactive ion etching using CHF₃/O₂, with Cr/Au (5nm/60nm) deposited to contact graphene. After the transport, only the TBG side was usable, and therefore,

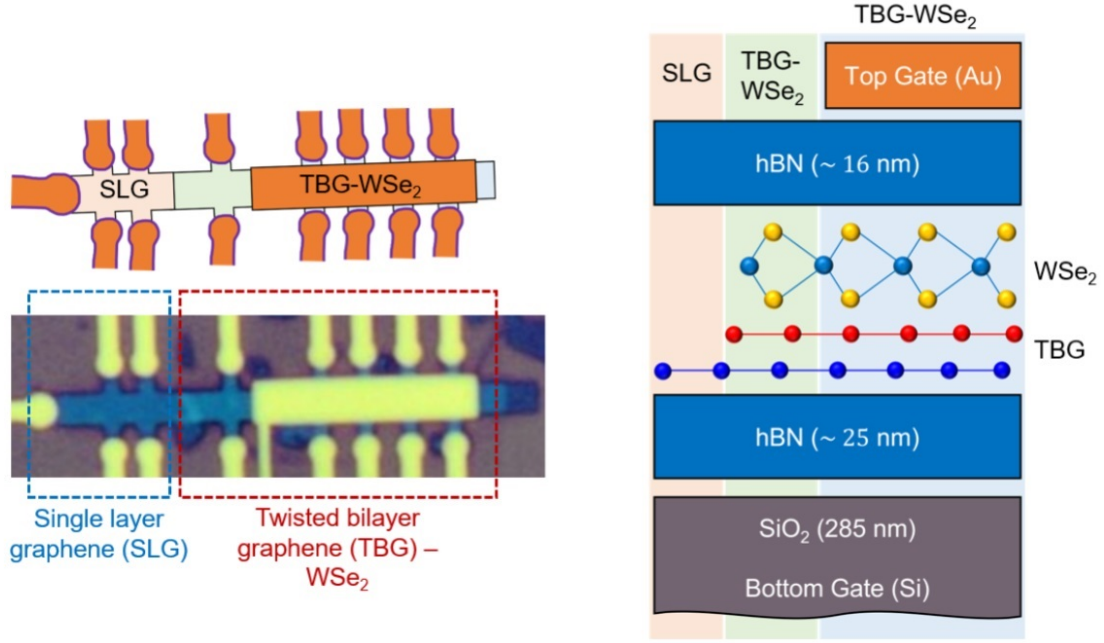


Figure 5.1: **TBG- WSe_2 device architecture and its different region.** (a) SLG region (orange) and TBG- WSe_2 region with (blue) and without (green) a top gate (b) side view of the device architecture. The TBG- WSe_2 is encapsulated between $\approx 16\text{nm}$ (top) and $\approx 25\text{nm}$ (bottom) of hBN. The material is contacted with a Au top gate (orange) and the substrate, Si/SiO_2 285nm of oxide (gray), used as back gate.

the focus was on this side.

Martin Gmitra. et al. modeled the Hamiltonian of single-layer graphene in contact with various TMD. They concluded that SOC by proximity results in spin degeneracy and subsequent band inversion of TBG's band structure [97]. Among the TMDs studied, MoS_2 , WS_2 , $MoSe_2$, and WSe_2 , only WSe_2 exhibited SOC strong enough to induce a band inversion. Additionally, TBG- WSe_2 heterostructures break both inversion and TR symmetry, making them an ideal platform for studying Chern insulating phases [98].

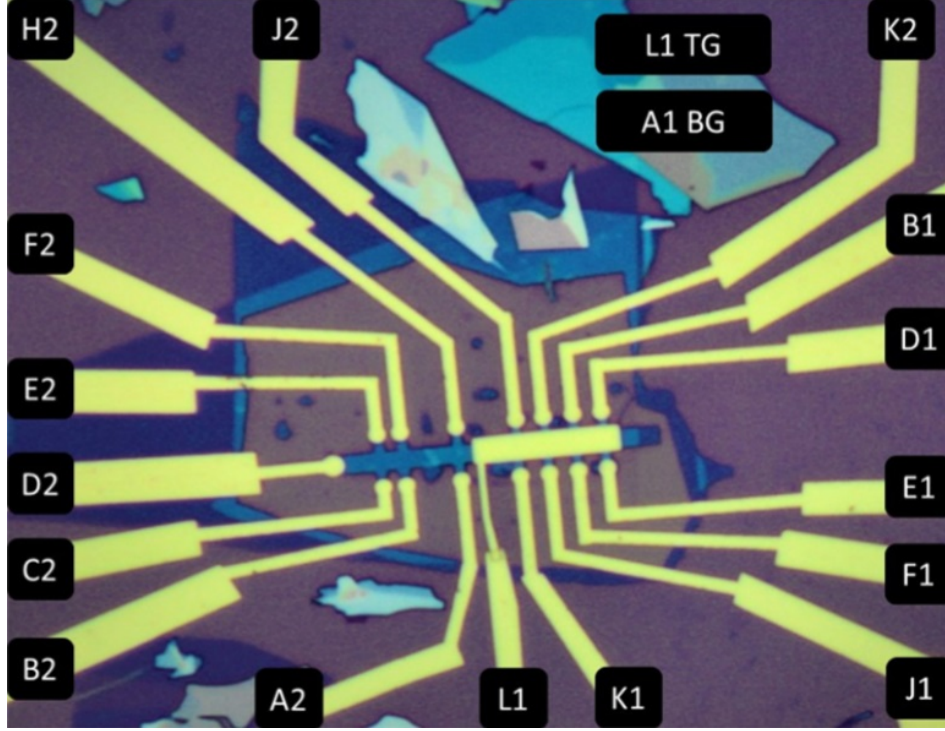


Figure 5.2: **Contact diagram of TBG- WSe_2 device.** Top view of the contact diagram of the TBG- WSe_2 device.

5.1 Transport Characterization

The device was received pre-mounted in a Leadless-Chip-Carrier (LCC) socket and was connected using a wiring diagram shown in Figure 3.2. The LCC socket is mounted on an LCC adapter fitting on the probe to be cooled down. Magnetotransport measurements were conducted using a standard AC lock-in measurement technique. Both 2-terminal and 4-terminal measurements were performed in a pumped $^3He/{}^4He$ wet dilution refrigerator with the sample being loaded from the top and reaching temperatures as low as 11mK. This equipment can reach high magnetic fields up to 20T. The same instrumentation was used for the lock-in and the pre-amplifier, which are from Stanford Research Systems Model SR830DSP and Model SR560, respectively and used a SIM900 GSM voltage source.

The measurements began with assessing ohmic's quality and the impact of the metal-work function. This was achieved using a 2-terminal measurement setup, as explained in the previous chapter. Table 5.1 shows the ohmic contact resistance measured for the magnetic field, TBG's sheet resistance, and peak mobility at various time points, with the data presented chronologically. Between the first and second sets of measurements, the device was brought to room temperature and went through a thermal cycle. Since the device

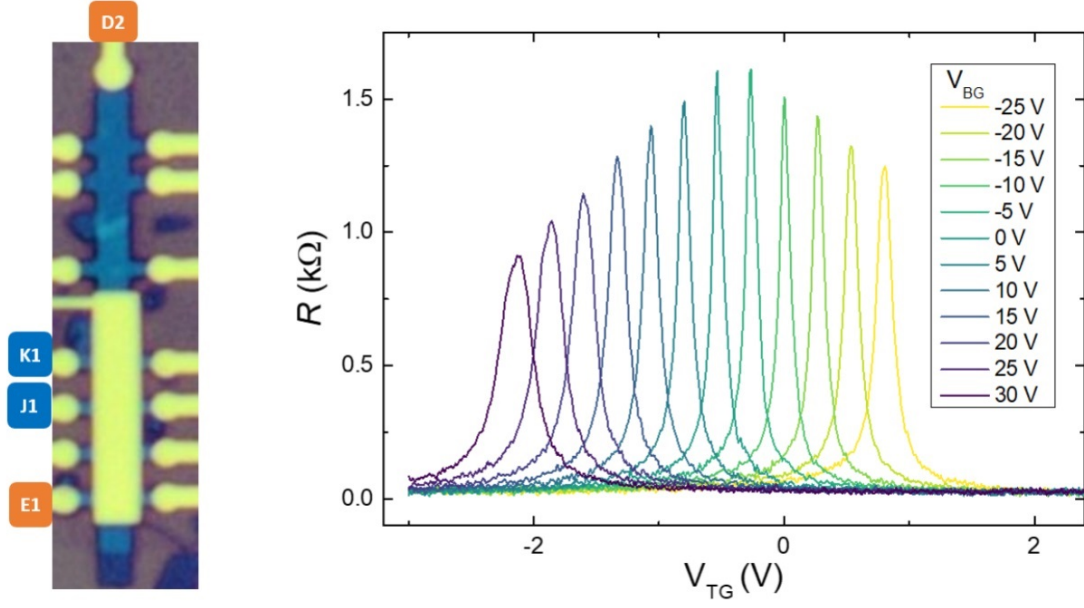
	0T	18T	0T	10T	0T	15T
$I_{K1-J1} (k\Omega)$	2	-	4	42(62)	5	157
$I_{K1-F1} (k\Omega)$	-	-	4	42(57)	5	249
$I_{J1-F1} (k\Omega)$	-	-	3	42(69)	5	217
$I_{K1-J2} (k\Omega)$	26	113	37	60(69)	66	164
$I_{J1-K2} (k\Omega)$	-	-	27	100(88)	16	193
$I_{F1-B1} (k\Omega)$	-	-	27	58(67)	41	250
$I_{A2-D1} (k\Omega)$	18	500	12	42(62)	10	128
Sheet resistance ($\Omega/\square$)	88.1		90.8		115	
Peak Mobility ($cm^2 V^{-1} s^{-1}$)	195 750		355 163		8259	

Table 5.1: **Ohmic contact resistance as a function of magnetic field.** Hall voltage contacts (I_{K1-J2} , I_{J1-k2} , and I_{F1-B1}), and the longitudinal voltage contacts (I_{K1-J1} , I_{K1-F1} , and I_{J1-F1} for holes (electrons). Sample sheet resistance and peak mobility are measured chronologically in time following events that may change the sample's behavior.

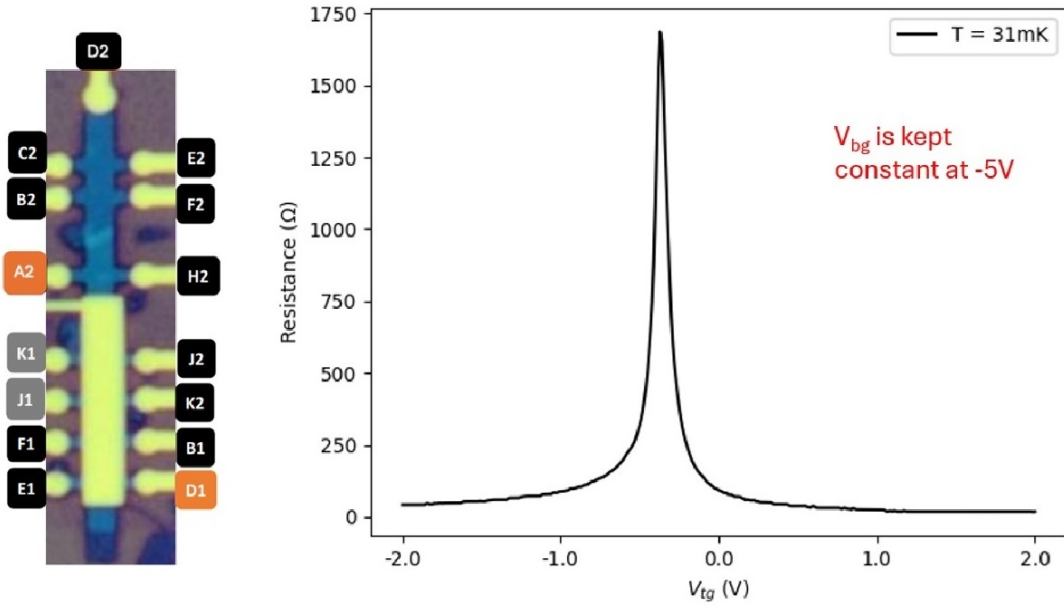
experiences significant temperature variations, its sensitivity to change can be improved or diminished. For example, the ohmic contact resistance improved for I_{A2-D1} between series compared to I_{K1-J1} , which decreased. The ohmic contact resistance increases as a function of the field, with the best ohmic contact resistance of 42 K Ω for the hole carriers in the intermediate magnetic field. Longitudinal contact pairs I_{K1-J1} , I_{K1-F1} , and I_{J1-F1} exhibit lower resistivity than all Hall contact pairs I_{K1-J2} , I_{J1-k2} , and I_{F1-B1} , ranging between 2-5 k Ω and 16-66 k Ω respectively.

In Figure 5.3, 4-terminal measurements were used to observe the sample's resistance as the top gate voltages varied at different back gate voltages. The device schematic for the ohmic contacts shows where the current is measured (gray contacts) and where the constant bias voltage is applied (orange contacts). The device behavior was initially observed in a cryostat at T=4K at the India Institute of Science and then reproduced at a lower temperature, T=31mK, in Waterloo. The bag gate voltage was set to the level with the sharpest CNP peak and highest resistivity, corresponding to the lowest metal work function. Preliminary results presented in Figure 5.3(a) show the ideal back gate setting at $V_{bg} = -5V$ with CNP's $R_{xx} \approx 1650\Omega$. This sweep was replicated in our lab with CNP's $R_{xx} = 1684\Omega$ at $V_{tg} = -0.31V$, so the bag gate was set to $V_{bg} = -5V$ for subsequent measurements.

Figure 5.4 presents the device magnetoresistance as a function of top gate voltage at a fixed field of B= 18T. Initially, the CNP shifted in the field at $V_{tg} = -0.18V$. The signal



(a)



(b)

Figure 5.3: *TBG* – WSe_2 sheet resistance as a function of V_{tg} . (a) reference from the India Institute of Science of the sample's resistance for different back gate voltages taken at $T = 4K$ (b) reproduced in Waterloo with a 4-terminal setup ($\pm I$ (orange) $\pm V_{xx}$ (blue or gray)) at $T = 31mK$.

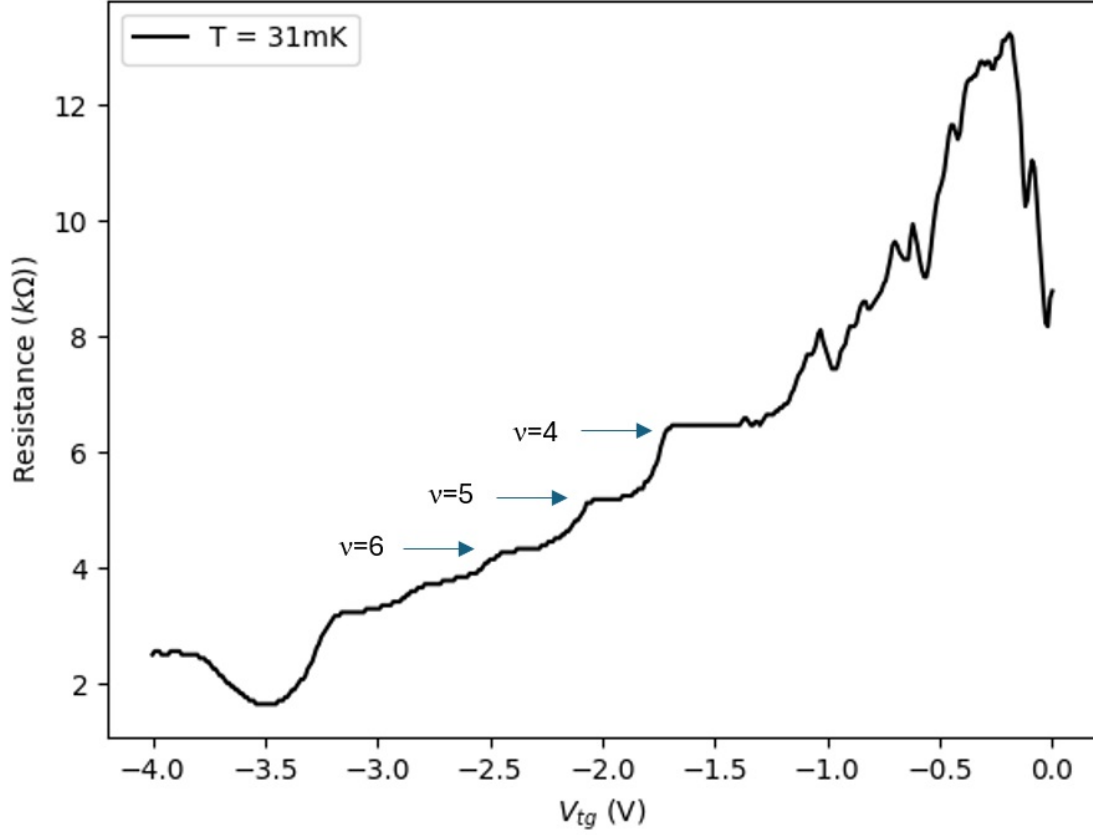


Figure 5.4: **TBG- WSe_2 magnetoresistance as a function of V_{tg} at $B= 18T$ and $V_{bg} = -5V$. CNP is found at $V_{tg} = -0.18V$ and plateaus appears at R_{xy} at $R_{xy} = 6470$, 5188 and 4333 Ω . The device is measured at $T = 31mK$.**

