STRUCTURAL AND ELECTRONIC PROPERTIES OF GRAPHENE ON 4H- AND 3C-SiC

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Cover

Atomic force microscopy topographic image of graphene on C-face 4H-SiC(000-1) grown by high-temperature sublimation in argon atmosphere.

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Je dédie cette thèse pour ceux qui sont très loin de moi et très proches à mon cœur:

Pour celle qui vient de l'île des rêves et qui a changé ma vie au plus beau rêve.

Pour celle que je dois ma vie.

Pour ma famille.

Pour ceux qui ne perdent jamais la foi en l'humanité.

ABSTRACT

Graphene is a one-atom-thick carbon layer arranged in a honeycomb lattice. Graphene was first experimentally demonstrated by Andre Geim and Konstantin Novoselov in 2004 using mechanical exfoliation of highly oriented pyrolytic graphite (exfoliated graphene flakes), for which they received the Nobel Prize in Physics in 2010. Exfoliated graphene flakes show outstanding electronic properties, e.g., very high free charge carrier mobility parameters and ballistic transport at room temperature. This makes graphene a suitable material for next generation radio-frequency and terahertz electronic devices. Such applications require fabrication methods of large-area graphene compatible with electronic industry. Graphene grown by sublimation on silicon carbide (SiC) offers a viable route towards production of large-area, electronic-grade material on semi-insulating substrate without the need of transfer. Despite the intense investigations in the field, uniform wafer-scale graphene with very high-quality that matches the properties of exfoliated graphene has not been achieved yet. The key point is to identify and control how the substrate affects graphene uniformity, thickness, layer stacking, structural and electronic properties. Of particular interest is to understand the effects of SiC surface polarity and polytype on graphene properties in order to achieve large-area material with tailored properties for electronic applications. The main objectives of this thesis are to address these issues by investigating the structural and electronic properties of epitaxial graphene grown on 4H-SiC and 3C-SiC substrates with different surface polarities.

The first part of the thesis includes a general description of the properties of graphene, bilayer graphene and graphite. Then, the properties of epitaxial graphene on SiC by sublimation are detailed. The experimental techniques used to characterize graphene are described. A summary of all papers and contribution to the field is presented at the end of Part I. Part II consists of seven papers.

Paper I reports on the structural, vibrational, and dielectric function properties of graphene grown on the C-face of 4H-SiC(000 – 1) with surface defects. We have shown that the average number of graphene layers, the size of the domains with uniform thickness and the crystallite size increase with the increase of temperature. This improved graphene quality is attributed to an enhanced sublimation of Si from the SiC and to the elimination of SiC surface defects by surface restructuring during the sublimation growth. Central result of the paper is the transition from decoupled to Bernal stacked graphene layers with the increase in growth temperature, which is explained by a competition between growth mechanisms. We also determined the thickness dependence of graphene dielectric function. Fi-

nally, we reported the first observation of an interface layer that forms between SiC and graphene and it is composed of amorphous carbon, silicon and oxygen. We have established the evolution of the interface layer with growth temperature and outlined its implications for potential applications of graphene.

Paper II reports a detailed study of the interface layer properties and its evolution with time for a few layer graphene (FLG) sample with large homogeneous areas of monolayer (ML), bi-layer (BL) and tree-layer (TL) on the C-face of 4H-SiC(000 – 1) without any defects. A SiO_x layer is identified at the interface between graphene and SiC independently of graphene thickness and domain size. We have found that the chemical composition of the interface layer changes towards SiO_2 and its thickness increases with aging in normal ambient conditions. We have shown that the presence of the interface layer causes the formation of non-ideal Schottky contact behavior for electrical transport between ML graphene and SiC, which has significant implications for device applications. Finally, BL and FLG are shown to be composed of decoupled graphene layers. However, contrary to previous works on decoupled C-face graphene, our investigations indicate that the adjacent layers in the BL and FLG stacks may not be rotationally disordered.

Paper III reports Landau level spectroscopy, measured using mid-infrared optical Hall effect in combination with low energy electron microscopy and low-energy electron diffraction investigations of FLG grown on the C-face of 3C-SiC (111). We show for the first time that FLG on 3C-SiC (111) consists of decoupled graphene sheets and behaves effectively as a single layer graphene with linearly dispersing bands (Dirac cones) at the graphene K point. Low-energy electron diffraction mapping suggests that the azimuth rotation occurs between adjacent domains within the same sheet rather than vertically in the stack. While the origin of the decoupling between the individual sheets still remains unknown, the fact that FLG on 3C-SiC(111) behaves as a single layer graphene with carrier mobility of $33000 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ at 1.5 K gives good prospects for its applications in future electronic devices.

Paper IV reports on the Landau level (LL) splitting in epitaxial graphene grown on the C-terminated face of 4H-SiC (000–1). Infrared optical Hall effect is employed to measure LL spectroscopy in reflection mode. We find that the LL transitions in epitaxial graphene exhibit polarization preserving selection rules and the transition energies obey a square-root dependence on the magnetic field strength for the two sets of LL. We find Fermi velocity values of $v_{F1} = 1.03 \times 10^6 \text{ ms}^{-1}$ and $v_{F2} = 1.09 \times 10^6 \text{ ms}^{-1}$ for the two sets, respectively. The origin of the LL splitting is discussed and it is suggested that the most likely explanation is the appearance of extra localized levels due to vacancy defects.

Paper V reports on cavity-enhanced optical Hall effect experiments at terahertz (THz) frequencies to determine the free charge carrier properties in graphene with different number of layers grown on Si-face 4H-SiC(0001). We have found that i) monolayer graphene possesses p-type conductivity with a free hole concentration in the low 10^{12} cm^{-2} range and a free hole mobility parameter as high as $1550 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, ii) 6 monolayers graphene shows n-type doping behavior with a much lower free electron mobility parameter of $470 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ and an order of magnitude higher free electron density in the low 10^{13} cm^{-2} range. The observed differences in the carrier type of the two samples are suggested to be due to increased hydrophobicity of graphene with increasing number of graphene layers, which significantly diminishes adsorption of p-type dopants from the environment. The reduced mobility parameter in the thick graphene sample was attributed to the higher free charge carrier density, higher effective mass and enhanced scattering between the graphene sheets in the thick graphene. The cavity-enhanced THz optical Hall effect is demonstrated to be an excellent tool for contactless access to the type of free charge carriers and their properties in two-dimensional materials such as graphene.

Paper VI reports the first in-situ experiments on the effect of ambient gas exposure on the free charge carrier concentration and mobility of monolayer graphene on 4H-SiC(0001) using contactless in-situ cavity-enhanced THz optical Hall effect. The exposure of graphene to cycles of different inert gases (for example: helium and nitrogen) and air, shows that exposure to ambient causes an initial rapid change in the carrier properties, followed by a gradual change for the rest of the exposure time. This indicates that the sample could take longer than one day to reach its final ambient state. Furthermore, we have found that exposure to an inert gas reverses the electron withdrawal caused by air. The doping trend is essentially repeatable when switching between inert gases and air. We found that the mobility variation as a function of sheet density obtained from the different doping cycles shows a linear dependence. This suggests that the dominant scattering mechanism related to ambient doping originates from charged impurities. The charge impurities are presumed to be by products of the doping redox reaction involving O_2 , H_2O , and CO_2 caused by ambient exposure.

Paper VII reports a new crucible design for the sublimation growth of graphene and the optimization of growth conditions to achieve large-area homogeneous monolayer graphene on Si-face 4H-SiC(0001). The effect of buffer layer growth temperature on the thickness homogeneity and free charge carrier properties is established. We show that at the best conditions 99% monolayer graphene with uniform surface morphology can be grown over areas of $15 \times 15 \text{ mm}^2$.

POPULÄRVETENSKAPLIG

Materialvetenskapen har fått en uppmärksamhet utöver det vanliga ända sedan upptäckten av grafen år 2004. En stor mängd fysikaliska fenomen och potentiella applikationer associerade till grafens unika natur har föranlett en forskningsaktivitet utan motstycke. Grafen är mirakelmaterialet vars upphovsmakare, Novoselov och Geim, blev tilldelade Nobelpriset i fysik år 2010. Denna tvådimensionella kristall bestående av endast ett atomlager kol arrangerat likt en bivaxkaka är stabil i normal omgivning. Grafen har dessutom hög elektronmobilitet, hög elektrisk och termisk ledningsförmåga, optiskt transparent samt hög mekanisk tålighet. Utöver detta är grafen en semi-metall innehavande av en linjär energispridning, även kallat Dirac cone. Detta medför en spännande avvikelse i kontrast till konventionella halvledare och är därför mycket intressant inom framtida halvlederapplikationer. Den verkliga utmaningen är däremot uppskalningen från forskningsnivå till produktionsnivå i industrin. Ett av de stora problemen idag är att de mest enastående egenskaperna har uppmätts på mekaniskt exfolierat grafen vilket är den metod som framställer materialet i högsta kvalitet. Den metoden är inte tillämpbar för storskalig produktion, därför behövs ett alternativ, nämligen epitaxiell tillväxt av grafen med önskvärda egenskaper. För att åstadkomma detta har jag i min avhandling fokuserat på tillväxt och karaktärisering av epitaxiell grafen på SiC via sublimering. Metoden för högtemperatur upplösning av SiC för att bilda grafen på dess yta har utvecklats av Rositsa Yakimova och kan leverera material med hög homogenitet som är kompatibel med industriell framställning. I avhandlingen presenterar jag en egenutvecklad smältdegel designad för tillväxt av grafen, själva tillväxten av materialet samt karaktäriseringen av de strukturella egenskaperna. Ett antal olika karaktäriseringstekniker har använts i detta syfte för att belysa och optimera grafenets strukturella och elektroniska egenskaper. Detta inkluderar spektroskopisk ellipsometri och optiska Hall-effekten, Raman spektroskopi, röntgen-fotoelektron-spektroskopi / mikroskopi, atomkraftsmikroskopi, kelvinsondmikroskopi, vridningsresonant ledande atomkraft-mikroskopi, transmissionselektronmikroskopi, lågenergielektronmikroskopi, och lågenergi-elektron-diffraktion.

PREFACE

This Doctoral thesis is the results of my doctoral studies in Semiconductor materials division at the department of physics, chemistry and biology (IFM) at Linköping University between 2012 and 2016. The main objective of this thesis is to investigate the structural and electronic properties of graphene on 4H-SiC(0001) and on 3C-SiC(111) with different surface polarities. The thesis also includes designing a crucible with improved temperature homogeneity and a optimization of growth conditions for a monolayer graphene on the Si-face of 4H-SiC(0001) substrates. The results are presented in seven papers proceeded by an introduction. This thesis was financed by: the Marie Curie actions under the Project No.264613-NetFISiC, the centre of Nano Science and Nano technology (CeNano), the Swedish Research Council (VR Contract 2013 – 5580), the Swedish Governmental Agency for Innovation Systems (VINNOVA) under the VINNMER international qualification program Grant No.2011 – 03486, the Swedish foundation for strategic research (SSF) under Grants No. FFL12 – 0181 and No. RIF14 – 055, the Swedish Government Strategic Research Area in Materials Science on Functional Materials at Linköping University (Faculty Grant SFO Mat LiU No2009 00971).

INCLUDED PAPERS

- **Paper I**

Structural properties and dielectric function of graphene grown by high-temperature sublimation on 4H-SiC(000 – 1)

C. Bouhafs, V. Darakchieva, I. L. Persson, A. Tiberj, P. O. Á. Persson, M. Paillet, A.-A. Zahab, P. Landois, S. Juillaguet, S. Schöche, M. Schubert, and R. Yakimova.

Journal of Applied Physics 117, 085701 (2015)

- **Paper II**

Interface and electrical properties, ordering and decoupling of few layer graphene on C-face 4H-SiC

C. Bouhafs, A. A. Zakharov, I. G. Ivanov, F. Giannazzo, J. Eriksson, V. Stanishev, P. Kühne, T. Iakimov, T. Hofmann, M. Schubert, F. Roccaforte, R. Yakimova, V. Darakchieva.

Carbon, under review

- **Paper III**

Decoupling and ordering of multilayer graphene on C-face 3C-SiC(111)

C. Bouhafs, V. Stanishev, A. A. Zakharov, T. Hofmann, P. Kühne, T. Iakimov, R. Yakimova, M. Schubert, V. Darakchieva.

Applied Physics Letters, under review

- **Paper IV**

On the Landau level splitting in few layer epitaxial graphene

C. Bouhafs, P. Kühne, V. Stanishev, I. G. Ivanov, T. Iakimov, R. Yakimova, M. Schubert, T. Hofmann and V. Darakchieva.

Manuscript

- **Paper V**

Cavity-enhanced optical Hall in epitaxial graphene detected at terahertz frequencies

N. Armakavicius, C. Bouhafs, V. Stanishev, P. Kühne, R. Yakimova, S. Knight,

T. Hofmann, M. Schubert, and V. Darakchieva.

Applied Surface Science, in press

(DOI: 10.1016/j.apsusc.2016.10.023)

- **Paper VI**

Terahertz optical Hall effect and cyclic gas doping reveal impurity-induced carrier scattering mechanism in epitaxial graphene

S. Knight, C. Bouhafs, T. Hofmann, N. Armakavicius, P. Kühne, V. Stanishev, I. G. Ivanov, R. Yakimova, S. Wimer, V. Darakchieva and M. Schubert.

Manuscript

- **Paper VII**

Effect of buffer layer growth conditions on the properties of monolayer graphene on Si-face 4H-SiC

V. Stanishev, C. Bouhafs, A. A. Zakharov, I. G. Ivanov, N. Armakavicius, P. Kühne, R. Yakimova, and V. Darakchieva.

Manuscript

MY CONTRIBUTION TO THE PAPERS

- **Paper I**

I contributed to the planning. I have participated in the measurements of micro-Raman, the AFM measurements, in the discussion of the TEM results. I have analyzed the spectroscopic data ellipsometry with my supervisor and the Raman data and i have written the first version of the paper.

- **Paper II**

I have participated in the measurements of conductive-AFM, Kelvin probe, Raman, reflectance, micro- LEED and LEEM. I have analyzed micro- LEED, LEEM, XPS, Raman, reflectance, Kelvin probe and mid-infrared optical Hall effect data. I have interpret the measurements together with my co-authors. I have written the first version of the paper.