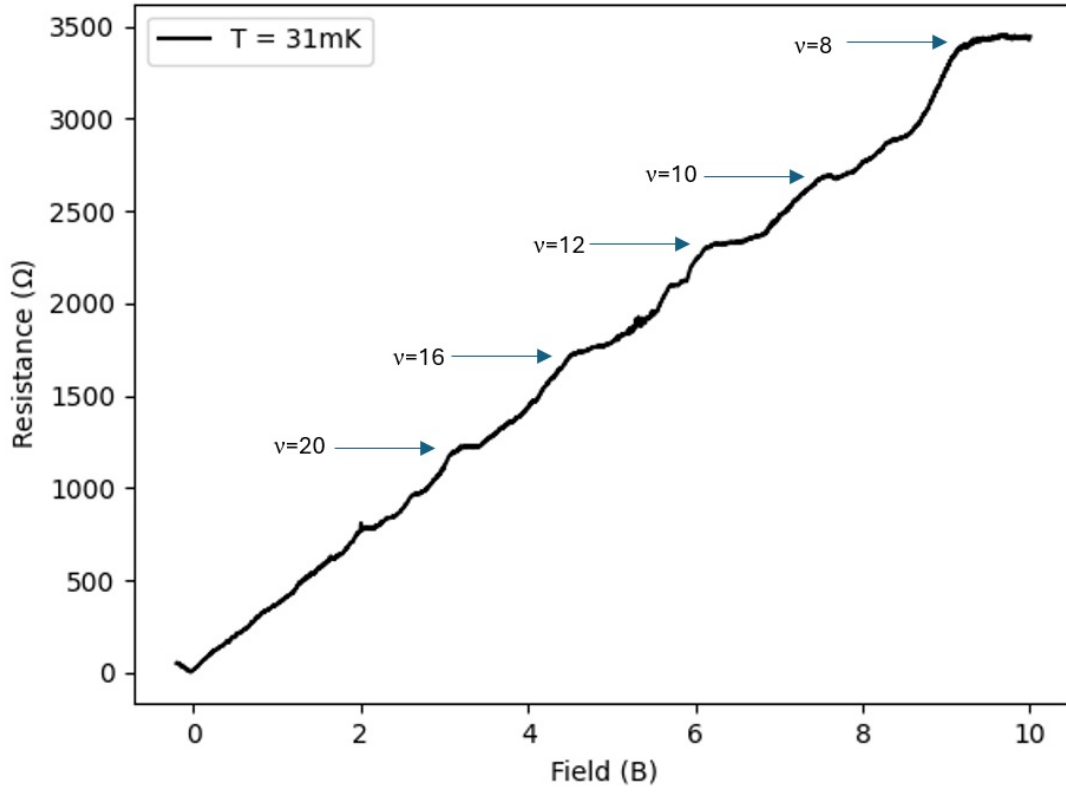


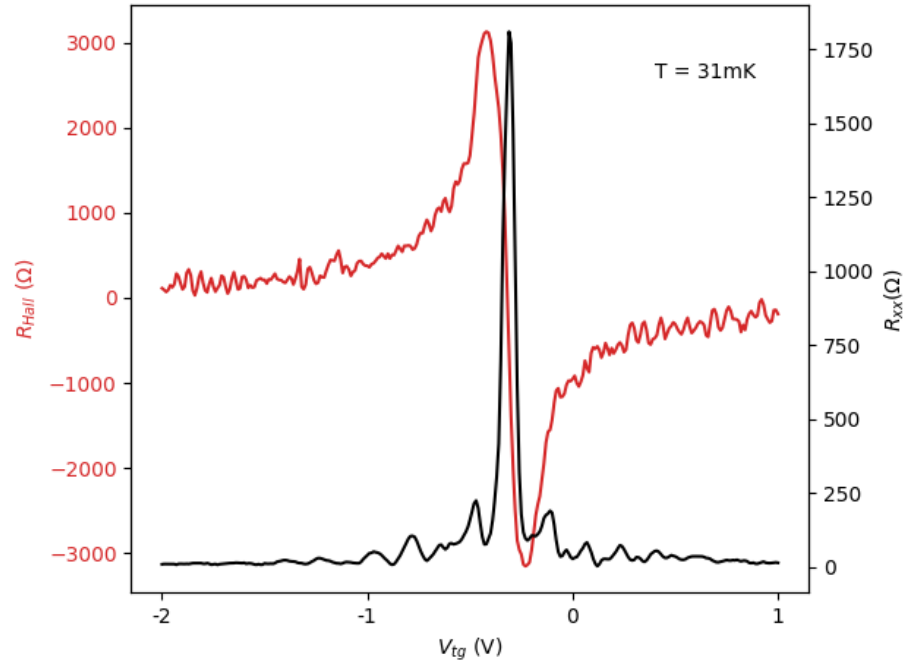
Figure 5.5: **TBG-WSe₂** magnetoresistance as a function of B at $V_{tg} = -2V$ and $V_{bg} = -5V$. plateaus are starting to form in R_{xy} at $\nu = 8, 10, 12, 16$ and 20 . The device is measured from B= -0.2T to 10T at T = 31mK.

is noisy in the low-density regime near the CNP, with no quantized resistance observed in that region. Hall plateaus are visible at $R_{xy} = 6470, 5188, \text{ and } 4333 \, \Omega$, corresponding to the filling factors $\nu = 4, 5, 6$ with no apparent SdH oscillations in R_{xx} . It's worth noting that filling factors 5 and 6 are uncommon for TBG and thus require further verification before drawing any conclusions. However, filling factor 4, typically associated with BLG, is identified over a range of 0.54 V in the top gate voltage. At higher top-gate voltages $V_{tg} > -3V$, the ohmic contacts became very resistive, and it was no longer possible to perform Hall measurements in a magnetic field.

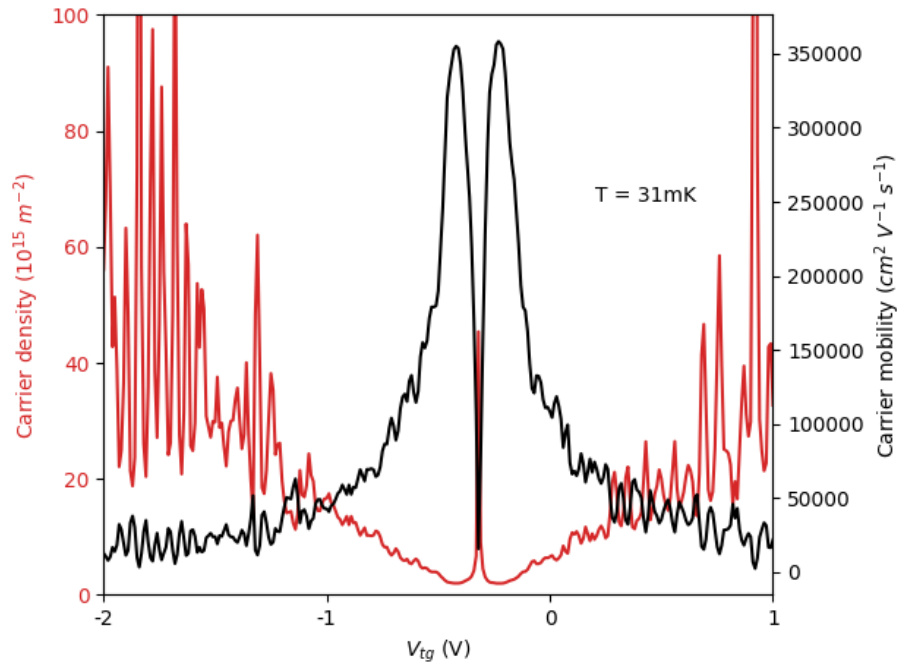
In Figure 5.5, magnetoresistance is shown as a function of the magnetic field ranging from -0.2T to 10T at a constant top-gate voltage of $V_{tg} = -2V$. A plateau begins to take form at filling factors $\nu = 8, 10, 12, 16, 20$ with no Shubnikov-de Haas (SdH) oscillations in R_{xx} . The ohmic contact resistivity also significantly increased for both electron and hole carriers.

Figure 5.6 and Figure 5.7 illustrates the carrier's density and mobility as a function of the top-gate voltage at fixed magnetic fields of 1T and 3T, respectively. The lower magnetic field sweep displayed the highest measured mobility at $V_{tg} = -32$, with a carrier mobility of $355\,163 \, cm^2V^{-1}s^{-1}$ and a carrier density of $2.0010^{15}m^{-2}$. The higher field sweep revealed a peak mobility at $V_{tg} = -28$, with a carrier mobility of $149\,988 \, cm^2V^{-1}s^{-1}$ and a carrier density of $4.73 \, 10^{15}m^{-2}$.

Figure 5.8 shows the Hall resistance as a function of the top-gate voltage at a fixed magnetic field of $B = \pm 3T$. The voltage sweep was conducted at 1.8V per hour to minimize noise from the ohmic contacts. For both electrons and holes, a plateau is observed at $\nu = 8$ with $R_{Hall} \approx 3226\Omega$. Although Shubnikov-de Haas (SdH) oscillations are present, they do not fully reach $R_{xx} = 0$ when the Hall plateaus are observed. Additionally, they exhibit an asymmetric shape rather than the typical sin-cardinal function-like shape. As the sweep was repeated to assess the repeatability, an incident at the beginning of the sweep altered the sample sensitivity, preventing the observation of Hall plateaus even following an anti-symmetrization of V_{xy} . Consequently, a thermal cycle was performed to reset the device.

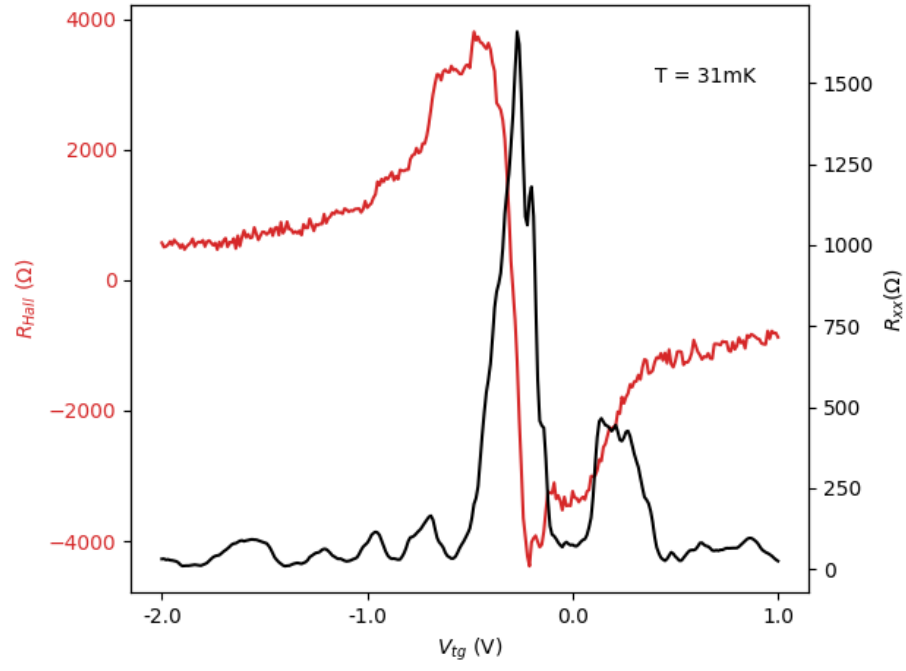


(a)

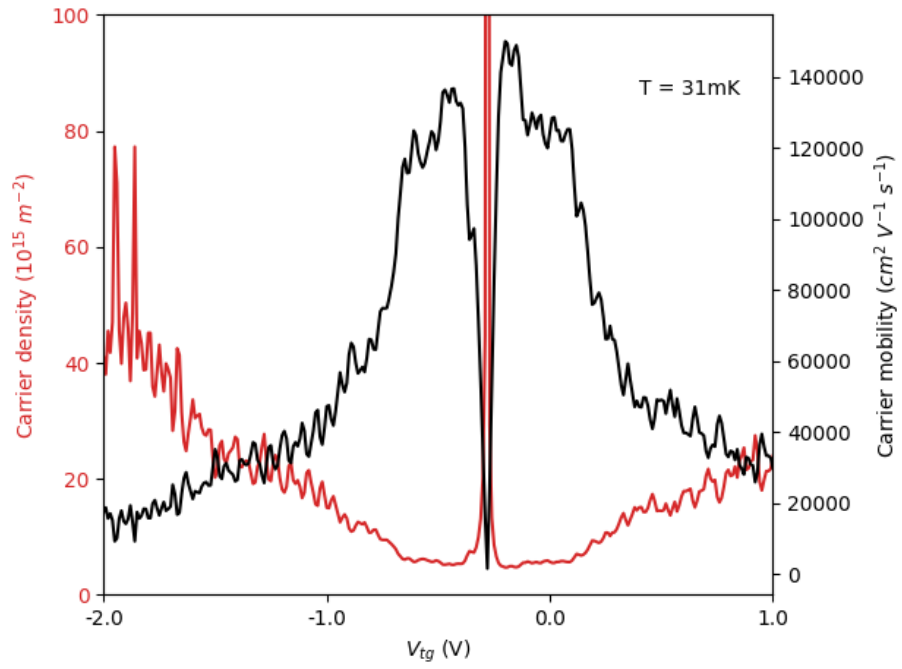


(b)

Figure 5.6: **TBG- WSe_2 Magnetoresistance and respective carrier density and mobility as function of V_{tg} and fixed $B \pm 1T$ and $V_{bg} = -5V$.** (a) Hall resistance (left) and longitudinal resistance (right) taken at $B \pm 1T$. CNP is found at $V_{tg} = -0.32V$. (b) Carrier density (left) and mobility (right) taken at $B \pm 1T$. Measurements are performed at $T=31mK$.

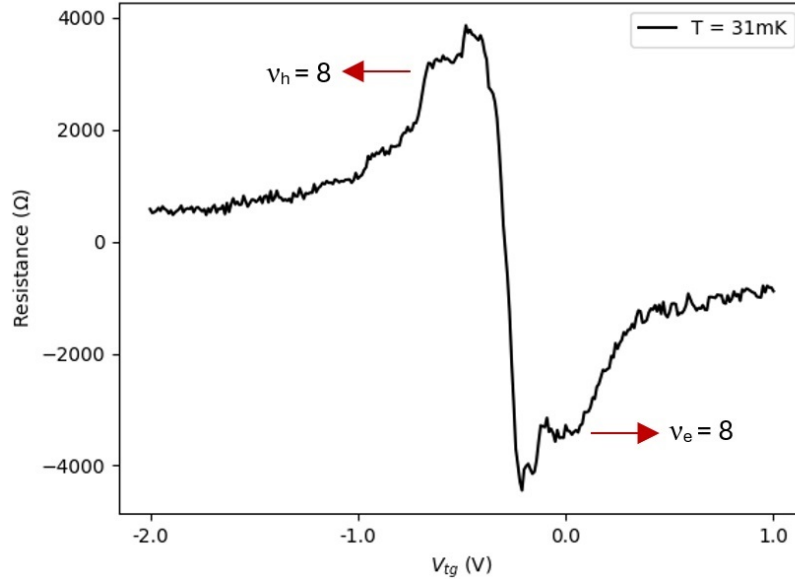


(a)

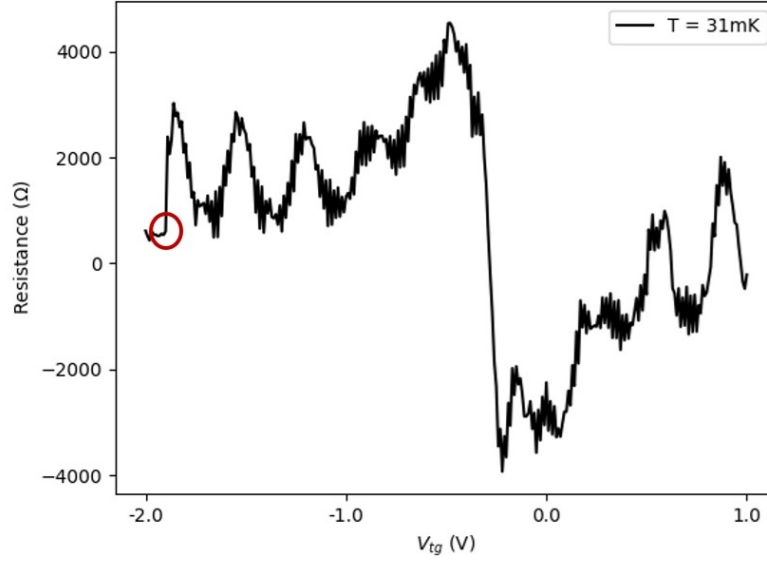


(b)

Figure 5.7: **TBG- WSe_2 Magnetoresistance and respective carrier density and mobility as function of V_{tg} and fixed $B \pm 3\text{T}$ and $V_{bg} = -5\text{V}$.** (a) Hall resistance (left) and longitudinal resistance (right) taken at $B \pm 3\text{T}$. CNP is found at $V_{tg} = -0.28\text{V}$. (b) Carrier density (left) and mobility (right) taken at $B \pm 3\text{T}$. Measurements are performed at $T=31\text{mK}$.



(a)



(b)

Figure 5.8: **TBG- WSe_2 magnetoresistance as a function of V_{tg} and fixed $B \pm 3\text{T}$ and $V_{bg} = 0\text{V}$.** (a) A Hall plateau appears $R_{Hall} \approx 3226\Omega$ (b) repeated measurement with sample behavior changing at $V_{tg} = -1.92\text{V}$. Measurements are performed at $T=31\text{mK}$.

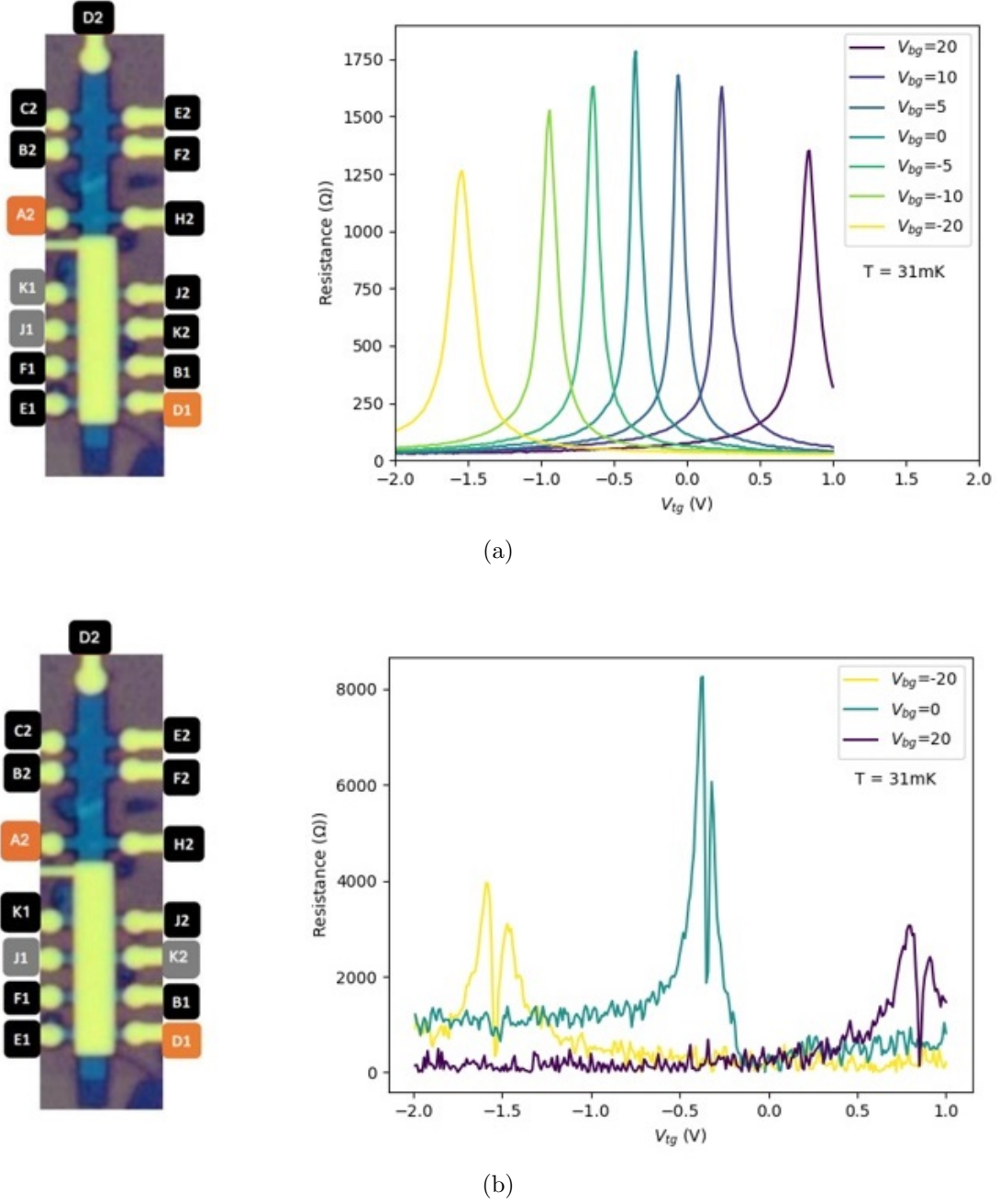


Figure 5.9: **TBG-WSe₂ sample sheet resistance as a function of the V_{tg} and its respective carrier mobility** (a) repeated measurement 4 terminal measurements ($\pm I \pm V_{xx}$) of the sample sheet resistance as a function of the V_{tg} for different V_{bg} . (b) Carrier's mobility as a function of top gate voltage for the $V_{bg} = -20, 0$ and 20V . Measurements are performed at $T=31\text{mK}$.

5.2 Discussion

After conducting the thermal cycle, we re-evaluated the contact metal-work function. Figure 5.9 shows the sample sheet resistance as a function of top gate voltage for various back-gate voltages. We adjusted the settings to lower the metal-work function with the back-gate at $V_{bg} = 0V$ rather than $V_{bg} = -5V$, resulting in $R_{xx} = 1749\Omega$ at the CNP. Despite this, the sample's sheet resistance increased from 90.8 to 115 Ω , and the mobility dropped significantly to below 10,000 $cm^2V^{-1}s^{-1}$.

Our measurements are significantly limited due to the high ohmic contact resistance, typically in the $k\Omega$ compared to the sample's sheet resistance of approximately 100 Ω . Despite our efforts to improve it, the ohmic contact resistance for measuring the Hall Voltage effect has not been below 15 $k\Omega$. A solution for this issue would be to use a different metal with lower contact resistance. Pd is a strong candidate for this purpose, as it is known to provide the lowest ohmic contact resistance with graphene[92]. It's important to mention that the ohmic contact resistance tends to increase for electrons compared to hole carriers.

During the magnetic field sweep in the intermediate field (Figure 5.5), the top gate voltage was set to -2V to avoid the noisy region near the charge neutrality point (CNP). Under these conditions, the Hall plateau for $\nu=8$ appears only at 9T, whereas the corresponding plateau was observed at 3T for a $V_{tg} \approx -0.6V$ in later measurements (Figure 5.8 a)). This suggests that the chosen carrier density wasn't optimal, although the correct filling factors are still observed.

The highest mobility was measured at a magnetic field of 1T. A lower mobility is expected in a higher field as V_{xx} increases with the magnetic field. The decrease in mobility at B=3T is consistent with the field-induced broadening of the SdH oscillations, which become less pronounced and noisier at 1T and 3T despite a top gate sweeping rate of 1.7V per hour.

The repeating measurements changed the sample's behavior, making it unusable for further Hall measurements. These new characteristics include a shift in the CNP toward p-doping, an increase in the sample's sheet resistance, and reduced carrier mobility. Figure 5.9 shows that the mobility decreased significantly, almost 50 times lower, even with the proper top and back gate settings. This plot also highlights the inverse relationship between high contact resistance and carrier mobility, where a wrong back gate setting can considerably reduce carrier mobility.

Furthermore, a different measurement setup could be used to perform a first assessment of Chern insulating phases, which requires low magnetic fields and temperatures in the

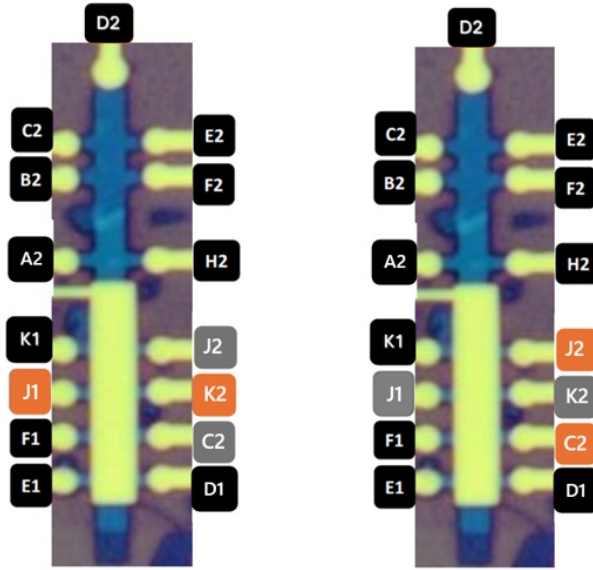


Figure 5.10: **Proposed setup to measure the AQHE.** Setup to perform the Onsager anti-symmetrization in low $B \approx 50mT$

range of millikelvins. Our collaborator demonstrated this measurement setup in a recent study [98]. Figure 5.10 illustrates the configuration, showing the contacts permutation of $\pm V$ and $\pm I$. Anti-symmetrization of the signal was required for Hall measurements, which still applies here. For this setup, an Onsager anti-symmetrization approach can be used. This anti-symmetrization is performed by interchanging $\pm I$ and $\pm V$ contacts. The Detection of a hysteresis loop in V_{Hall} in a low-energy regime indicates the presence of graphene's local valley magnetization and confirms the existence of Chern insulating phases. Following this first assessment, the characterization could then be extended to higher magnetic fields for further analysis.

Chapter 6

Conclusion

The recent ability to synthesize graphene represents a significant breakthrough in studying condensed matter physics and its practical applications. Graphene's planar lattice structure creates a band structure where charge carriers behave like relativistic massless particles at low carrier densities. This unique electrical property has shown potential in various applications. Among these, SLG shows promise as a possible resistance standard in metrology. High mobility and low defects graphene demonstrate the possibility of observing the Hall effect under less stringent measurement conditions than the current GaAs/AlGaAs resistance standard used by NIST. Furthermore, the possibility of confinement in BLG's band structure and TBG's tunable superconducting and insulating phases opens up the potential for their use in quantum topological computing. These unique properties have sparked interest in utilizing graphene to study strongly correlated states and as a platform for superconducting quantum devices. While CVD provides a convenient method for synthesizing large quantities of graphene, its reliability and high quality still require improvement. Our research project focuses on synthesizing high-quality, low-defect single-layer graphene using the LPCVD system available at the QNFCF.

This thesis first introduces the crystalline and band structures of SLG, BLG, and TBG and briefly covers the topological band theory. We then discuss the application of SLG, mainly for metrology applications, and the potential application of BLG and TBG for quantum computation. The second chapter covers different growth recipes for synthesizing SLG using LPCVD. Aiming to grow large-area single-crystal graphene, parameters such as the temperature and the position in the loading boat have been explored and compared to improve the QNFCF reference growth recipe. The synthesized materials were then identified and characterized using AFM and Raman spectroscopy. Mapping of the materials suggests the synthesis of high-quality graphene with few defects. However, preliminary

transport measurements of the devices aren't characterized by high carrier mobility superior of $5000\text{cm}^2\text{ V}^{-1}\text{ s}^{-1}$, and thus, no Hall plateaus were observed. A deeper investigation is needed to understand the discrepancy with Raman mappings. However, mobility is similar to our group's, which was previously measured using purchased CVD-grown graphene. The last part of this thesis discusses the transport characterization of the TBG- WSe_2 device where conventional hall states were observed but no signature of chern insulating phases.

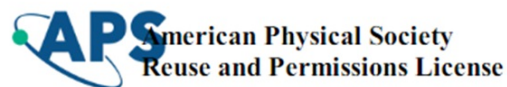
The CVD synthesis of graphene was completed on a liquid Cu substrate, and the Hall bar devices were patterned by photolithography. As shown in the scope pictures and the Raman mappings in Chapter 2, CVDHT graphene crystals are characterized by multilayer graphene nucleation centers. The quadratic dependency observed for the longitudinal voltage in a magnetic field, characteristic of multilayer graphene, confirms the first observation. Despite the non-repeatability of the growth recipe, the initial results are promising concerning the potential of growing SLG graphene at the QNFCF.

The magnetotransport performance of graphene devices is heavily influenced by their quality and interactions with the material's surface. The wet-transfer techniques used to transfer the graphene film add polymer residues, which are hardened by the baking step in our process. To avoid this, a dry-transfer technique could be used to encapsulate SLG with hBN crystals and protect it for the subsequent fabrication steps.

It is important to note that the issues encountered with the previous student persisted throughout this project. Residual photoresists get stuck on the graphene channel and are hard to remove. These residues are the limiting factors to this process yield, making these Hall bars unusable for measurement. With an initial hypothesis of skin forming between photoresists, other UV-photoresist developers could be tried out to avoid its formation. Another possibility would be to change the use of photolithography for beam lithography, as it is primarily done in the literature.

The TBG- WSe_2 structure enables the study of Chern insulating states, although it requires improved contact resistance to be observed. Developing a chip holder compatible with our group's dilution refrigerator would benefit us, especially since observing the AQHE does not require high magnetic fields.

Letters of Copyright Permission



15-Aug-2024

This license agreement between the American Physical Society ("APS") and Camille Lacroix ("You") consists of your license details and the terms and conditions provided by the American Physical Society and SciPris.

Licensed Content Information

License Number:	RNP/24/AUG/082327
License date:	15-Aug-2024
DOI:	10.1103/RevModPhys.81.109
Title:	The electronic properties of graphene
Author:	A. H. Castro Neto et al.
Publication:	Reviews of Modern Physics
Publisher:	American Physical Society
Cost:	USD \$ 0.00

Request Details

Does your reuse require significant modifications:	No
Specify intended distribution locations:	Canada
Reuse Category:	Reuse in a thesis/dissertation
Requestor Type:	Student
Items for Reuse:	Figures/Tables
Number of Figure/Tables:	2
Figure/Tables Details:	FIG. 2 and FIG. 9
Format for Reuse:	Electronic

Information about New Publication:

University/Publisher:	University of Waterloo
Title of dissertation/thesis:	Development and Electronic Characterization of Graphene-Based Hall Effect Devices
Author(s):	Camille Lacroix
Expected completion date:	Sep. 2024

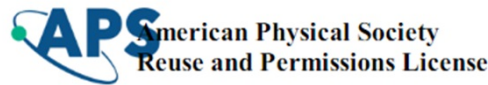
License Requestor Information

Name:	Camille Lacroix
Affiliation:	Individual
Email Id:	c5lacroix@uwaterloo.ca
Country:	Canada

Figure 6.1: Reuse and permissions license for Figure 1.4 (a).

License Number	5850270659498
License date	Aug 15, 2024
Licensed Content Publisher	Springer Nature
Licensed Content Publication	Nature
Licensed Content Title	Direct observation of a widely tunable bandgap in bilayer graphene
Licensed Content Author	Yuanbo Zhang et al
Licensed Content Date	Jun 11, 2009
Type of Use	Thesis/Dissertation
Requestor Type	academic/university or research institute
Format	electronic
Portion	figures/tables/illustrations
Number of figures/tables/illustrations	1
Would you like a high resolution image with your order?	no
Will you be translating?	no
Circulation/distribution	1 - 29
Author of this Springer Nature content	no
Title of new work	Development and Electronic Characterization of Graphene-Based Hall Effect Devices
Institution name	University of Waterloo
Expected presentation date	Sep 2024
Portions	Figure 1 a)
The Requesting Person / Organization to Appear on the License	Camille Lacroix
Requestor Location	University of Waterloo

Figure 6.2: Reuse and permissions license for Figure 1.4 (b).



15-Aug-2024

This license agreement between the American Physical Society ("APS") and Camille Lacroix ("You") consists of your license details and the terms and conditions provided by the American Physical Society and SciPris.

Licensed Content Information

License Number: RNP/24/AUG/082328
 License date: 15-Aug-2024
 DOI: 10.1103/PhysRevB.84.205440
 Title: Berry phase and pseudospin winding number in bilayer graphene
 Author: Cheol-Hwan Park and Nicola Marzari
 Publication: Physical Review B
 Publisher: American Physical Society
 Cost: USD \$ 0.00

Request Details

Does your reuse require significant modifications: No
 Specify intended distribution locations: Canada
 Reuse Category: Reuse in a thesis/dissertation
 Requestor Type: Student
 Items for Reuse: Figures/Tables
 Number of Figure/Tables: 1
 Figure/Tables Details: FIG. 2
 Format for Reuse: Electronic

Information about New Publication:

University/Publisher: University of Waterloo
 Title of dissertation/thesis: Development and Electronic Characterization of Graphene-Based Hall Effect Devices
 Author(s): Camille Lacroix
 Expected completion date: Sep. 2024

License Requestor Information

Name: Camille Lacroix
 Affiliation: Individual
 Email Id: c5lacroix@uwaterloo.ca

Figure 6.3: Reuse and permissions license for Figure 1.5.