- **Paper III**

I have analyzed the micro- LEED, LEEM and mid-infrared optical Hall effect data. I have written the first version of the paper.

- **Paper IV**

I have performed the Raman polarization measurements. I have interpreted the data together with my supervisor.

- **Paper V**

I have participated in the growth of the graphene samples and reflectance measurements. I took part in the discussion of the results.

- **Paper VI**

I have participated in the growth of the graphene samples, the reflectance and Raman measurements. I have participated to the building of the experimental setup. I took part in the interpretation and the discussion of the results.

- **Paper VII**

I have participated the optimization of the growth. I have participated in the growth of the graphene samples and reflectance, AFM and Raman measurements. I have participated in the reflectance and Raman data analysis. I took part in the interpretation and the discussion of the results.

RELATED BUT NOT INCLUDED PAPERS

- **Morphological and electronic properties of epitaxial graphene on SiC**

R. Yakimova, T. Iakimov, G. R. Yazdi, C. Bouhafs, J. Eriksson, A. Zakharov, A. Boosalis, M. Schubert, and V. Darakchieva
Physics B, 439, 59 (2014)

NOT RELATED AND NOT INCLUDED PAPERS

- **Effect of nitrogen on the $\text{GaAs}_{0.9-x}\text{N}_x\text{Sb}_{0.1}$ dielectric function from the near-infrared to the ultraviolet**

N. Ben. Sedrine, C. Bouhafs, J.C. Harmand, R. Chtourou, V. Darakchieva.

Applied Physics Letters 97, 201903 (2010).

- **Optical properties of $\text{GaAs}_{0.9-x}\text{N}_x\text{Sb}_{0.1}$ alloy films studied by spectroscopic ellipsometry**

N. Ben. Sedrine, C. Bouhafs, M. Schubert, J.C. Harmand, R. Chtourou, V. Darakchieva.

Thin Solid Films 519 (9), 2838-2842 (2011).

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Contents

Contents	xvii
1 Introduction to graphene	1
1.1 Crystal and electronic structure of graphene	1
1.2 Bilayer graphene	4
1.3 Graphite	6
1.4 Vibrational properties of graphene	7
1.5 Optical properties of graphene	7
1.6 Transport properties of graphene	10
1.7 Graphene and graphite in magnetic field	11
2 Epitaxial graphene on SiC	15
2.1 Introduction	15
2.2 Background of epitaxial graphene on SiC	18
2.3 EG on Si-face SiC(0001) in UHV	20
2.4 Graphene on C-face SiC(000-1) in UHV	21
2.5 Low-temperature EG on Si-face SiC (0001)	23
2.6 Low-temperature graphene on C-face SiC (000-1)	24
2.7 High-temperature EG on Si-face SiC (0001)	29
2.8 High-temperature graphene on C-face SiC (000-1)	31
2.9 Si- and C-face graphene on 3C-SiC(111)	32
2.10 Samples studied in the thesis	34
3 Experimental techniques	35
3.1 Raman scattering Spectroscopy	35
3.1.1 The effects of doping	36
3.1.2 The effects of strain	37
3.1.3 The effects of number of layers and stacking	38
3.1.4 Raman Spectroscopy of graphene on SiC	38
3.2 Reflectance	39

3.3	Scanning probe microscopy techniques	40
3.3.1	Atomic force microscopy	40
3.3.2	Conductive atomic force microscopy	41
3.3.3	Scanning Kelvin probe microscopy	42
3.4	Surface techniques	44
3.4.1	Low-energy electron microscopy	44
3.4.2	Low-energy electron diffraction	46
3.4.3	X-ray photoelectron spectroscopy and microscopy	47
3.5	Spectroscopic ellipsometry	48
3.5.1	Types of ellipsometry	48
3.5.1.1	Standard spectroscopic ellipsometry	48
3.5.1.2	Generalized spectroscopic ellipsometry	48
3.5.2	Optical Hall effect	50
3.5.2.1	The Optical Hall effect	50
3.5.2.2	Cavity-enhanced and in-situ cavity-enhanced THz optical Hall effect	51
3.5.3	Optical models	52
3.5.3.1	Dielectric tensor	53
3.5.3.2	Visible to vacuum ultraviolet optical models	53
3.5.3.3	Mid-infrared/terahertz optical models	54
3.5.4	Instrumentation	57
4	Summary of the results	59
	References	61
	List of Figures	73

Chapter 1

Introduction to graphene

A. Geim and K. Novoselov reported the isolation of graphene using mechanical exfoliation in 2004. They first experimentally demonstrated the outstanding physical properties of graphene, such as massless Dirac fermions with extremely high mobility parameters. In 2010, A. Geim and K. Novoselov were awarded the Nobel prize for Physics for groundbreaking experiments regarding the two-dimensional material graphene [1].

1.1 Crystal and electronic structure of graphene

The outstanding properties of graphene originate from its unique two-dimensional lattice structure. Graphene consists of a single layer of sp^2 -hybridized carbon atoms that are arranged in a honeycomb lattice. The crystal lattice of graphene contains two triangular sub-lattices composed of atoms A and B, as shown in Fig.1.1(a). The unit cell of graphene (black-dotted line) is rhombic and contains two non equivalent carbon atoms per unit cell (A and B) with unit cell vectors

$$\vec{a}_1 = \left(\frac{3}{2}a - \frac{\sqrt{3}}{2}a \right) \quad \text{and} \quad \vec{a}_2 = \left(\frac{3}{2}a, \frac{\sqrt{3}}{2}a \right), \quad (1.1)$$

where $a = 1.42 \text{ \AA}$ is the carbon-carbon bond length. The reciprocal lattice of graphene is also hexagonal as shown in Fig.1.1(b). The corresponding reciprocal lattice vectors are

$$\vec{g}_1 = \frac{4\pi}{3\sqrt{3}a} \left(\frac{\sqrt{3}}{2}, -\frac{3}{2} \right) \quad \text{and} \quad \vec{g}_2 = \frac{4\pi}{3\sqrt{3}a} \left(\frac{\sqrt{3}}{2}, \frac{3}{2} \right). \quad (1.2)$$

The high symmetry points in the first Brillouin zone (BZ) (gray hexagon in Fig. 1.1(b)) are the Γ point at the zone center (origin of the reciprocal space with

Figure 1.1: (a) Periodic lattice of graphene. The unit cell is indicated by dashed lines and the two sub-lattices composed of atoms A and B are shown by dotted triangles. γ_0 is the hopping energy between the nearest neighbour carbon atoms. (b) Reciprocal lattice and high symmetry points of graphene. The first BZ is indicated in gray.

$k = 0$), the $\mathbf{M}$ point in the middle of the hexagonal sides, and the two non equivalent $\mathbf{K} = \left(\frac{2\pi}{3a}, \frac{2\pi}{3\sqrt{3}a}\right)$ and $\mathbf{K}' = \left(\frac{2\pi}{3a}, -\frac{2\pi}{3\sqrt{3}a}\right)$ points at the hexagon corners. The $\mathbf{K}$ and $\mathbf{K}'$ points are known as the Dirac points.