License Number	5850280906403
License date	Aug 15, 2024
Licensed Content Publisher	Springer Nature
Licensed Content Publication	Nature
Licensed Content Title	Correlated insulator behaviour at half-filling in magic-angle graphene superlattices
Licensed Content Author	Yuan Cao et al
Licensed Content Date	Mar 5, 2018
Type of Use	Thesis/Dissertation
Requestor Type	academic/university or research institute
Format	electronic
Portion	figures/tables/illustrations
Number of figures/tables/illustrations	1
Would you like a high resolution image with your order?	no
Will you be translating?	no
Circulation/distribution	1 - 29
Author of this Springer Nature content	no
Title of new work	Development and Electronic Characterization of Graphene-Based Hall Effect Devices
Institution name	University of Waterloo
Expected presentation date	Sep 2024
Portions	Figure 1 c) to i) disposed differently and, if possible, Figure b) modified without the zoom the TBG section in a)
The Requesting Person / Organization to Appear on the License	Camille Lacroix
Requestor Location	University of Waterloo

Figure 6.4: Reuse and permissions license for Figure 1.6.

License Number	5850290069669
License date	Aug 15, 2024
Licensed Content Publisher	Springer Nature
Licensed Content Publication	La Rivista del Nuovo Cimento
Licensed Content Title	Fundamentals and functionalities of silicene, germanene, and stanene
Licensed Content Author	M. Ezawa et al
Licensed Content Date	Feb 16, 2018
Type of Use	Thesis/Dissertation
Requestor Type	academic/university or research institute
Format	electronic
Portion	figures/tables/illustrations
Number of figures/tables/illustrations	1
Will you be translating?	no
Circulation/distribution	1 - 29
Author of this Springer Nature content	no
Title of new work	Development and Electronic Characterization of Graphene-Based Hall Effect Devices
Institution name	University of Waterloo
Expected presentation date	Sep 2024
Portions	Figure 5
The Requesting Person / Organization to Appear on the License	Camille Lacroix
Requestor Location	University of Waterloo

Figure 6.5: Reuse and permissions license for Figure 1.8 (a).

License Number	5850281375160
License date	Aug 15, 2024
Licensed Content Publisher	Springer Nature
Licensed Content Publication	Nature Physics
Licensed Content Title	Probing bulk topological invariants using leaky photonic lattices
Licensed Content Author	Daniel Leykam et al
Licensed Content Date	Feb 11, 2021
Type of Use	Thesis/Dissertation
Requestor Type	academic/university or research institute
Format	electronic
Portion	figures/tables/illustrations
Number of figures/tables/illustrations	1
Would you like a high resolution image with your order?	no
Will you be translating?	no
Circulation/distribution	1 - 29
Author of this Springer Nature content	no
Title of new work	Development and Electronic Characterization of Graphene-Based Hall Effect Devices
Institution name	University of Waterloo
Expected presentation date	Sep 2024
Portions	Figure 4 c)
The Requesting Person / Organization to Appear on the License	Camille Lacroix
Requestor Location	University of Waterloo

Figure 6.6: Reuse and permissions license for Figure 1.8 (b).

License Number	5850350180839
License date	Aug 15, 2024
Licensed Content Publisher	Springer Nature
Licensed Content Publication	Nature Materials
Licensed Content Title	The topology of electronic band structures
Licensed Content Author	Prineha Narang et al
Licensed Content Date	Nov 2, 2020
Type of Use	Thesis/Dissertation
Requestor Type	academic/university or research institute
Format	electronic
Portion	figures/tables/illustrations
Number of figures/tables/illustrations	1
Would you like a high resolution image with your order?	no
Will you be translating?	no
Circulation/distribution	1 - 29
Author of this Springer Nature content	no
Title of new work	Development and Electronic Characterization of Graphene-Based Hall Effect Devices
Institution name	University of Waterloo
Expected presentation date	Sep 2024
Portions	Box 1
The Requesting Person / Organization to Appear on the License	Camille Lacroix
Requestor Location	University of Waterloo

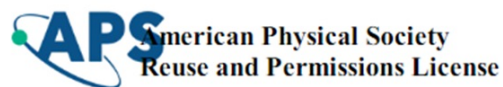
Figure 6.7: Reuse and permissions license for Figure 1.9.

Order License ID	1517105-1	Type of Use	Republish in a thesis/dissert...
Order detail status	Completed	Publisher	IOP Publishing
ISSN	0034-4885	Portion	Image/photo/illustration
		0.00 CAD	
Hide Details		Republication Permission Publisher Terms and Conditions	
LICENSED CONTENT			
Publication Title	Reports on Progress in Physi...	Country	United Kingdom of Great Bri...
Author / Editor	Institute of Physics (Great Br...	Rightsholder	IOP Publishing, Ltd
Date	01/01/1934	Publication Type	Journal
Language	English		
REQUEST DETAILS			
Portion Type	Image/photo/illustration	Distribution	Canada
Number of Images / Photos / Illustrations	3	Translation	Original language of publica...
Format (select all that apply)	Electronic	Copies for the Disabled?	No
Who Will Republish the Content?	Academic institution	Minor Editing Privileges?	Yes
Duration of Use	Life of current edition	Incidental Promotional Use?	No
Lifetime Unit Quantity	Up to 499	Currency	CAD
Rights Requested	Main product		
NEW WORK DETAILS			
Title	Development and Electronic...	Institution Name	University of Waterloo
Instructor Name	Jonathan Baugh	Expected Presentation Date	2024-08-21
ADDITIONAL DETAILS			
The Requesting Person / Organization to Appear on the License	Camille Lacroix		
REQUESTED CONTENT DETAILS			
Title, Description or Numeric Reference of the Portion(s)	Figure 2 a and b, Figure 3 an...	Title of the Article / Chapter the Portion Is From	NA
Editor of Portion(s)	N/A	Author of Portion(s)	Institute of Physics (Great Br...
Volume / Edition	N/A	Publication Date of Portion	1934-01-01
Page or Page Range of Portion	N/A		

Figure 6.8: Reuse and permissions license for Figure 1.10 and Figure 1.11.

License Number	5853140454805
License date	Aug 20, 2024
Licensed Content Publisher	John Wiley and Sons
Licensed Content Publication	Advanced Materials
Licensed Content Title	The Material Efforts for Quantized Hall Devices Based on Topological Insulators
Licensed Content Author	Baigeng Wang, Xuefeng Wang, Fengqi Song, et al
Licensed Content Date	Dec 16, 2019
Licensed Content Volume	32
Licensed Content Issue	27
Licensed Content Pages	25
Type of Use	Dissertation/Thesis
Requestor type	University/Academic
Format	Electronic
Portion	Figure/table
Number of figures/tables	1
Will you be translating?	No
Title of new work	Development and Electronic Characterization of Graphene-Based Hall Effect Devices
Institution name	University of Waterloo
Expected presentation date	Sep 2024
Portions	Figure 1
The Requesting Person / Organization to Appear on the License	Camille Lacroix
Requestor Location	University of Waterloo

Figure 6.9: Reuse and permissions license for Figure 1.12.



20-Aug-2024

This license agreement between the American Physical Society ("APS") and Camille Lacroix ("You") consists of your license details and the terms and conditions provided by the American Physical Society and SciPris.

Licensed Content Information

License Number:	RNP/24/AUG/082475
License date:	20-Aug-2024
DOI:	10.1103/PhysRevLett.96.086805
Title:	Landau-Level Degeneracy and Quantum Hall Effect in a Graphite Bilayer
Author:	Edward McCann and Vladimir I. Fal'ko
Publication:	Physical Review Letters
Publisher:	American Physical Society
Cost:	USD \$ 0.00

Request Details

Does your reuse require significant modifications:	No
Specify intended distribution locations:	Canada
Reuse Category:	Reuse in a thesis/dissertation
Requestor Type:	Student
Items for Reuse:	Figures/Tables
Number of Figure/Tables:	1
Figure/Tables Details:	Fig. 4
Format for Reuse:	Electronic

Information about New Publication:

University/Publisher:	University of Waterloo
Title of dissertation/thesis:	Development and Electronic Characterization of Graphene-Based Hall Effect Devices
Author(s):	Camille Lacroix
Expected completion date:	Aug. 2024

License Requestor Information

Name:	Camille Lacroix
Affiliation:	Individual
Email Id:	c5lacroix@uwaterloo.ca
Country:	Canada

Figure 6.10: Reuse and permissions license for Figure 1.13.

License Number	5850290872998
License date	Aug 15, 2024
Licensed Content Publisher	The American Association for the Advancement of Science
Licensed Content Publication	Science
Licensed Content Title	The Complete Quantum Hall Trio
Licensed Content Author	Seongshik Oh
Licensed Content Date	Apr 12, 2013
Licensed Content Volume	340
Licensed Content Issue	6129
Type of Use	Thesis / Dissertation
Requestor type	Scientist/individual at a research institution
Format	Electronic
Portion	Text Excerpt
Number of pages requested	1
Title of new work	Development and Electronic Characterization of Graphene-Based Hall Effect Devices
Institution name	University of Waterloo
Expected presentation date	Sep 2024
Portions	Figure Quantum Hall trio
The Requesting Person / Organization to Appear on the License	Camille Lacroix
Requestor Location	University of Waterloo

Figure 6.11: Reuse and permissions license for Figure 1.14.

License Number	5850290201332
License date	Aug 15, 2024
Licensed Content Publisher	Springer Nature
Licensed Content Publication	Nature Nanotechnology
Licensed Content Title	Quantum Hall resistance standard in graphene devices under relaxed experimental conditions
Licensed Content Author	R. Ribeiro-Palau et al
Licensed Content Date	Sep 7, 2015
Type of Use	Thesis/Dissertation
Requestor Type	academic/university or research institute
Format	electronic
Portion	figures/tables/illustrations
Number of figures/tables/illustrations	1
Would you like a high resolution image with your order?	no
Will you be translating?	no
Circulation/distribution	1 - 29
Author of this Springer Nature content	no
Title of new work	Development and Electronic Characterization of Graphene-Based Hall Effect Devices
Institution name	University of Waterloo
Expected presentation date	Sep 2024
Portions	Figure 2 d)
The Requesting Person / Organization to Appear on the License	Camille Lacroix
Requestor Location	University of Waterloo

Figure 6.12: Reuse and permissions license for Figure 1.15.

License Number	5850291238374
License date	Aug 15, 2024
Licensed Content Publisher	Springer Nature
Licensed Content Publication	Springer eBook
Licensed Content Title	Characterization of Graphene by Confocal Raman Spectroscopy
Licensed Content Author	Christoph Neumann, Christoph Stampfer
Licensed Content Date	Jan 1, 2018
Type of Use	Thesis/Dissertation
Requestor Type	academic/university or research institute
Format	electronic
Portion	figures/tables/illustrations
Number of figures/tables/illustrations	3
Will you be translating?	no
Circulation/distribution	1 - 29
Author of this Springer Nature content	no
Title of new work	Development and Electronic Characterization of Graphene-Based Hall Effect Devices
Institution name	University of Waterloo
Expected presentation date	Sep 2024
Portions	Figure 8.4, Figure 8.5, Figure 8.13
The Requesting Person / Organization to Appear on the License	Camille Lacroix
Requestor Location	University of Waterloo 84 Union Boulevard Kitchener, ON N2G2K2 Canada Attn: University of Waterloo
Billing Type	Invoice
Billing address	University of Waterloo

Figure 6.13: Reuse and permissions license for Figure 2.4 and Figure 2.5.

References

- [1] B Andrei Bernevig. *Topological insulators and topological superconductors*. Princeton University Press, Princeton, NJ, April 2013.
- [2] P R Wallace. The band theory of graphite. *Phys. Rev.*, 71(9):622–634, May 1947.
- [3] J W McClure. Band structure of graphite and de haas-van alphen effect. *Phys. Rev.*, 108(3):612–618, November 1957.
- [4] J C Slonczewski and P R Weiss. Band structure of graphite. *Phys. Rev.*, 109(2):272–279, January 1958.
- [5] Gordon W Semenoff. Condensed-matter simulation of a three-dimensional anomaly. *Phys. Rev. Lett.*, 53(26):2449–2452, December 1984.
- [6] F D Haldane. Model for a quantum hall effect without landau levels: Condensed-matter realization of the “parity anomaly”. *Phys. Rev. Lett.*, 61(18):2015–2018, October 1988.
- [7] C L Kane and E J Mele. Quantum spin hall effect in graphene. *Phys. Rev. Lett.*, 95(22):226801, November 2005.
- [8] C L Kane and E J Mele. Z₂ topological order and the quantum spin hall effect. *Phys. Rev. Lett.*, 95(14):146802, September 2005.
- [9] Jian Kang and Oskar Vafek. Symmetry, maximally localized wannier states, and a low-energy model for twisted bilayer graphene narrow bands. *Phys. Rev. X.*, 8(3), September 2018.
- [10] K S Novoselov, A K Geim, S V Morozov, D Jiang, Y Zhang, S V Dubonos, I V Grigorieva, and A A Firsov. Electric field effect in atomically thin carbon films. *Science*, 306(5696):666–669, October 2004.

- [11] V P Gusynin and S G Sharapov. Unconventional integer quantum hall effect in graphene. *Phys. Rev. Lett.*, 95(14):146801, September 2005.
- [12] N M R Peres, F Guinea, and A H Castro Neto. Electronic properties of disordered two-dimensional carbon. *Phys. Rev. B Condens. Matter Mater. Phys.*, 73(12), March 2006.
- [13] Yuanbo Zhang, Yan-Wen Tan, Horst L Stormer, and Philip Kim. Experimental observation of the quantum hall effect and berry’s phase in graphene. *Nature*, 438(7065):201–204, November 2005.
- [14] K S Novoselov, Z Jiang, Y Zhang, S V Morozov, H L Stormer, U Zeitler, J C Maan, G S Boebinger, P Kim, and A K Geim. Room-temperature quantum hall effect in graphene. *Science*, 315(5817):1379, March 2007.
- [15] Angelo Armano and Simonpietro Agnello. Two-dimensional carbon: A review of synthesis methods, and electronic, optical, and vibrational properties of single-layer graphene. *C*, 5(4):67, November 2019.
- [16] Eduardo V Castro, K S Novoselov, S V Morozov, N M R Peres, J M B Lopes dos Santos, Johan Nilsson, F Guinea, A K Geim, and A H Castro Neto. Biased bilayer graphene: semiconductor with a gap tunable by the electric field effect. *Phys. Rev. Lett.*, 99(21):216802, November 2007.
- [17] Aaron Bostwick, Taisuke Ohta, Thomas Seyller, Karsten Horn, and Eli Rotenberg. Quasiparticle dynamics in graphene. *Nat. Phys.*, 3(1):36–40, January 2007.
- [18] P Plochocka, C Faugeras, M Orlita, M L Sadowski, G Martinez, M Potemski, M O Goerbig, J-N Fuchs, C Berger, and W A de Heer. High-energy limit of massless dirac fermions in multilayer graphene using magneto-optical transmission spectroscopy. *Phys. Rev. Lett.*, 100(8):087401, February 2008.
- [19] M S Dresselhaus and G Dresselhaus. Intercalation compounds of graphite. *Adv. Phys.*, 51(1):1–186, January 2002.
- [20] Edward McCann and Vladimir I Fal’ko. Landau-level degeneracy and quantum hall effect in a graphite bilayer. *Phys. Rev. Lett.*, 96(8):086805, March 2006.
- [21] Yuanbo Zhang, Tsung-Ta Tang, Caglar Girit, Zhao Hao, Michael C Martin, Alex Zettl, Michael F Crommie, Y Ron Shen, and Feng Wang. Direct observation of a widely tunable bandgap in bilayer graphene. *Nature*, 459(7248):820–823, June 2009.

- [22] Taisuke Ohta, Aaron Bostwick, Thomas Seyller, Karsten Horn, and Eli Rotenberg. Controlling the electronic structure of bilayer graphene. *Science*, 313(5789):951–954, August 2006.
- [23] K S Novoselov, E McCann, S V Morozov, V I Fal’ko, M I Katsnelson, U Zeitler, D Jiang, F Schedin, and A K Geim. Unconventional quantum hall effect and berry’s phase of 2π in bilayer graphene. *Nat. Phys.*, 2(3):177–180, March 2006.
- [24] Cheol-Hwan Park and Nicola Marzari. Berry phase and pseudospin winding number in bilayer graphene. *Phys. Rev. B Condens. Matter Mater. Phys.*, 84(20), November 2011.
- [25] Yuan Cao, Valla Fatemi, Ahmet Demir, Shiang Fang, Spencer L Tomarken, Jason Y Luo, Javier D Sanchez-Yamagishi, Kenji Watanabe, Takashi Taniguchi, Efthimios Kaxiras, Ray C Ashoori, and Pablo Jarillo-Herrero. Correlated insulator behaviour at half-filling in magic-angle graphene superlattices. *Nature*, 556(7699):80–84, April 2018.
- [26] Rafi Bistritzer and Allan H MacDonald. Moiré bands in twisted double-layer graphene. *Proc. Natl. Acad. Sci. U. S. A.*, 108(30):12233–12237, July 2011.
- [27] Hoi Chun Po, Liujun Zou, T Senthil, and Ashvin Vishwanath. Faithful tight-binding models and fragile topology of magic-angle bilayer graphene. *Phys. Rev. B.*, 99(19), May 2019.
- [28] Simone Lisi, Xiaobo Lu, Tjerk Benschop, Tobias A de Jong, Petr Stepanov, Jose R Duran, Florian Margot, Irène Cucchi, Edoardo Cappelli, Andrew Hunter, Anna Tamai, Viktor Kandyba, Alessio Giampietri, Alexei Barinov, Johannes Jobst, Vincent Stalman, Maarten Leeuwenhoek, Kenji Watanabe, Takashi Taniguchi, Louk Rademaker, Sense Jan van der Molen, Milan P Allan, Dmitri K Efetov, and Felix Baumberger. Observation of flat bands in twisted bilayer graphene. *Nat. Phys.*, 17(2):189–193, February 2021.
- [29] Prineha Narang, Christina A C Garcia, and Claudia Felser. The topology of electronic band structures. *Nat. Mater.*, 20(3):293–300, March 2021.
- [30] R V Gorbachev, J C W Song, G L Yu, A V Kretinin, F Withers, Y Cao, A Mishchenko, I V Grigorieva, K S Novoselov, L S Levitov, and A K Geim. Detecting topological currents in graphene superlattices. *Science*, 346(6208):448–451, October 2014.

- [31] B Hunt, J D Sanchez-Yamagishi, A F Young, M Yankowitz, B J LeRoy, K Watanabe, T Taniguchi, P Moon, M Koshino, P Jarillo-Herrero, and R C Ashoori. Massive dirac fermions and hofstadter butterfly in a van der waals heterostructure. *Science*, 340(6139):1427–1430, June 2013.
- [32] C R Dean, A F Young, I Meric, C Lee, L Wang, S Sorgenfrei, K Watanabe, T Taniguchi, P Kim, K L Shepard, and J Hone. Boron nitride substrates for high-quality graphene electronics. *Nat. Nanotechnol.*, 5(10):722–726, October 2010.
- [33] The nobel prize in physics 2016. <https://www.nobelprize.org/prizes/physics/2016/haldane/facts/>. Accessed: 2024-6-28.
- [34] Srijata Lahiri and Saurabh Basu. Second order topology in a band engineered chern insulator. *Sci. Rep.*, 14(1):1880, January 2024.
- [35] Sambit Mitra, Álvaro Jiménez-Galán, Mario Aulich, Marcel Neuhaus, Rui E F Silva, Volodymyr Pervak, Matthias F Kling, and Shubhadeep Biswas. Light-wave-controlled haldane model in monolayer hexagonal boron nitride. *Nature*, 628(8009):752–757, April 2024.
- [36] M Ezawa, E Salomon, P De Padova, D Solonenko, P Vogt, M E Dávila, A Molle, T Angot, and G Le Lay. Fundamentals and functionalities of silicene, germanene, and stanene. *Riv. Nuovo Cimento*, 41(3):175–224, February 2018.
- [37] Daniel Leykam and Daria A Smirnova. Probing bulk topological invariants using leaky photonic lattices. *Nat. Phys.*, 17(5):632–638, May 2021.
- [38] E H Hall. On a new action of the magnet on electric currents. *Amer. J. Math.*, 2(3):287, September 1879.
- [39] T J B M Janssen, A Tzalenchuk, S Lara-Avila, S Kubatkin, and V I Fal’ko. Quantum resistance metrology using graphene. *Rep. Prog. Phys.*, 76(10):104501, October 2013.
- [40] Klaus von Klitzing. The quantized hall effect. *Rev. Mod. Phys.*, 58(3):519–531, July 1986.
- [41] B I Halperin. Quantized hall conductance, current-carrying edge states, and the existence of extended states in a two-dimensional disordered potential. *Phys. Rev. B Condens. Matter*, 25(4):2185–2190, February 1982.
- [42] M Büttiker. Absence of backscattering in the quantum hall effect in multiprobe conductors. *Phys. Rev. B Condens. Matter*, 38(14):9375–9389, November 1988.

- [43] L Landau. Diamagnetismus der metalle. *Eur. Phys. J. A*, 64(9-10):629–637, September 1930.
- [44] Fucong Fei, Shuai Zhang, Minhao Zhang, Syed Adil Shah, Fengqi Song, Xuefeng Wang, and Baigeng Wang. The material efforts for quantized hall devices based on topological insulators. *Adv. Mater.*, 32(27):e1904593, July 2020.
- [45] Seongshik Oh. Physics. the complete quantum hall trio. *Science*, 340(6129):153–154, April 2013.
- [46] Wang-Kong Tse, Zhenhua Qiao, Yugui Yao, A H MacDonald, and Qian Niu. Quantum anomalous hall effect in single-layer and bilayer graphene. *Phys. Rev. B Condens. Matter Mater. Phys.*, 83(15), April 2011.
- [47] Zhenhua Qiao, Hua Jiang, Xiao Li, Yugui Yao, and Qian Niu. Microscopic theory of quantum anomalous hall effect in graphene. *Phys. Rev. B Condens. Matter Mater. Phys.*, 85(11), March 2012.
- [48] Zhiyong Wang, Chi Tang, Raymond Sachs, Yafis Barlas, and Jing Shi. Proximity-induced ferromagnetism in graphene revealed by the anomalous hall effect. *Phys. Rev. Lett.*, 114(1):016603, January 2015.
- [49] M Z Hasan and C L Kane. Colloquium: Topological insulators. *Rev. Mod. Phys.*, 82(4):3045–3067, November 2010.
- [50] B N Taylor and T J Witt. New international electrical reference standards based on the josephson and quantum hall effects. *Metrologia*, 26(1):47–62, January 1989.
- [51] S G Semenchinskiy. The quantum hall effect and von klitzing constant. *Meas. Tech.*, 64(1):8–12, April 2021.
- [52] A Hartland, K Jones, J M Williams, T Galloway, B L Gallagher, C R H White, and M Henini. A direct comparison of the quantized hall resistance in high critical current gallium arsenide and silicon devices. *Surf. Sci.*, 263(1-3):112–115, February 1992.
- [53] R Ribeiro-Palau, F Lafont, J Brun-Picard, D Kazazis, A Michon, F Cheynis, O Couturaud, C Consejo, B Jouault, W Poirier, and F Schopfer. Quantum hall resistance standard in graphene devices under relaxed experimental conditions. *Nat. Nanotechnol.*, 10(11):965–971, November 2015.
- [54] Félicien Schopfer and Wilfrid Poirier. Graphene-based quantum hall effect metrology. *MRS Bull.*, 37(12):1255–1264, December 2012.

- [55] W Poirier and F Schopfer. Resistance metrology based on the quantum hall effect. *Eur. Phys. J. Spec. Top.*, 172(1):207–245, June 2009.
- [56] F Delahaye and B Jeckelmann. Revised technical guidelines for reliable dc measurements of the quantized hall resistance. *Metrologia*, 40(5):217–223, October 2003.
- [57] W Gannett, W Regan, K Watanabe, T Taniguchi, M F Crommie, and A Zettl. Boron nitride substrates for high mobility chemical vapor deposited graphene. *Appl. Phys. Lett.*, 98(24):242105, June 2011.
- [58] D G Purdie, N M Pugno, T Taniguchi, K Watanabe, A C Ferrari, and A Lombardo. Cleaning interfaces in layered materials heterostructures. *Nat. Commun.*, 9(1):5387, December 2018.
- [59] Min Yi and Zhigang Shen. A review on mechanical exfoliation for the scalable production of graphene. *J. Mater. Chem. A Mater. Energy Sustain.*, 3(22):11700–11715, May 2015.
- [60] K S Novoselov, A K Geim, S V Morozov, D Jiang, M I Katsnelson, I V Grigorieva, S V Dubonos, and A A Firsov. Two-dimensional gas of massless dirac fermions in graphene. *Nature*, 438(7065):197–200, November 2005.
- [61] L Banszerus, T Sohler, A Epping, F Winkler, F Libisch, F Haupt, K Watanabe, T Taniguchi, K Müller-Caspary, N Marzari, F Mauri, B Beschoten, and C Stampfer. Extraordinary high room-temperature carrier mobility in graphene-WSe₂ heterostructures. September 2019.
- [62] Sungjin Park and Rodney S Ruoff. Chemical methods for the production of graphenes. *Nat. Nanotechnol.*, 4(4):217–224, April 2009.
- [63] Domenico De Fazio, David G Purdie, Anna K Ott, Philipp Braeuninger-Weimer, Timofiy Khodkov, Stijn Goossens, Takashi Taniguchi, Kenji Watanabe, Patrizia Livreri, Frank H L Koppens, Stephan Hofmann, Ilya Goykhman, Andrea C Ferrari, and Antonio Lombardo. High-mobility, wet-transferred graphene grown by chemical vapor deposition. *ACS Nano*, 13(8):8926–8935, August 2019.
- [64] Daniel R Cooper, Benjamin D’Anjou, Nageswara Ghattamaneni, Benjamin Harack, Michael Hilke, Alexandre Horth, Norberto Majlis, Mathieu Massicotte, Leron Vandsburger, Eric Whiteway, and Victor Yu. Experimental review of graphene. *ISRN Condens. Matter Phys.*, 2012:1–56, April 2012.

- [65] Björn Trauzettel, Denis V Bulaev, Daniel Loss, and Guido Burkard. Spin qubits in graphene quantum dots. *Nat. Phys.*, 3(3):192–196, March 2007.
- [66] Chuyao Tong, Rebekka Garreis, Angelika Knothe, Marius Eich, Agnese Sacchi, Kenji Watanabe, Takashi Taniguchi, Vladimir Fal’ko, Thomas Ihn, Klaus Ensslin, and Annika Kurzmann. Tunable valley splitting and bipolar operation in graphene quantum dots. *Nano Lett.*, 21(2):1068–1073, January 2021.
- [67] R Garreis, A Knothe, C Tong, M Eich, C Gold, K Watanabe, T Taniguchi, V Fal’ko, T Ihn, K Ensslin, and A Kurzmann. Shell filling and trigonal warping in graphene quantum dots. *Phys. Rev. Lett.*, 126(14):147703, April 2021.
- [68] Annika Kurzmann, Yaakov Kleeorin, Chuyao Tong, Rebekka Garreis, Angelika Knothe, Marius Eich, Christopher Mittag, Carolin Gold, Folkert Kornelis de Vries, Kenji Watanabe, Takashi Taniguchi, Vladimir Fal’ko, Yigal Meir, Thomas Ihn, and Klaus Ensslin. Kondo effect and spin-orbit coupling in graphene quantum dots. *Nat. Commun.*, 12(1):6004, October 2021.
- [69] Rebekka Garreis, Chuyao Tong, Jocelyn Terle, Max Josef Ruckriegel, Jonas Daniel Gerber, Lisa Maria Gächter, Kenji Watanabe, Takashi Taniguchi, Thomas Ihn, Klaus Ensslin, and Wei Wister Huang. Long-lived valley states in bilayer graphene quantum dots. *Nat. Phys.*, 20(3):428–434, March 2024.
- [70] Lisa Maria Gächter, Rebekka Garreis, Jonas Daniel Gerber, Max Josef Ruckriegel, Chuyao Tong, Benedikt Kratochwil, Folkert Kornelis de Vries, Annika Kurzmann, Kenji Watanabe, Takashi Taniguchi, Thomas Ihn, Klaus Ensslin, and Wister Wei Huang. Single-shot spin readout in graphene quantum dots. *PRX quantum*, 3(2), May 2022.
- [71] L Banszerus, S Möller, C Steiner, E Icking, S Trellenkamp, F Lentz, K Watanabe, T Taniguchi, C Volk, and C Stampfer. Spin-valley coupling in single-electron bilayer graphene quantum dots. *Nat. Commun.*, 12(1):5250, September 2021.
- [72] Marius Eich, František Herman, Riccardo Pisoni, Hiske Overweg, Annika Kurzmann, Yongjin Lee, Peter Rickhaus, Kenji Watanabe, Takashi Taniguchi, Manfred Sigrist, Thomas Ihn, and Klaus Ensslin. Spin and valley states in gate-defined bilayer graphene quantum dots. *Phys. Rev. X.*, 8(3), July 2018.
- [73] Zhengguang Lu, Tonghang Han, Yuxuan Yao, Aidan P Reddy, Jixiang Yang, Junseok Seo, Kenji Watanabe, Takashi Taniguchi, Liang Fu, and Long Ju. Fractional quantum

- anomalous hall effect in multilayer graphene. *Nature*, 626(8000):759–764, February 2024.
- [74] Long Ju, Allan H MacDonald, Kin Fai Mak, Jie Shan, and Xiaodong Xu. The fractional quantum anomalous hall effect. *Nat. Rev. Mater.*, 9(7):455–459, June 2024.
 - [75] Yagang Yao, Zhuo Li, Ziyin Lin, Kyoung-Sik Moon, Josh Agar, and Chingping Wong. Controlled growth of multilayer, few-layer, and single-layer graphene on metal substrates. *J. Phys. Chem. C Nanomater. Interfaces*, 115(13):5232–5238, April 2011.
 - [76] Ruiwen Xue, Irfan H Abidi, and Zhengtang Luo. Domain size, layer number and morphology control for graphene grown by chemical vapor deposition. *Funct. Mater. Lett.*, 10(04):1730003, August 2017.
 - [77] Mohamed Fahmy Taha, Hager Ashraf, and Wahyu Caesarendra. A brief description of cyclic voltammetry transducer-based non-enzymatic glucose biosensor using synthesized graphene electrodes. *Appl. Syst. Innov.*, 3(3):32, August 2020.
 - [78] Welyson T S Ramos, Thiago H R Cunha, Ingrid D Barcelos, Douglas R Miquita, Gustavo A Ferrari, Sergio de Oliveira, Luciana M Seara, Eliel G Silva Neto, Andre S Ferlauto, and Rodrigo G Lacerda. The role of hydrogen partial pressure on the annealing of copper substrates for graphene CVD synthesis. *Mater. Res. Express*, 3(4):045602, April 2016.
 - [79] Benjamin Huet and Jean-Pierre Raskin. Role of cu foil in-situ annealing in controlling the size and thickness of CVD graphene domains. *Carbon N. Y.*, 129:270–280, April 2018.
 - [80] Kamal P Sharma, Sachin M Shinde, Mohamad Saufi Rosmi, Subash Sharma, Golap Kalita, and Masaki Tanemura. Effect of copper foil annealing process on large graphene domain growth by solid source-based chemical vapor deposition. *J. Mater. Sci.*, 51(15):7220–7228, August 2016.
 - [81] Xiaohua Yang, Gaixia Zhang, Jai Prakash, Zhangsen Chen, Marc Gauthier, and Shuhui Sun. Chemical vapour deposition of graphene: layer control, the transfer process, characterization, and related applications. *Int. Rev. Phys. Chem.*, 38(2):149–199, April 2019.
 - [82] Christoph Neumann and Christoph Stampfer. Characterization of graphene by confocal raman spectroscopy. In *Confocal Raman Microscopy*, Springer series in surface sciences, pages 177–194. Springer International Publishing, Cham, 2018.