An isolated carbon atom has the configuration of $1s^2 2s^2 2p^2$ and it possesses four valence electrons to form chemical bonds. In graphene, three out of the four valence electrons are hybridized into three sp^2 orbitals and form in-plane σ -bonds, while the remaining electron of each carbon atom forms π - (or P_z -) orbitals perpendicular to the graphene plane. The σ -bond is the strongest covalent chemical bond, which is the reason for graphene outstanding mechanical properties [2]. The π -orbitals determine the low-energy electronic structure of graphene and are responsible for its high electrical conductivity.

The electronic structure of graphene can be calculated using a tight binding model as demonstrated first by P. R. Wallace [3]. The tight binding model only takes into account the interaction between the nearest neighbor carbon atoms (A-B) with hopping energy γ_0 . The energy dispersion relation obtained from tight binding model calculations gives

$$E(\vec{k}) = \pm \gamma_0 \sqrt{1 + 4 \cos^2 \left(\frac{\sqrt{3} k_y a}{2} \right) + 4 \cos \left(\frac{3 k_x a}{2} \right) \cos \left(\frac{\sqrt{3} k_y a}{2} \right)}, \quad (1.3)$$

where $\gamma_0 = 3.12 - 3.15$ eV is the nearest neighbor hopping energy [3], k_x and k_y are the $\vec{k}$ momentum components in the x and y in-plane directions. Fig.1.2 shows the

Figure 1.2: Electronic structure of graphene. The valence band (lower red band) and conduction band (upper blue band) touch at the $\mathbf{K}$ -points of the BZ. In the vicinity of these points, the energy dispersion relation is linear. Reprinted with permission from Ref. 4.

electronic structure of graphene obtained from Eqn. 1.3, where the conduction and valence bands are connected at the six non equivalent $\mathbf{K}$ and $\mathbf{K}'$ points of the first BZ. Therefore, graphene is considered as a gapless semiconductor or a semimetal. For undoped graphene, the Fermi energy lies exactly at the Dirac points. Close to the $\mathbf{K}$ and $\mathbf{K}'$ points, where $\vec{k} = \vec{K} + \delta\vec{k}$, the graphene band structure can be described by

$$E_{\pm}(\vec{k}) = \pm \hbar v_f \left| \vec{\delta k} \right|, \quad (1.4)$$

where $|\vec{\delta k}| \ll |\vec{K}|$ and v_f is the Fermi velocity, given by

$$v_f = \frac{3\gamma_0 a}{2\hbar} \approx 1 \times 10^6 \text{ ms}^{-1}. \quad (1.5)$$

Equation 1.4 shows that the electronic structure of graphene exhibits a linear energy dispersion as a function of the wave vector close to the Dirac points. As a result, the free charge carriers in graphene behave exactly as massless relativistic Dirac-fermions (quasi-particles) with speed v_f . Consequently, the electrons (holes) in graphene near the $\mathbf{K}$ ($\mathbf{K}'$) points can be described by the Dirac equation instead of the Schrödinger equation, which is used to describe electron (holes) in conventional semiconductors.

$$H_{\mathbf{K}} = \pm \hbar v_f \vec{\sigma} \vec{k}, \quad (1.6)$$

where $\vec{\sigma} = (\sigma_x, \sigma_y)$ are the Pauli matrix vectors.

Figure 1.3: (a) Top and (b) side view of the crystal structure of AB-stacked bilayer graphene. Reprinted with permission from Ref. 7. (c) Electronic band structure of bilayer graphene near the K point obtained by taking into account inter-layer hopping γ_1 and γ_3 , zero layer asymmetry and with $v_3/v_f = 0.1$. Reprinted with permission from Ref. 8.

The Dirac fermions in graphene exhibit two-component wave function that describes the sublattices A and B with a pseudospin $\pm\sigma$, leading to a different chirality in the graphene conduction and valence bands at the K and K' points. Therefore, the band structure of graphene at the different Dirac points is not equivalent.

The linear energy dispersion of graphene at the Dirac points is of particular interest since many novel physical phenomena and extraordinary electronic properties found in graphene have been correlated to this unusual band structure. The density of states (DOS) of graphene near the Dirac points is given by [5]

$$\rho(E) = \frac{g_s g_v |E|}{2\pi\hbar^2 v_f^2}, \quad (1.7)$$

where v_f , $g_s = 2$ and $g_v = 2$ are the Fermi velocity, the spin and the valley degeneracy, respectively. The density of state of graphene increases linearly by increasing $|E|$ and vanishes at $|E| = 0$ allowing the possibility of carrier modulation unlike conventional 2D semiconductors with a parabolic electronic structure and a constant DOS ($\rho(E) = m^*/\pi\hbar^2$, where m^* is the effective mass). Consequently, graphene can find applications in ambipolar field effect transistors [6].

1.2 Bilayer graphene

Bilayer graphene consists of two coupled monolayers that are stacked in a structured order with a layer spacing of $d \approx 0.334$ nm. The AB stacking order of bilayer graphene (or Bernal stacking) is the most common and stable phase among all the different reported stacking orders (such as AAA , ABC , etc) [9]. In AB -stacking

configuration, the unit cell has four carbon atoms where (A_1, B_1) and (A_2, B_2) are the non equivalent carbon atoms of the upper and lower layer, respectively (Fig. 1.3(a)). The AB -staging is formed when A_2 -type carbon atoms in the upper layer sit on top of B_1 -type carbon atoms of the adjacent lower layer, while the B_2 -type (upper layer) atoms sit over the center of a hexagon, as illustrated in Fig. 1.3(a). The band structure of bilayer graphene can be calculated similarly to the one of graphene using tight binding model [7, 10–12]. However, in addition to the in-plane interaction between the nearest neighbour carbon atoms of the upper ($A_2 - B_2$) and the lower layer ($A_1 - B_1$), with hopping energy $\gamma_{A_1B_1} = \gamma_{A_2B_2} = \gamma_0$ and velocity $v_f = 3\gamma_0 a / 2\hbar$, the strongest inter-layer interactions γ_1 , γ_3 and γ_4 , are included in the model (see Fig. 1.3(b)) [8]. The $A_1 - B_2$ interaction is weak ($v_3 \ll v_f$), thus it can be neglected. When $\gamma_3 = 0$, the resulting electronic band structure near the $\mathbf{K}$ ($\mathbf{K}'$) points obtained from tight binding calculation is given by [8]

$$\varepsilon_{\pm}^{(\alpha)}(p) = \pm \sqrt{\frac{\gamma_1^2}{2} + \frac{\Delta^2}{4} + v_f^2 p^2 + (-1)^\alpha \sqrt{\frac{\gamma_1^4}{4} + (\gamma_1^2 + \Delta^2)v_f^2 p^2}}, \quad (1.8)$$

where Δ is the asymmetry between on-site energies in the two layers, p is the momentum close to the $\mathbf{K}$ ($\mathbf{K}'$) points and $\alpha = 1, 2$.