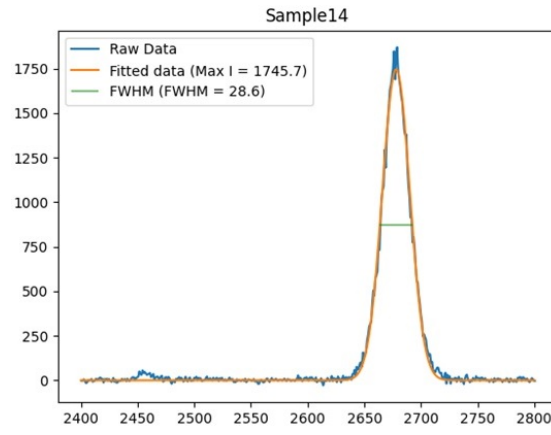
- [83] Indu Sharma, Girija Shankar Papanai, Sharon Jyotika Paul, and Bipin Kumar Gupta. Partial pressure assisted growth of single-layer graphene grown by low-pressure chemical vapor deposition: Implications for high-performance graphene FET devices. *ACS Omega*, 5(35):22109–22118, September 2020.
- [84] Cameron J Shearer, Ashley D Slattey, Andrew J Stapleton, Joseph G Shapter, and Christopher T Gibson. Accurate thickness measurement of graphene. *Nanotechnology*, 27(12):125704, March 2016.
- [85] P Blake, E W Hill, A H Castro Neto, K S Novoselov, D Jiang, R Yang, T J Booth, and A K Geim. Making graphene visible. *Appl. Phys. Lett.*, 91(6):063124, August 2007.
- [86] Yi Zhang, Zhen Li, Pyojae Kim, Luyao Zhang, and Chongwu Zhou. Anisotropic hydrogen etching of chemical vapor deposited graphene. *ACS Nano*, 6(1):126–132, January 2012.
- [87] Grzegorz Romaniak, Peifu Cheng, Konrad Dybowski, Piotr Kula, and Piran R Kidambi. Assessing the quality of large-area monolayer graphene grown on liquid copper for size-selective ionic/molecular membrane separations. *Mater. Res. Express*, 10(10):105101, October 2023.
- [88] Dechao Geng, Bin Wu, Yunlong Guo, Liping Huang, Yunzhou Xue, Jianyi Chen, Gui Yu, Lang Jiang, Wenping Hu, and Yunqi Liu. Uniform hexagonal graphene flakes and films grown on liquid copper surface. *Proc. Natl. Acad. Sci. U. S. A.*, 109(21):7992–7996, May 2012.
- [89] Xudong Xue, Qiang Xu, Huaping Wang, Shuwei Liu, Qianqing Jiang, Zhiwei Yu, Xiahong Zhou, Tianbao Ma, Liping Wang, and Gui Yu. Gas-flow-driven aligned growth of graphene on liquid copper. *Chem. Mater.*, 31(4):1231–1236, February 2019.
- [90] Jacob Amontree, Xingzhou Yan, Christopher S DiMarco, Pierre L Levesque, Tehseen Adel, Jordan Pack, Madisen Holbrook, Christian Cupo, Zhiying Wang, Dihao Sun, Adam J Biacchi, Charlezetta E Wilson-Stokes, Kenji Watanabe, Takashi Taniguchi, Cory R Dean, Angela R Hight Walker, Katayun Barmak, Richard Martel, and James Hone. Reproducible graphene synthesis by oxygen-free chemical vapour deposition. *Nature*, 630(8017):636–642, June 2024.
- [91] Mai. Sukuragi. Electronic transport properties in single-layer cvd graphene, 2022.

- [92] Teresa Cusati, Gianluca Fiori, Amit Gahoi, Vikram Passi, Max C Lemme, Alessandro Fortunelli, and Giuseppe Iannaccone. Electrical properties of graphene-metal contacts. *Sci. Rep.*, 7(1):5109, July 2017.
- [93] J Martin, N Akerman, G Ulbricht, T Lohmann, J H Smet, K von Klitzing, and A Yacoby. Observation of electron–hole puddles in graphene using a scanning single-electron transistor. *Nat. Phys.*, 4(2):144–148, February 2008.
- [94] Kalon Gopinadhan, Young Jun Shin, Rashid Jalil, Thirumalai Venkatesan, Andre K Geim, Antonio H Castro Neto, and Hyunsoo Yang. Extremely large magnetoresistance in few-layer graphene/boron-nitride heterostructures. *Nat. Commun.*, 6(1):8337, September 2015.
- [95] Jiang-Xiazi Lin, Ya-Hui Zhang, Erin Morissette, Zhi Wang, Song Liu, Daniel Rhodes, K Watanabe, T Taniguchi, James Hone, and J I A Li. Spin-orbit-driven ferromagnetism at half moiré filling in magic-angle twisted bilayer graphene. *Science*, 375(6579):437–441, January 2022.
- [96] Tianle Wang, Nick Bultinck, and Michael P Zaletel. Flat-band topology of magic angle graphene on a transition metal dichalcogenide. *Phys. Rev. B.*, 102(23), December 2020.
- [97] Martin Gmitra, Denis Kochan, Petra Högl, and Jaroslav Fabian. Trivial and inverted dirac bands and the emergence of quantum spin hall states in graphene on transition-metal dichalcogenides. *Phys. Rev. B.*, 93(15), April 2016.
- [98] Saisab Bhowmik, Bhaskar Ghawri, Youngju Park, Dongkyu Lee, Suvronil Datta, Radhika Soni, K Watanabe, T Taniguchi, Arindam Ghosh, Jeil Jung, and U Chandni. Spin-orbit coupling-enhanced valley ordering of malleable bands in twisted bilayer graphene on WSe₂. *Nat. Commun.*, 14(1):4055, July 2023.

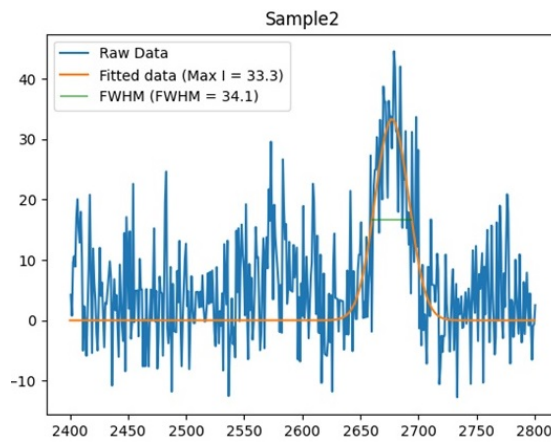
Appendix A

Data Reprocessing

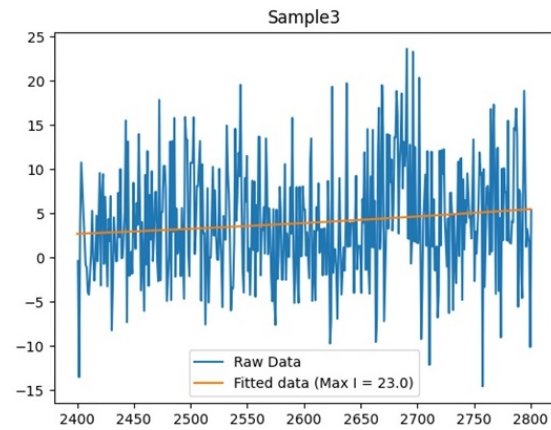
Following the mapping of the samples, the resulting data are stacked in a text file and need to be reprocessed to map the desired parameters. Additionally, the mapping is cut into 2 acquisition ranges to accelerate the mapping. A first range of 1300 cm^{-1} to 1800 cm^{-1} cover the D and G band region. the second range of 2400 cm^{-1} to 2800 covers the range of the 2D band. The peaks are fitted to a Gaussian function. Figure A.1 percent the peak fitting on real data, in the case of clear data and noisy data. Even in the case of a signal-to-noise ratio peak can be distinguished from the background. The I(2D)/I(G) band ratio is found by comparing the height or peak intensity of the 2 peaks. Figure A.2 presents the resulting reprocessing of spectra with an I(2D)/I(G) band ratio of 3.2 and FWHM of the 2D band of 31.4 cm^{-1} . Figure A.3 presents the case of an I(2D)/I(G) band ratio of 1.4 and increased FWHM of the 2D band of 46.6 cm^{-1} . The presence of high-quality SLG is only considered with an I(2D)/I(G) ratio greater than 2 and with FWHM under 35 cm^{-1} . Figure A.3 and Figure A.4 present the I(2D)/I(G) band ratio and I(D)/I(G) band ratio in the case of no or low defect density and high defect density graphene. Graphene is considered to have a low defect density for I (D)/I(G) ratio < 0.1 . Figure The I(2D)/I(G) band ratio is 2.8, and the I(D)/I(G) band ratio is 0.0. In the case of Figure A.4, the I(2D)/I(G) is 1.2, and the I(D)/I(G) band ratio is 2.8 for an I(D)/I(G) of Figure A.4.



(a)



(b)



(c)

Figure A.1: **Peak fitting of Raman spectra.** a) Clear data. b) noisy data. c) pure noise. The peak can be fitted with a signal where the signal-to-noise ratio is < 3 .

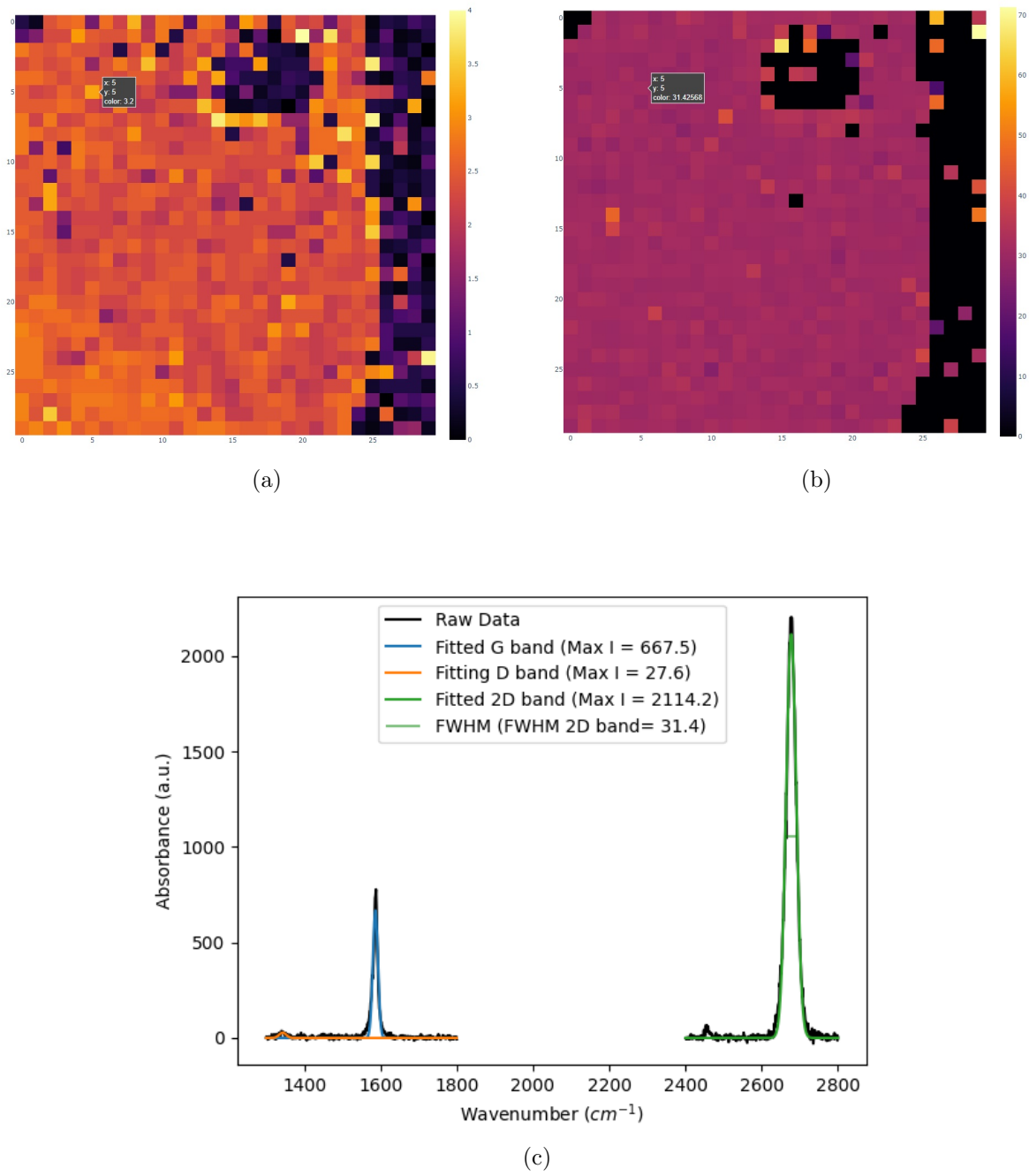


Figure A.2: **Data reprocessing of high quality graphene.** a) mapping of the I(2D)/I(G) band ratio showing 3.2 for sample 274. b) The mapping of the 2D band FWHM is showing 31.4 cm^{-1} for sample 274. c) Raman spectra of sample 274. Mapping of a CVDCV graphene sample.

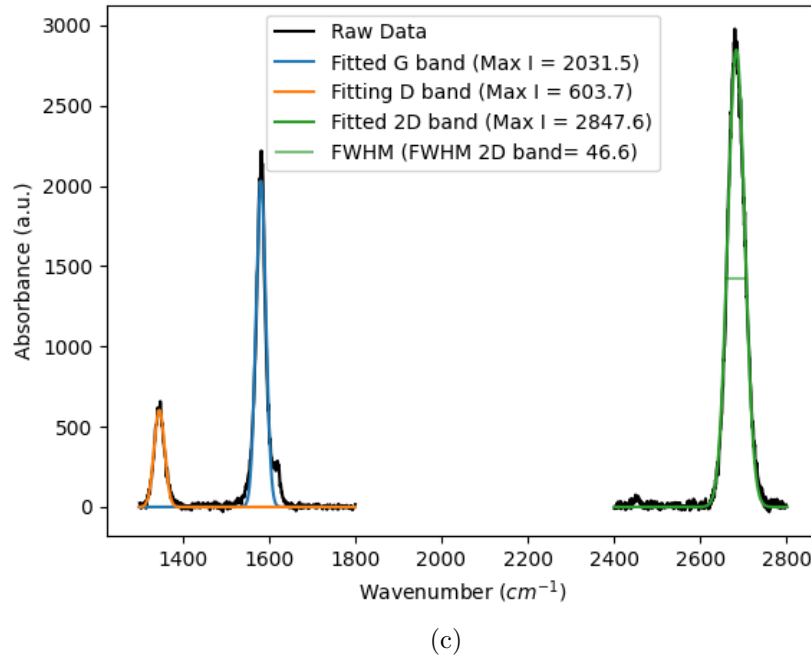
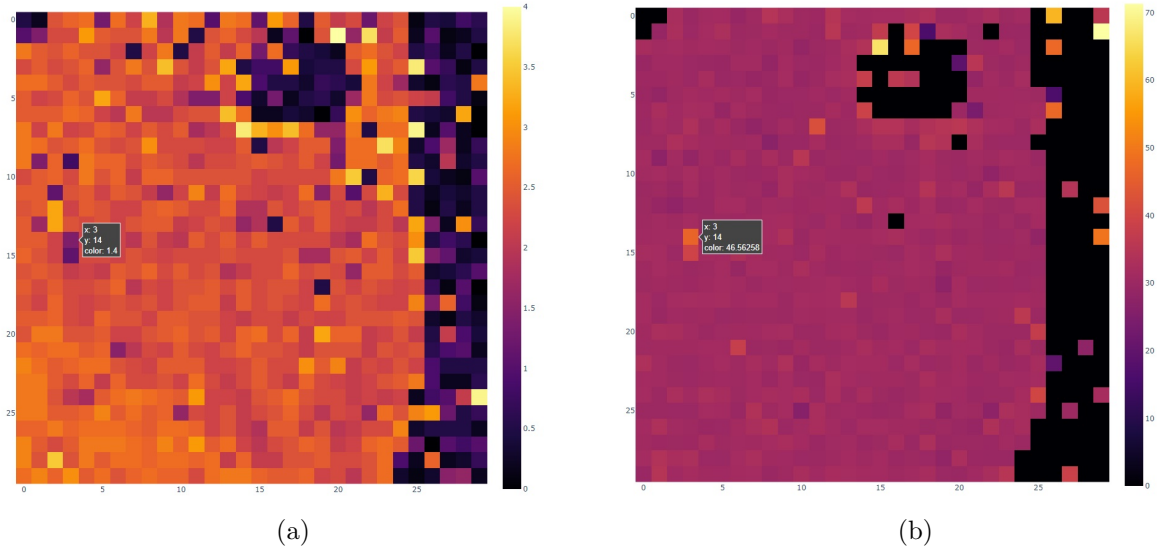


Figure A.3: **Data reprocessing of low quality graphene** a) mapping of the I(2D)/I(G) band ratio showing 1.4 for sample 274. b) The mapping of the 2D band FWHM is showing 46.6 cm^{-1} for sample 424. c) Raman spectra of sample 424. Mapping of a CVDCV graphene sample.