$\varepsilon_{\pm}^2(p)$ represent the higher energy conduction and valence bands of bilayer graphene. These bands are the result of the strong inter-layer coupling and are separated by $\gamma_1 = 0.39$ [13]. $\varepsilon_{\pm}^1(p)$ represent the lower conduction and valence bands of bilayer graphene for zero asymmetry ($\Delta = 0$) (Fig. 1.3(c)), which can be approximated by [14]

$$\varepsilon_{\pm}^{(1)}(p) = \pm \frac{\gamma_1}{2} \left[\sqrt{1 + 4v_f^2 p^2 / \gamma_1^2} - 1 \right]. \quad (1.9)$$

In contrast to monolayer graphene, bilayer graphene shows a parabolic band structure that is connected at $\mathbf{K}$ ($\mathbf{K}'$) points with a zero bandgap. Consequently, the bilayer graphene can be described as massive Dirac-fermions with an effective mass $m^* = \gamma_1 / 2v_f^2$ for which the DOS is independent on the energy.

Interaction between graphene sheets plays an important role in the electronic band structure. Fig. 1.4 shows the electronic band structure obtained by density functional theory of monolayer graphene (dotted line), AB -stacked bilayer graphene (dashed line) and twisted bilayer graphene by an angle $\pm 2.204^\circ$ (solid line) at the $\mathbf{K}$ point [15]. In contrast to AB -stacked bilayer graphene, which has a parabolic band structure, twisted bilayer graphene exhibits a linear band structure similar to monolayer graphene.

Figure 1.4: Band structure of monolayer graphene (dotted line), AB-stacked bilayer graphene (dashed line) and bilayer graphene twisted by an angle $\pm 2.204^\circ$ (solid line) calculated by density functional theory. Reprinted with permission from Ref. 15.

1.3 Graphite

Three-dimensional (3D) graphite crystal is composed of N graphene layers ($N \geq 10$) stacked in AB-stacking order as shown in Fig. 1.5(a). The band structure of graphite was investigated by Slonczewski, Weiss and McClure using tight binding calculations (SWM model) [3, 16–18] (see Fig. 1.5(b)). The SWM model for graphite considers two additional interactions between the second-neighbour layers, γ_2 and γ_5 compared to the tight bonding model for bilayer graphene, as shown in Fig. 1.5(a).

Following the same approach as for bilayer, and neglecting all inter-layer interactions (γ_1 - γ_5) except γ_1 , the band structure of graphite can be described by [19]

$$\varepsilon_{\pm}^{(\alpha)}(p) = \pm \sqrt{\frac{(\lambda\gamma_1)^2}{2} + v_f^2 p^2 + (-1)^\alpha \sqrt{\frac{(\lambda\gamma_1)^4}{4} + v_f^2 p^2 (\lambda\gamma_1)^2}}, \quad (1.10)$$

where $\lambda = 2 \cos(\pi K_z)$ is the effective coupling.

At the **K** point ($k_z = 0$, $\lambda = 2$), graphite shows a parabolic band structure. The electrons in graphite behave similarly as in bilayer graphene (massive-Dirac fermions) with an effective mass ($m^* = \lambda\gamma_1 / (2v_f^2)$), two times higher compared to the one of bilayer graphene [19]. At the **H** point ($k_z = 0.5$, $\lambda = 0$), the inter-layer coupling between the different graphene layers disappears and graphite shows a linear band structure similarly to graphene.

Figure 1.5: (a) Crystal structure of AB-stacked graphite. Different inter-layer interactions γ_1 - γ_5 used in the standard SWM model are indicated. (b) First BZ and electronic band structure of graphite along **H-K-H** line of the 3D first BZ. Reprinted with permission from Ref. 19.

1.4 Vibrational properties of graphene

Monolayer graphene with two atoms per unit cell has six normal vibrational modes from which three are acoustic and three are optical vibrational modes. Fig. 1.6(a) shows the calculated phonon dispersion of graphene. The ZA and ZO modes (branches) correspond to the out-of-plane acoustic and optical vibrational mode. The LO and TO modes represent the in-plane longitudinal and transverse optical vibrational mode, respectively. The LO and TO modes describe the vibrations of the graphene sub-lattice A towards the sub-lattice B (See inset in Fig. 1.6(a)) and are degenerated at the Γ point [20]. The LA and TA modes represent the in-plane longitudinal and transverse acoustic vibrational mode, respectively. Graphene belongs to the space group $P6/mmm$ which corresponds to D_{6h} point group. The irreducible representation for the lattice vibrations ($\Gamma_{\text{lat.vib}}$) at the Γ point is

$$\Gamma_{\text{lat. vib.}} = A_{2u} + B_{2g} + E_{1u} + E_{2g}, \quad (1.11)$$

where A_{2u} and E_{1u} are acoustic vibration modes, B_{2g} is out-of-plane optical vibrational mode (silent mode). The E_{2g} is the only active Raman mode and correspond to the doubly degenerate TO and LO phonon mode at the Γ point (Fig. 1.6).

1.5 Optical properties of graphene

The optical response of graphene depends on the spectral range and doping properties. The optical conductivity of graphene results from both inter-band and

Figure 1.6: Phonon dispersions for monolayer graphene showing the LO, TO, ZO, LA and TA phonon branches. Adapted from Ref. 21. The inset shows E_{2g} vibrational modes in graphene.

intra-band processes (free charge carrier absorption). The inter-band transition originates from the transition of an electron from an occupied state in the valence band to an unoccupied state in the conduction band, as shown in Fig. 1.7(a), only when the energy of the incident photon is two-times higher than the Fermi energy of graphene ($\hbar\omega > 2E_f$). If $\hbar\omega < 2E_f$, the inter-band transition does not occur due to Pauli blocking, and in this case the optical conductivity is dominated by intra-band processes (free charge carrier absorption), as illustrated in Figs. 1.7(a) and (b).

For undoped graphene at zero temperature, the calculated optical conductivity $\sigma(\omega)$ near the Dirac points was found to be independent on the frequency of the light (ω) (i. e. universal optical conductivity) and can be described by [26–28]

$$\sigma(\omega) = \frac{\pi e^2}{2\hbar}. \quad (1.12)$$

The absorbance of graphene $A(\omega)$ can be related to the optical conductivity by

$$A(\omega) = \frac{4\pi}{c} \sigma(\omega). \quad (1.13)$$

As a result of the universal conductivity of graphene, the absorbance of graphene is independent on the frequency $A(\omega) = \pi\alpha \approx 2.29\%$, where α denotes the fine structure constant. The optical transmittance $T(\omega)$ of graphene is defined by

$$T(\omega) = 1 - A(\omega) \approx 1 - \pi\alpha. \quad (1.14)$$

Figure 1.7: (a) Illustration of inter-band and intra-band (free charge carrier absorption) processes. (b) Illustration of a typical absorption spectrum of doped graphene, which shows a universal absorbance of 2.3 % in the visible range, graphene becomes transparent in the mid-infrared region, and shows a strong Drude absorption peak in the far-infrared and THz frequency regions (μ refers here to the Fermi energy). Reprint with permission from Ref. 22. (c) Photograph of a 50 μm aperture partially covered with monolayer and bilayer graphene. The line scan profile shows the intensity of transmitted white light along the yellow line. (d) Transmittance spectrum of monolayer graphene (open circles) and comparison with the theoretical transmission (Eqn. 1.14) (red line). Reprint with permission from Ref. 23. (e) Measured optical absorbance of monolayer graphene in the spectral range of 0.2 to 5.5 eV. The experimental spectrum shows an absorption peak energy at 4.62 eV. Reprint with permission from Ref. 24. (f) GW ab-initio calculations of the optical absorbance of graphene with (solid-blue line) and without (red-dashed line) excitonic effects. Reprint with permission from Ref. 25.

The universal optical conductivity (i.e. absorbance) of graphene was experimentally confirmed for suspended graphene [23, 29] in the spectral range of 0.5 – 1.0 eV (Fig. 1.7(d)). Figs. 1.7 (c) and (d) show the transmittance of suspended exfoliated monolayer and bilayer graphene membranes, in which the absorbance of a monolayer is $2.3 \pm 0.1\%$. Therefore, the absorbance increases with the graphene thickness by 2.3% for each graphene layer.

In the ultraviolet region, the optical conductivity (i.e. absorbance) becomes dependent on the frequency and shows a large asymmetric peak absorption at 4.62 eV (see Fig. 1.7(f)). The GW ab-initio calculations demonstrated that this absorption peak originates from the inter-band transitions near the saddle point

singularity at the **M**-point (Van Hove singularity) and that the absorption peak is symmetric and occurs at 5.1 eV [25]. The redshift of the peak near 4.5 eV and the different line shape was attributed to the strong resonant excitonic effects (see Fig. 1.7(e)).

In this thesis, we have investigated the optical properties of graphene on 4H-SiC(000 $\bar{1}$) grown by sublimation technique using spectroscopic ellipsometry in the visible to vacuum ultraviolet spectral range. We have found that graphene exhibits a critical point transition energy (CP) at 4.51 eV, associated with exciton enhanced van Hove singularity. We have investigated the graphene thickness dependence of the graphene dielectric function and we have found that the CP point transition energy redshifts with increasing the graphene thickness towards those reported for graphite (**Paper I**).

In the far-infrared and THz regions, the optical properties of graphene are dominated by the free charge carriers absorption (intra-band). The optical conductivity can be described by a classical Drude-model as discussed in more detail in chapter 3.

1.6 Transport properties of graphene

First transport experiments on graphene (exfoliated graphene on SiO₂/Si) have demonstrated high free charge carrier mobility in the range 10000 – 15000 cm² V⁻¹s⁻¹ at ambient conditions. Furthermore, graphene exhibits a strong ambipolar field effect due to the linear dependence of the carrier DOS as a function of the energy. The free charge carrier concentration in graphene can be tuned continuously from electrons to holes up to a concentration of $n = 10^{13}$ cm⁻², while the mobility parameter is as high as 15000 cm²V⁻¹s⁻¹, as presented in Fig. 1.8(a) [6, 30]. This is not the case of high-mobility-semiconductors, for which the mobility is high only for bulk undoped materials and decreases with increasing carrier concentration (see table 1.1).

Magneto-transport measurements realized on exfoliated graphene have provided the first evidence of massless-Dirac fermions in graphene [30, 31]. Fig. 1.8(a) shows the measured cyclotron mass of monolayer graphene as a function of carrier concentration (n) (varied by the field effect). The experimental cyclotron mass data show a square-root dependence with n and the corresponding fit using Eqn. 1.18 gives $v_f = 1 \times 10^6$ ms⁻¹.

Graphene shows the anomalous quantum Hall effect (QHE) or chiral QHE, which is the shift of the QHE levels by 1/2 [30, 31] and it is a direct consequence of the chirality of graphene carriers at the Dirac points (see Fig. 1.8(c)).

Figure 1.8: (a) Resistivity of graphene as a function of gate bias (Fermi energy), showing a strong ambipolar field effect where carrier concentration can be tuned from holes to electrons. Insets show low-energy band structure of graphene indicating changes in the position of the Fermi energy with changing gate bias. Reprinted with permission from Ref. 6. (b) Cyclotron mass of electrons and holes as a function of their concentrations. Symbols indicate experimental data and solid curves represent the best fit to theory using Eqn. 1.18. Reprinted with permission from Ref. 30. (c) Chiral quantum Hall effects of monolayer graphene. Reprinted with permission from Ref. 30.

Table 1.1: Properties of high mobility semiconductors [39] and exfoliated graphene on SiO₂ at room temperature [6].

	Si	GaAs	InSb	Exfoliated graphene
Electron mobility (cm ² V ⁻¹ s ⁻¹)	1417	8800	77000	10000—15000
Hole mobility (cm ² V ⁻¹ s ⁻¹)	471	400	850	10000—15000
Band gap (eV)	1.12	1.42	0.17	0

The “half-integer” QHE is considered as the unique fingerprint of high-quality monolayer graphene. Furthermore, graphene is the only material that possesses a room-temperature QHE [32].

Bilayer graphene also possesses high carrier mobility parameters, in the range of 3000 – 8000 cm²V⁻¹s⁻¹ at 300 K [30, 33, 34], but lower than the mobility of monolayer graphene. Interestingly, a narrow band gap of 250 meV can be created in bilayer graphene, in the presence of a potential difference between the adjacent graphene layers. This can be achieved via the creation of different doping levels between the top and the bottom layers [35] or by application of an electric field perpendicular to the graphene planes [36–38].

1.7 Graphene and graphite in magnetic field

When a magnetic field B is applied perpendicularly to the plane of a two-dimensional electron gas (2DEG), the electronic band structure is quantized into discrete

electronic levels (E_n), so called Landau levels (LLs)

$$E_n = \hbar\omega_c \left(n + \frac{1}{2} \right), \quad (1.15)$$

where $\omega_c = eB/m^*$ is the cyclotron frequency, e the electron charge and n the quantum number of the individual LL which is a positive (negative) integer for electron- (hole-) like LLs. Conventional 2DEG semiconductor heterostructures show a linear dependence of the LL energy with the magnetic field and the LL-energies are equally separated. However, graphene shows unique LLs due to its linear band structure at the Dirac point. The LL energy position in graphene are described by [32]

$$E_n = \text{sign}(n)v_f\sqrt{e\hbar B |n|} = \text{sign}(n)E_0\sqrt{|n|}, \quad (1.16)$$

with $E_0 = v_f\sqrt{2e\hbar B}$.

In contrast to 2DEG, the LLs of graphene show a square-root dependence on the magnetic field and are not equally separated. The fundamental Landau level ($n = 0$) for graphene is $E_0 = 0$, which can be equally shared by holes and electrons for undoped graphene. The cyclotron mass (in the semi-classical approximation) of graphene can be described by [5]

$$m_c = \frac{1}{2\pi} \left[\frac{\partial A(E)}{\partial E} \right]_{E=E_f}, \quad (1.17)$$

where $A(E)$ is the area in k -space enclosed by the orbit, such as $A(E) = \pi k^2 = \pi E^2/v_f^2$ and E_f is the Fermi energy. The resulting cyclotron mass m_c is [5]

$$m_c = \frac{\sqrt{\pi}}{v_f} \sqrt{n}. \quad (1.18)$$

The LL-energies of bilayer graphene are given by [26, 40, 41]

$$E_n^\alpha = \text{sign}(n) \frac{1}{\sqrt{2}} \sqrt{\gamma_1^2 + (2|n| + 1)E_0^2 - (1)^\alpha \sqrt{\gamma_1^4 + 2(2|n| + 1)E_0^2\gamma_1^2 + E_0^4}}. \quad (1.19)$$

Figures 1.9 (a) and (b) show the LL-energies (obtained for $\alpha = 1$) of monolayer and bilayer graphene, respectively. In contrast to monolayer graphene, the LL-energies of bilayer graphene follow a quasi-linear dependence with the magnetic field.