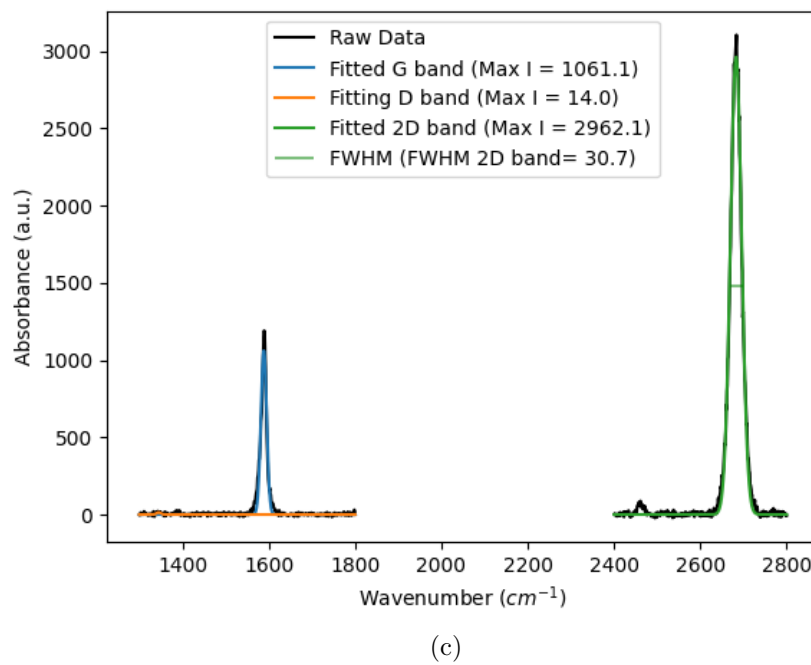
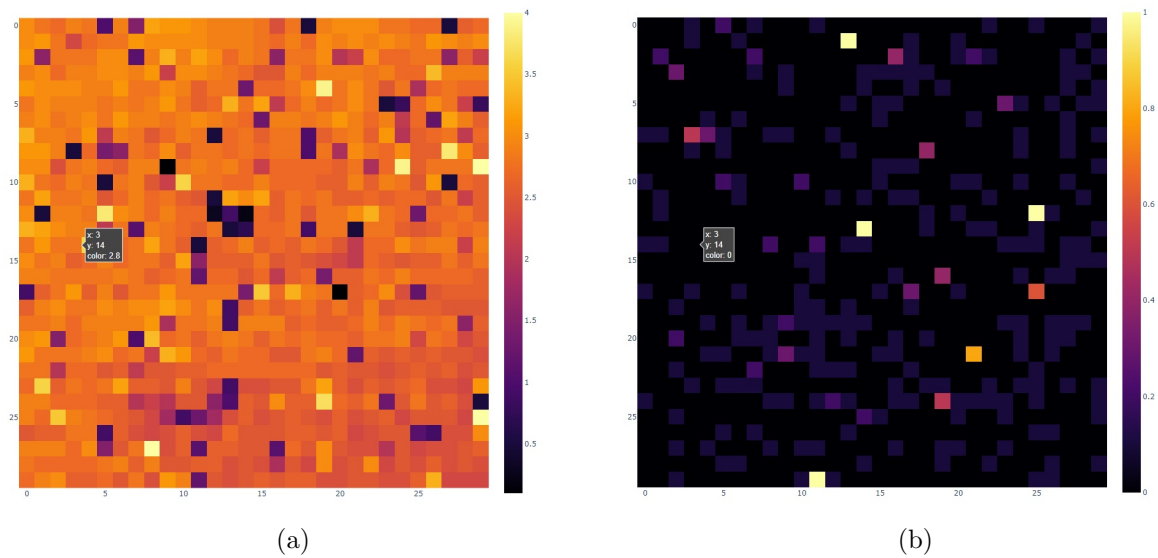


Figure A.4: **Data reprocessing of low defect density graphene.** a) mapping of the I(2D)/I(G) band ratio showing 2.8 for sample 424. b) The mapping of the I(D)/I(G) is showing 0.0 for sample 424. c) Raman spectra of sample 424. Mapping of a CVDHT graphene sample.

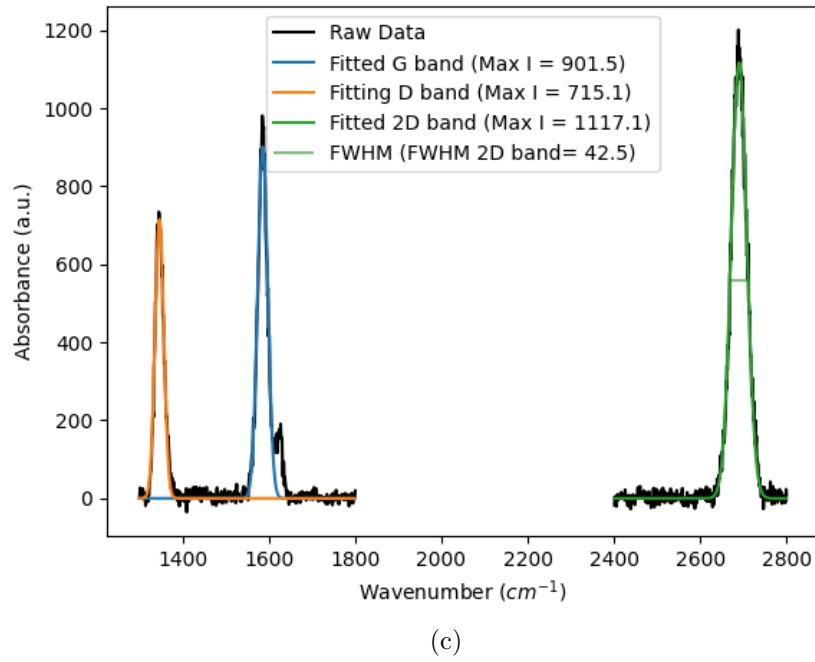
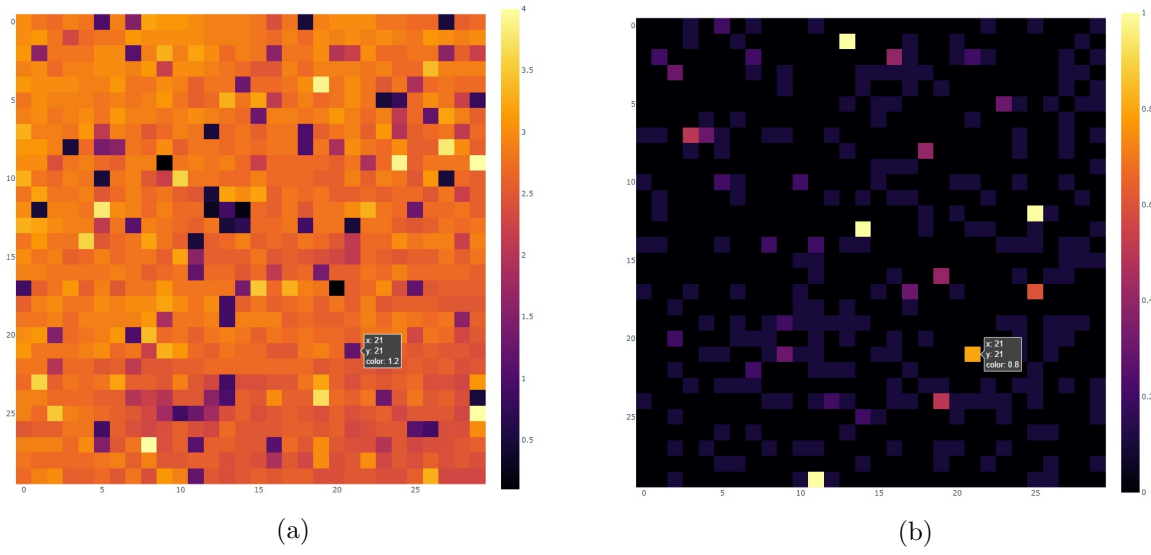


Figure A.5: **Data reprocessing of high defect density graphene.** a) mapping of the $I(2D)/I(G)$ band ratio showing 1.2 for sample 652. b) The mapping of the $I(D)/I(G)$ is showing 0.8 for sample 652. c) Raman spectra of sample 652. Mapping of a CVDHT graphene sample.

Appendix B

Optical Microscope Pictures

The following section extends the optical microscope pictures in Chapter 2. Pictures taken using an Olympus BX63 microscope at low magnification (2.5x, 10x, and 20x) are used to identify contamination and damage caused by the wet transfer and graphene coverage. Pictures taken at higher magnification (50x, 100x) are used to assess the crystal's shape and size as their domains become more discernible. Figures B.1 and B.2 present the microscope pictures of CVDREF samples, and Figures B.3 and B.4 show CVDHT and CVDCV microscope pictures, respectively.

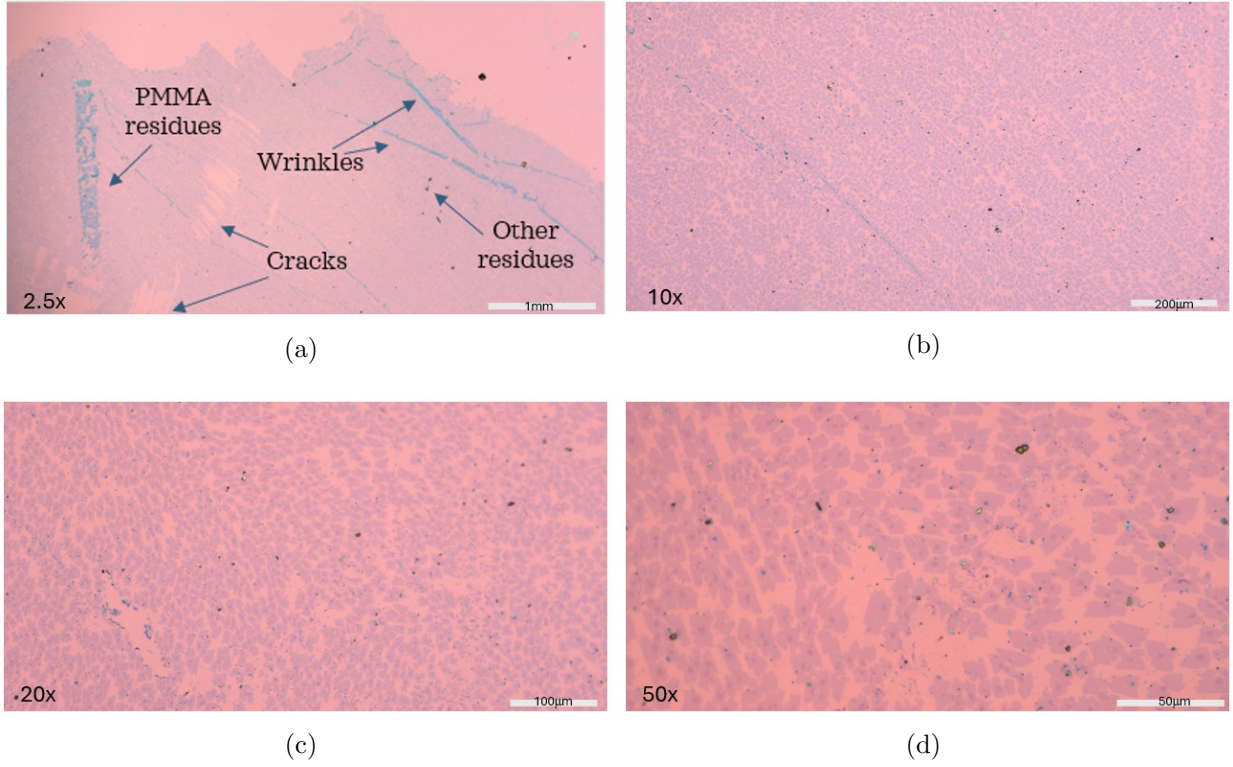


Figure B.1: **CVDREF-01** Microscope picture a)2.5x, b)10x, c)20x and d) 50x magnification. The crystal domains are irregularly shaped in size $\approx 10\mu m^2$ and are separated from each other. The graphene coverage is uniform but presents residues and damages from the transfer.

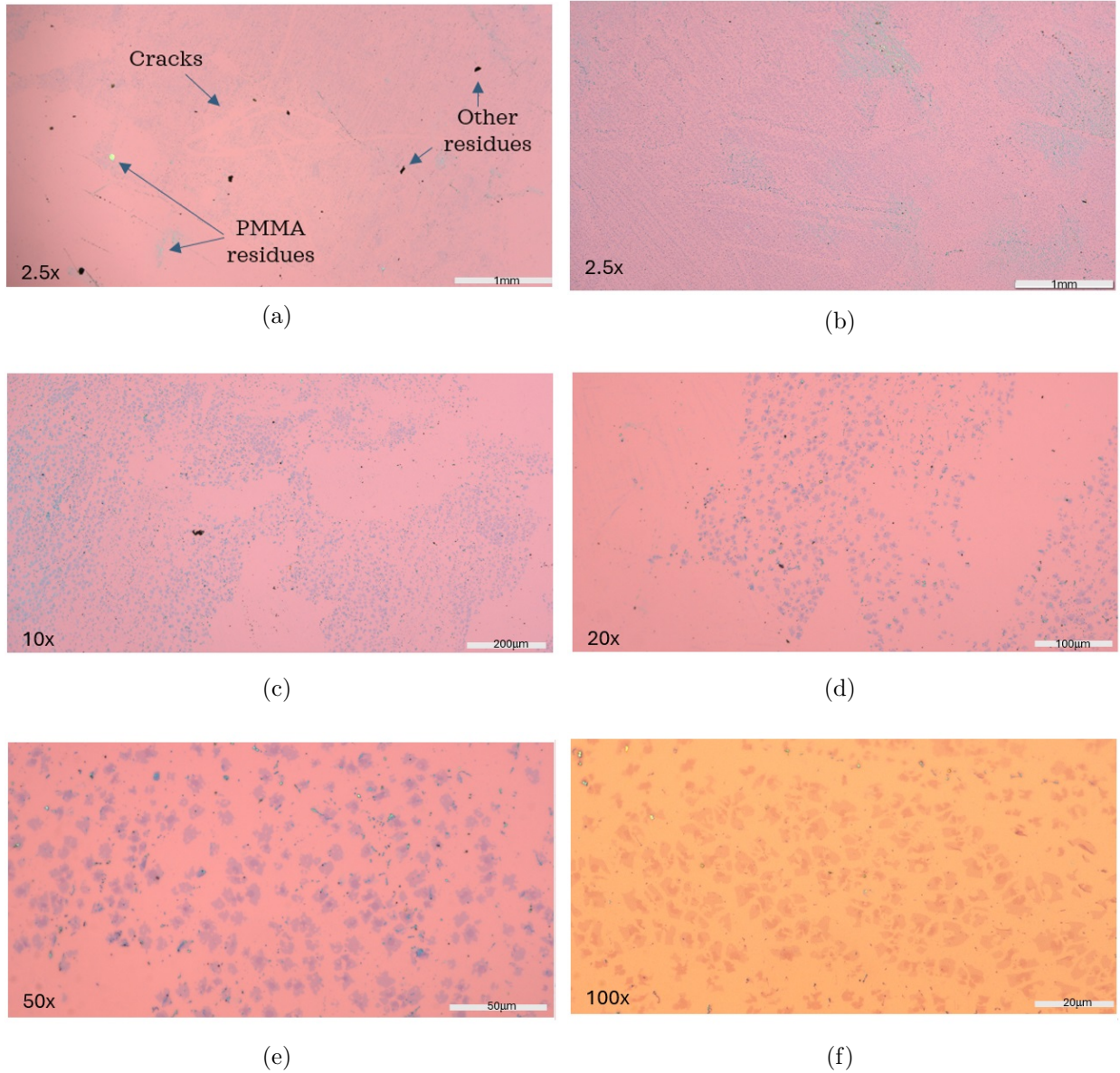


Figure B.2: **CVDREF-02 Microscope picture** a)2.5x, b)2.5x, c)10x, d)20x, e) 50x and f) 100x magnification. The crystal domains have an irregular shape but smaller domain size $\approx 7.5\mu m^2$ than CVDREF-01. The graphene coverage is uniform, not continuous. This sample is more damaged than the others but presents fewer photoresist residues.