In the presence of an electromagnetic radiation, the electrons are excited from an occupied Landau level state L_n to an unoccupied one L_n' by absorbing a photon,

Figure 1.9: (a) Landau level energy as a function of magnetic field for (a) monolayer graphene calculated using Eqn. 1.16 with $v_f = 1 \times 10^6 \text{ ms}^{-1}$ and (b) bilayer graphene calculated using Eqn. 1.19 with $v_f = 1 \times 10^6 \text{ ms}^{-1}$ and $\gamma_1 = 0.39$.

which is referred to as LL-transitions. The LL-transitions obey the optical selection rules, described for monolayer and bilayer graphene by the relationship

$$|n'| = |n| \pm 1. \quad (1.20)$$

The LL-transitions can be classified as following

- The inter-LL-transitions occur between LLs with opposite signs, where an electron is excited from the hole-LL to the electron-LL. The inter-bands LL-transitions energy is given by

$$E = v_f \sqrt{2e\hbar B} \left(\text{sign}(n') \sqrt{n'} - \text{sign}(n) \sqrt{n} \right) \quad (1.21)$$

- The intra-LL-transitions occur between LLs with the same sign, where an electron is excited from electron- (hole-) LL to electron- (hole-) LL.
- The mixture-LLs-transition involves LL-transition of the fundamental level (L_0). The fundamental-LL is shared by holes and electrons. Consequently, the LL-transitions $L_{-1} \rightarrow L_0$ and $L_0 \rightarrow L_1$ can be considered at the same time as inter- and intra-LL-transition.

Fig. 1.10 is an illustration of LL-energies for graphene at a constant magnetic field presenting the different possible allowed optical inter-, intra- and mixture-LL-transitions, labeled with *, # and †, respectively. The symmetric inter- and mixture-LL-transitions with $|n'| = |n| \pm 1$ (for example $L_{-3} \rightarrow L_4$ and $L_{-4} \rightarrow L_3$) are

Figure 1.10: Schematic presentation of LL-energies for graphene at a constant magnetic field, the dashed line indicates the Fermi energy and the optically allowed LL-transition-energies are indicated by arrows (a) *n*-type doped graphene excited with unpolarized light, (b) undoped graphene excited with circularly polarized light. The inter-, intra- and mixture-LL-transition are labeled with $*$, $\#$ and $+$. χ^+ and χ^- denote the right- and left-handed circularly polarized light. Adapted from Ref. 25.

energetically degenerated (Fig. 1.10 (a) and Eqn. 1.21). As a result, both transitions are excited simultaneously. The separation between the symmetric transitions can be achieved by using circularly polarized radiation [25], as shown in Fig. 1.10(b).

Chapter 2

Epitaxial graphene on SiC

2.1 Introduction

Most of the excellent properties of graphene discussed in the previous chapter were demonstrated on exfoliated graphene flakes with limited domain size. The mechanical exfoliation method is a cumbersome preparation method, which makes it unsuitable for large-scale production. Consequently, growth techniques that can produce large-area graphene with properties that match the high-quality of exfoliated graphene are needed in order to implement graphene in future applications. However, obtaining high-quality graphene with well-controlled properties (i.e. thickness, doping, etc.) over large-area remains a significant challenge. Despite the fact that several growth techniques have been developed during the last decade [42], only a few of them could be scaled up to mass production and are applicable at the industrial level. The most promising ways to fabricate large-area graphene are liquid-phase exfoliation of graphite (LPE), chemical vapor deposition of hydrocarbon precursors on transition-metal surfaces (CVD-graphene) and thermal decomposition of silicon carbide (SiC) by sublimation of Si atoms (see Fig. 2.1).

LPE can produce large quantities of graphene flakes by the oxidation of graphite in liquid environments and sonication to extract individual layers (Fig. 2.1). LPE is a cost-effective growth technique and LPE-graphene can be deposited on a wide range of different substrates. This makes LPE attractive for several applications, such as, graphene ink, coating, composite and transparent conductive electrodes. However, LPE-graphene is defective with a limited lateral size of the flakes, which makes LPE-graphene unsuitable for electronic-based application.

Large-area of high-quality graphene can be grown using CVD and sublimation (Fig. 2.1 and Tbl. 2.1). Graphene can be grown by CVD on a large variety of

transition metal substrates (Cu, Ru, Ir, Pt, Co, Pd, Re, etc.) using hydrocarbon reactants (such as methane). The transition metal substrate plays the role of a catalyst when maintained at high temperatures (400°C—1000°C), the hydrocarbon reactants are adsorbed at the metal surface and thermally decomposed to carbon species that enable the graphene growth. Large area monolayer graphene (up to 30 inches) is grown by using low pressure-CVD (LP-CVD) on polycrystalline Cu foil substrate and methane as a hydrocarbon reactant [43]. The as-produced monolayers are polycrystalline where grain boundaries are formed between the adjacent graphene domains. As a result, the carrier mobility is limited and there are large variations of the electronic properties of CVD-graphene, which renders its implementation in electronic devices challenging.

It was shown recently that oxygen-rich Cu substrate enable the large-area single crystal monolayer graphene growth by CVD up to several square-centimeters [44, 45]. The single-crystalline monolayer graphene shows high carrier mobility parameters similar to those of exfoliated graphene on silicon oxide substrate (Tab. 2.1). Despite the significant progress, the implementations of CVD-graphene in graphene-based electronics still faces several challenges. The growth rate of single-crystalline CVD graphene is very low, which leads to graphene domain in the centimeter-size range. The control of the size and the shape of single-crystalline graphene domains over large-area is still a challenge [46]. Besides, most of the electronic and optoelectronic applications require a transfer of CVD-graphene from the metal to a dielectric substrate. During the transfer process, defects (holes, cracks, and wrinkles with lengths of several micrometers), doping and residues are typically introduced into CVD-graphene [47], which can significantly degrade its electronic properties [48]. This transfer process is expensive, thus, limiting the implementation of CVD-graphene at industrial scale. CVD-graphene grown directly on a dielectric substrate has the advantage of avoiding the transfer process, but is far from having the desired crystalline quality and domain size needed for the integration of CVD-graphene in electronic applications [49, 50].

Uniform large-area of high-quality epitaxial graphene (EG) can be grown by sublimation, directly on semi-insulating hexagonal SiC wafers [51–53] without the need of transfer (Fig. 2.1). This is a significant advantage of the sublimation method for graphene-based electronic applications. Several EG-based devices have already been demonstrated, such as high-frequency field effect transistors with a cutoff frequency of 200 GHz [54]. In addition, EG finds application in metrological resistance standards [55]. A schematic summary of the different growth techniques and their main applications is presented in Fig. 2.1.