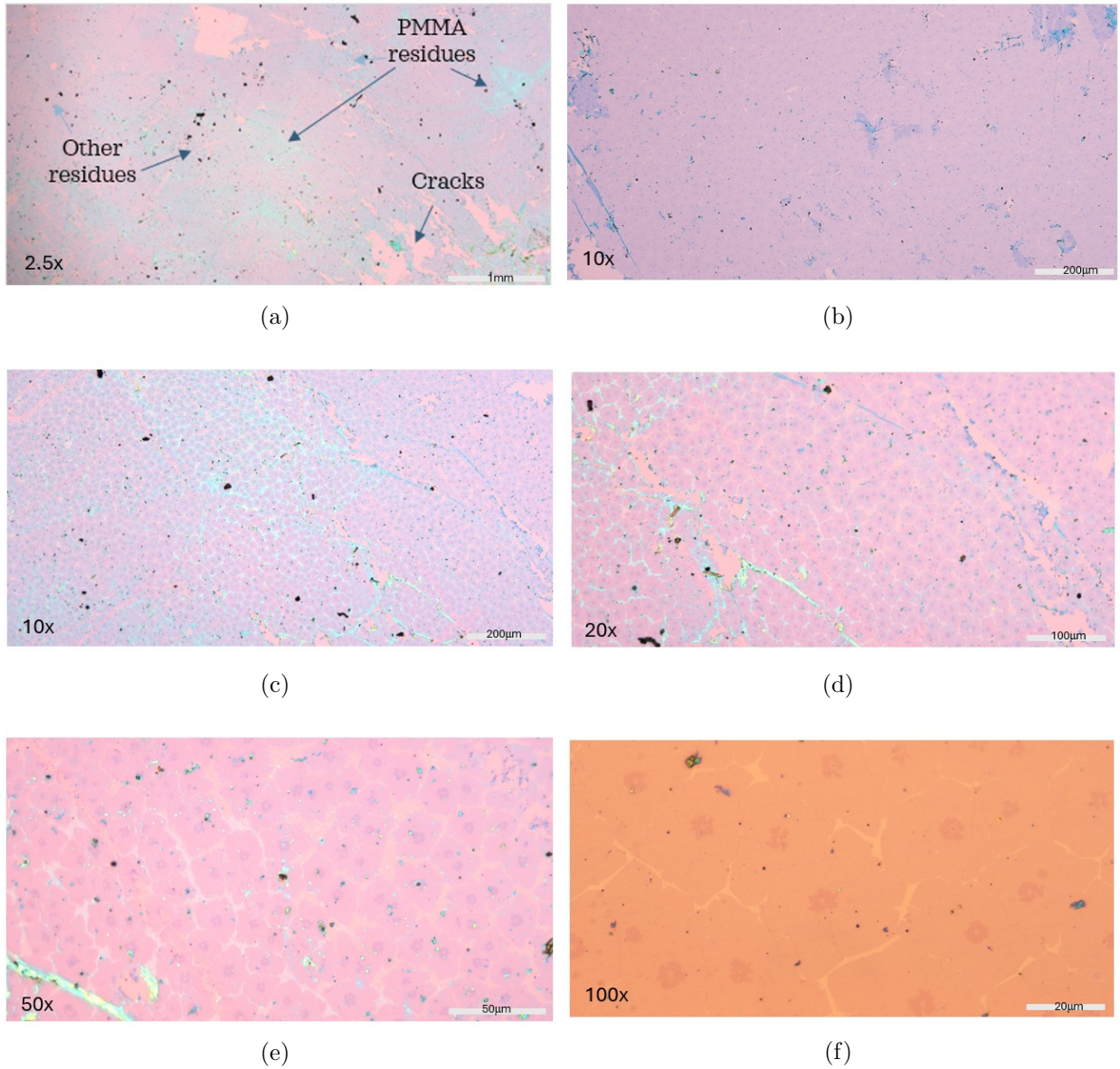


Figure B.3: **CVDHT-01 Microscope picture** a)2.5x, b)10x, c)10x, d)20x, e) 50x and f) 100x magnification. The crystal domains have a dendritic shape with large domain size $\approx 25\mu m^2$. The crystal's center appears in a darker shade. The graphene coverage is uniform, and the domains are close to each other. There is a noticeable amount of photoresist residues.

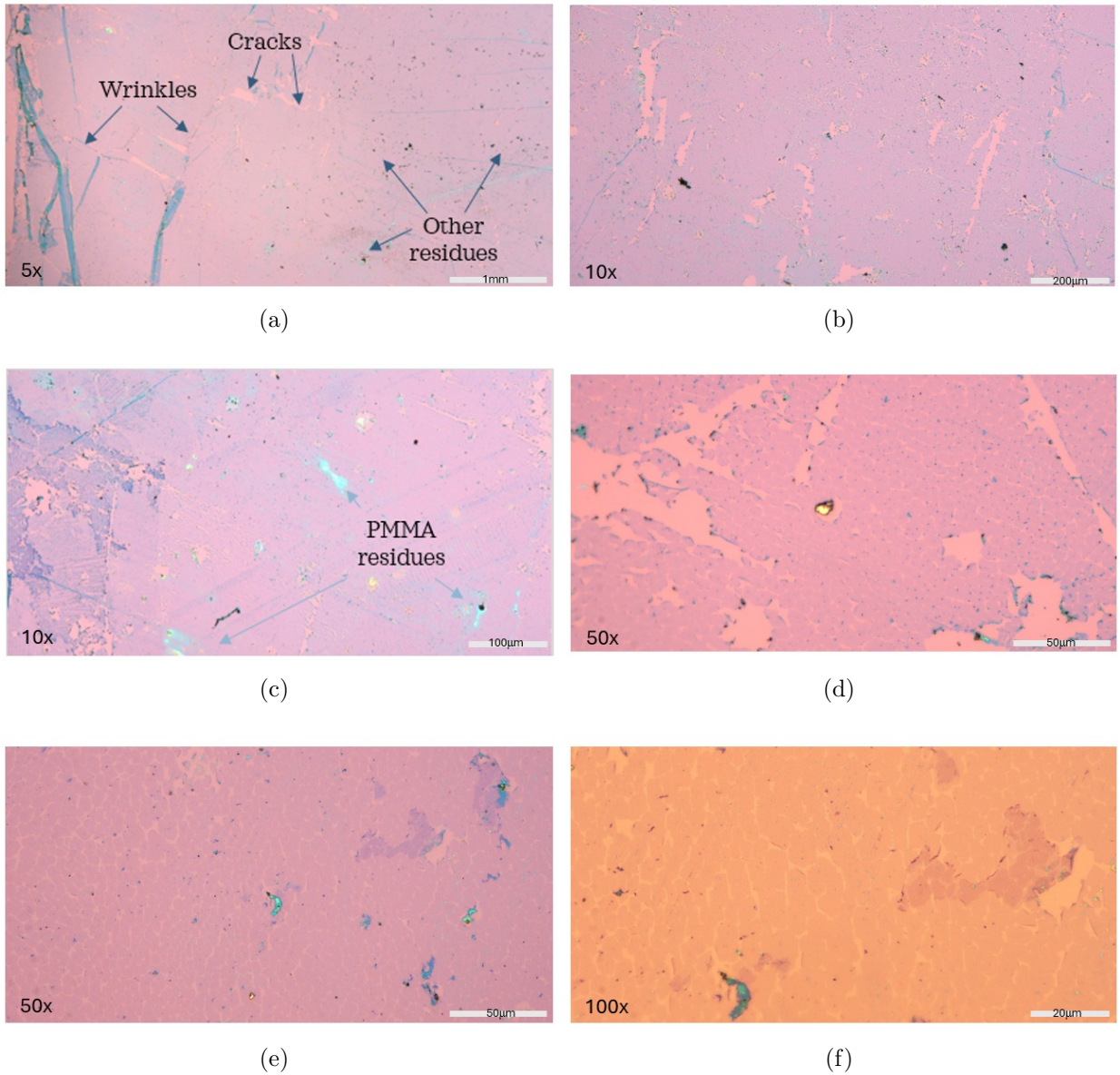


Figure B.4: **CVDCV-01 Microscope picture** a)2.5x, b)10x, c)10x, d)50x, e) 50x and f) 100x magnification. The crystal domains resemble hexagons with domain size $\approx 7.5\mu m^2$. The graphene coverage is uniform, and the domains are close to each other. Damages and residues from resulting from the transfer are also noticeable.

Appendix C

Nanofabrication

The nanofabrication of Hall devices is realized in the QNFCF cleanroom. The patterning process for each fabrication step is similar to Sakuragi's process but varies for the duration of the reflow and the etching steps[91]. The new process is described below.

Figure C.1 presents the evolution of graphene crystals during the nanofabrication process. As the process progresses, the crystal domain remains undamaged. However, the most significant issue in nanofabrication remains: the photoresist becoming stuck on the graphene channel renders the device unusable. One possible explanation is the creation of a skin at the interface of photoresists following the development of Shipley-1811. This is suggested by the relatively long development time of 90 seconds, which is unusual for similar nanofabrication processes and tends to indicate the presence of a hardened layer within the photoresists. One unexplored option is to use a different developer other than MF-319 for this step.

- Pre and post process backing step (QNFCF – FISHER oven)
 - (a) Gas: N_2
 - (b) Temperature: 180°
 - (c) Time: 30min
- 1. Photolithography (1^{st} and 3^{rd} step) - Alignment marks and tracks patterning.
 - (a) MMA 8.5 el 10 Spin-coating (QNFCF – REYNOLDSTECH-Twincoater or BREWER-Ebeamspinbake)
 - Spin-coating recipe:

- i. 5000 rpm, 500 rpm/sec, 60 sec
 - ii. 0 rpm, 500 rpm/sec, 10 sec
 - Baking recipe:
 - iii. 180°C for 5 min
 - (b) Shipley-1805 Spin-coating (QNFCF – REYNOLDSTECH-Twincoater or BREWER-UVspinbake)
 - Spin-coating recipe:
 - i. 500 rpm, 500 rpm/sec, 1 sec
 - ii. 5000 rpm, 1000 rpm/sec, 30 sec
 - iii. 0 rpm, 1000 rpm/s, 10 sec
 - Baking recipe:
 - iv. 120°C for 90 sec
 - (c) UV exposure(QNFCF – HEIDELBERG-MLA150)
 - Exposure with 405nm laser:
 - i. Dose 95 mJ/cm^2 , Defocus 2
 - (d) Shipley development (QNFCF – DEVELOPUV wetbench)
 - i. MF-319 for 1 min
 - ii. DI water
 - (e) MMA exposure (QNFCF – Novascan UV ozone)
 - * This tool is not available in the list of equipment you can require training on online. You need to ask the staff directly.
 - i. Reflow on a hot plate at 150°C for 3 min
 - ii. 25°C for 15 min with a stage height of 9 cm.
 - (f) Shipley development (QNFCF – SOLVENT 1, 2 or DEVELOPEBL wetbench)
 - i. IPA:DI (7:3) 35mL : 15mL for 2 min 40 sec
 - ii. DI water
2. Photolithography (2nd step) (Hall bars patterning)
- (a) MMA 8.5 el 10 Spin-coating (QNFCF – REYNOLDSTECH-Twincoater or BREWER-Ebeamspinbake)
 - Spin-coating recipe:
 - i. 5000 rpm, 500 rpm/sec, 60 sec

- ii. 0 rpm, 500 rpm/sec, 10 sec
 - Baking recipe:
 - iii. 180°C for 5 min
 - (b) Shipley-1811 Spin-coating (QNFCF – REYNOLDSTECH-Twincoater or BREWER-UVspinbake)
 - Spin-coating recipe:
 - i. 500 rpm, 500 rpm/sec, 1 sec
 - ii. 5000 rpm, 1000 rpm/sec, 30 sec
 - iii. 0 rpm, 1000 rpm/s, 10 sec
 - Baking recipe:
 - iv. 120°C for 90 sec
 - (c) UV exposure(QNFCF – HEIDELBERG-MLA150)
 - Exposure with 405nm laser:
 - i. Dose 95 mJ/cm^2 , Defocus -2
 - Inverted
 - margin: ± 4 mm in x and ± 3.4 mm in y
 - crosses: ± 3.9 mm : ± 3.2 mm and aligned the design
 - (d) Shipley development (QNFCF – DEVELOPUV wetbench)
 - i. MF-319 for 90 sec
 - ii. DI water
 - (e) MMA exposure (QNFCF – Novascan UV ozone)
 - i. Reflow on a hot plate at 150°C for 3 min
 - ii. 25°C for 15 min with a stage height of 9 cm.
 - (f) Shipley development (QNFCF [–] SOLVENT 1, 2 or DEVELOPEBL wetbench)
 - i. IPA:DI (7:3) 35mL : 15mL for 2 min 40 sec
 - ii. DI water
3. Etching (1st and 2rd step)
- (a) Recipe # 8 (QNFCF – YES-as):
 - i. RF power 200W
 - ii. Pressure: 300 mTorr
 - iii. Temperature: 25°C

- iv. O_2 flow: 40 sccm
 - v. Duration: 30 sec (1^{st} step) and 1min (3^{rd} step)
4. Metallization (1^{st} and 2^{nd} step)
- (a) (QNFCF – ANGSTROM - Ebeam)
 - Titanium/ Gold alignment marks and pads(1^{st} step):
 - i. Thickness: 20/80 nm
 - ii. Deposition rate: 3 Å/s
 - Palladium ohmic contacts (Step 3):
 - i. Thickness: 50 nm
 - ii. Deposition rate: 3 Å/s
5. Liftoff (1^{st} and 3^{nd} step)
- (a) (QNFCF – SOLVENT 1 or 2 wet bench)
 - i. Remover PG $\approx$ 30 min
 - ii. Acetone
 - iii. IPA
6. Photoresist removal (2^{nd} step)
- (a) (QNFCF – SOLVENT 1 or 2 wetbench)
 - i. Remover PG $100^\circ C$ for 2 hours
 - ii. Acetone
 - iii. IPA

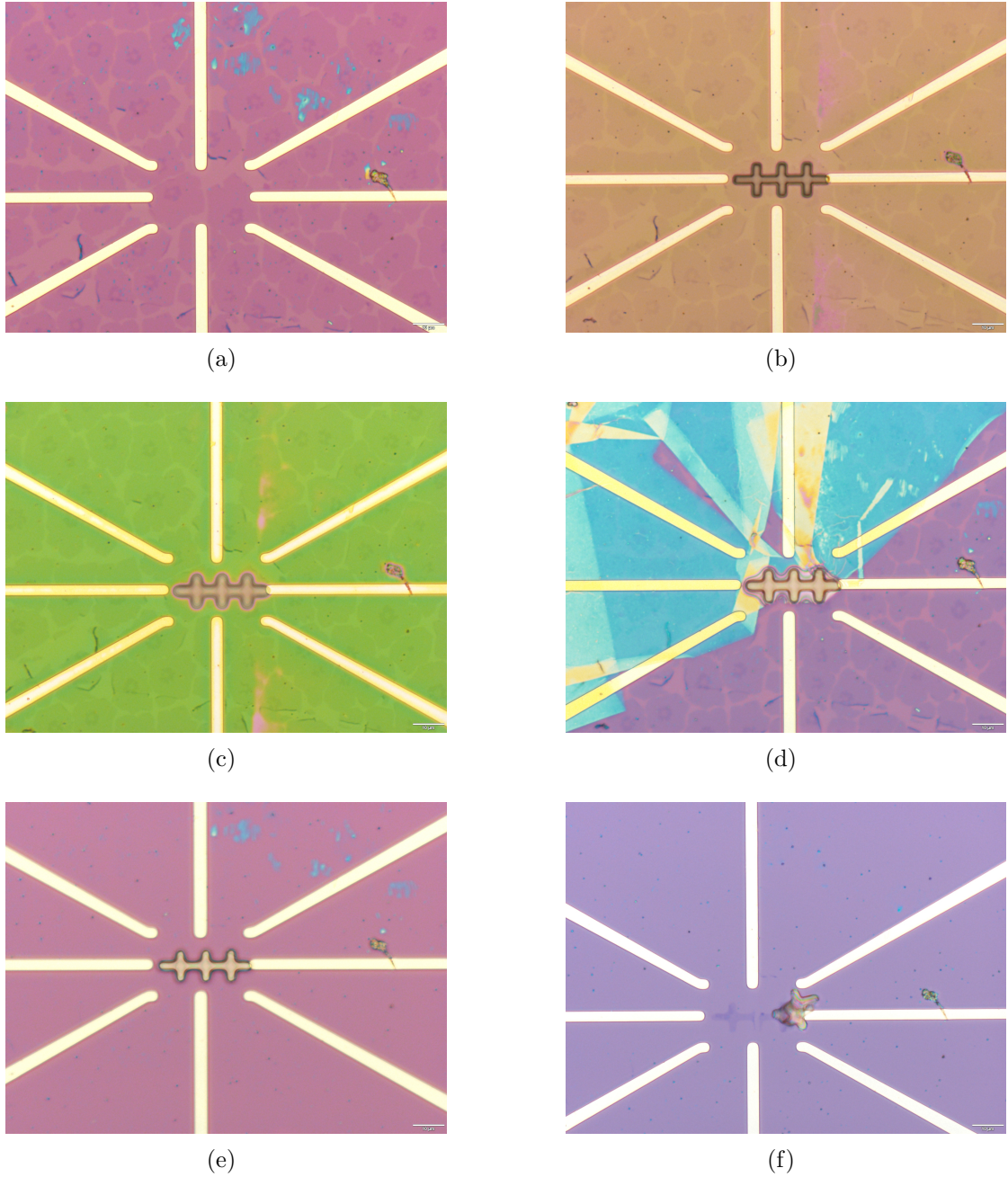


Figure C.1: **Microscope picture of the graphene domains during the fabrication process.** a) End of alignment mark and track patterning (yellow) with the presence of graphene (dark pink) on the substrate (light pink). b) Development of Shipley-1811. c) Reflow. This step leads to an enlargement of the Hall bars' features due to the melting of the polymers. d) Development of MMA (8.5). The blue-yellow polymeric skin layer isn't supposed to be present. e) graphene etching. f) End of graphene channel patterning. Harden photoresist remains on the graphene channel. Picture taken on CVDHT-01-H22-2 Hall device.