Properties	Mechanical exfoliation			CVD graphene		Epitaxial graphene on SiC	
	Exfoliated graphene	Suspended graphene	Poly-crystalline CVD graphene	Single-crystalline CVD graphene	Si-face	C-face	
	$\leq 1\text{ mm}^2$	$150\text{ }\mu\text{m}^2$	$\leq 30\text{ inch}$ [43]	$\leq 2\text{ cm}^2$ [44, 45]	Wafer size (76.2 mm)	Wafer size (76.2 mm)	
large-area scalability							
Domain with uniform thickness	$\leq 1\text{ mm}^2$	$150\text{ }\mu\text{m}^2$	95% monolayer	$\leq 2\text{ cm}^2$ [45]	60% to 98% monolayer [51, 52, 56]	$100\text{ }\mu\text{m}^2$ [57–59]	
Mobility at room temperature [cm ² V ⁻¹ s ⁻¹]	15000	120000 (at 240 K) [60]	≤ 5100 (at 295 K) [43]	≤ 25000 [61]	$\leq 2400\text{--}3100$ [62, 63]	≤ 18100 [64, 65]	
Half-integer QHE	[30, 31]	[60]	[43]	[44]	[62, 66, 67]	[68]	
Ballistic transport	–	[60]	–	[69]	[70]	–	
Applications	Fundamental research	Fundamental research	Transparent electrodes	Flexible electronics	Radio frequency-applications	Radio frequency-applications	

Table 2.1: Large-area scalability, size of graphene domains with uniform thickness and electronic properties of graphene obtained by mechanical exfoliation, CVD, and sublimation growth techniques.

Figure 2.1: Schematic summary of growth techniques used to fabricate large-area graphene.

2.2 Background of epitaxial graphene on SiC

The most common used SiC polytypes for the growth of epitaxial graphene are 3C-SiC (cubic), 4H-SiC (hexagonal) and 6H-SiC (hexagonal). Fig. 2.2(a) shows the different stacking of bilayers of 3C-, 4H- and 6H-SiC crystals in the (1120) plane. 3C-SiC, 4H-SiC, and 6H-SiC have bilayers Si-C stacking sequence of ABC..., ABCBABC..., and ABCACBABCACB..., respectively. Hexagonal SiC is a polar material with two non-equivalent polar faces when cut perpendicularly to the c-axis, where the Si-face corresponds to the (0001) surface and C-face corresponds to the (000 $\bar{1}$) surface. 3C-SiC also exhibits similar polar surfaces along the [111] direction.

Graphene can be grown on both SiC faces using sublimation. In the following, we will refer to epitaxial graphene grown on Si-face and C-face SiC(0001) as Si-face EG and C-face graphene, respectively. The 4H- and 6H-SiC substrate have been the substrate of choice for the growth of EG using sublimation, since their hexagonal surfaces offer an excellent template for EG and they are commercially available (up to 150 mm for 4H-SiC wafers). 3C-SiC has attracted less attention despite the fact that 3C-SiC(111) has a hexagonal surface, which can be used also as a template for EG growth. This is due to the difficulty to grow 3C-SiC(111) substrates (or films) with a similar high-quality as 4H-SiC (or 6H-SiC) wafers. The surface morphology and the off-cut angle of SiC also play important roles in the EG formation and properties [72].

Figure 2.2: Stacking sequence of bilayer Si-C of the 3C-, 4H and 6H-SiC polytypes in the (1120) plane and along the c-axis [0001]. Reprinted with permission from Ref. 71

Sublimation is a thermally driven growth process. When the SiC substrate is heated above the Si melting point (1150°C), the Si atoms sublime from the SiC surface (Fig. 2.3(a)). Fig. 2.3(b) shows the vapor pressure of different Si and C species present at the SiC surface when heated at different temperatures. In an ultra-high-vacuum (UHV) system, graphene can be grown at a temperature as high as 1200°C, since at this temperature, the Si atoms possess a vapor pressure of 10^{-10} bar and can be absorbed by the vacuum system, while the C atoms have a much lower vapor pressure [73] and remain at the surface. When a three bilayer Si-C are decomposed from the SiC, the remaining C atoms reconstruct via sp^2 hybridization and form a monolayer EG (Fig. 2.3(a)).

In UHV, the growth of EG occurs far from the thermodynamic equilibrium and the sublimation rate is high, which leads to a poor control of uniformity and thickness. EG grown by UHV-sublimation is defective and shows very rough surface morphology. As a result, the carrier mobility parameters of EG are very low: $\sim 300 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ [51] and $\sim 29 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ [75], for Si-face EG and C-face, respectively. In order to obtain EG graphene with good morphology, uniformity, and electronic properties, several advanced sublimation techniques have been developed. These include: low-temperature (1400°C–1650°C) sublimation in argon gas (low-temperature sublimation) [51], high-temperature (1800°C–2000°C) sublimation in argon atmosphere (high-temperature sublimation) [52] and confinement controlled sublimation (CCS) [53].

Figure 2.3: (a) Schematic illustration of the sublimation growth method. (b) Equilibrium partial pressures at different temperature shown for volatile Si species (Si, Si₂, Si₃, Si₂C, SiC and Si₃C₃) and C species (C, C₂, C₃, C₂Si) in SiC system assuming condensed SiC and carbon. Reprinted with permission from Ref. 74.

2.3 EG on Si-face SiC (0001) in UHV

Fig. 2.4 shows LEED patterns of Si-face SiC (0001) upon heating. SiC surfaces are usually covered with a native oxide layer (SiO_x), which has to be removed before the EG growth by annealing the SiC substrate under a Si flux at $\geq 800^\circ\text{C}$. In this case, the Si-face SiC (0001) shows Si-rich $(3 \times 3)_{\text{Si}}$, while the C-face SiC (000 $\bar{1}$) shows a Si-rich $(2 \times 2)_{\text{Si}}$. Note that the native oxide can also be removed by cleaning the SiC substrate with a hydrofluoric acid solution and by hydrogen etching. In such cases, the SiC surfaces show (1×1) surface reconstruction. For Si-face SiC (0001), the thermal annealing of the Si-rich $(3 \times 3)_{\text{Si}}$ surface results in a C-rich $(\sqrt{3} \times \sqrt{3})R30^\circ$ (Fig. 2.4(b)). By increasing the annealing temperature up to 1150°C , a C-rich phase with $(6\sqrt{3} \times 6\sqrt{3})R30^\circ$ surface reconstruction appears (Fig. 2.4(c)). This surface reconstruction was attributed to the formation of a carbon layer (so-called buffer layer) on top of SiC, rotated by 30° with respect to the SiC. Further heating (up to $\sim 1280^\circ\text{C}$) leads to the formation of a new carbon layer between the buffer layer and the SiC. The newly formed carbon layer interacts with the underlying SiC to form a new buffer layer, while the former buffer layer is detached from the SiC, leading to the formation of the first graphene layer on top with $(1 \times 1)_{\text{graphene}}$ (Fig. 2.4(d)). Further heating of Si-face SiC results in the formation of graphite with $(1 \times 1)_{\text{graphite}}$ LEED diffraction pattern (Fig. 2.4(e)).

It was found that Si-face EG has an intrinsic electron doping in UHV environment ($\sim 10^{13} \text{ cm}^{-2}$) [76–78]. The buffer layer exhibits σ -band similar to graphene, indicating that it has a similar atomic arrangement to the one of graphene. How-

Figure 2.4: LEED patterns of Si-face SiC (0001) upon annealing in UHV: (a) $(3 \times 3)_{\text{Si}}$, (b) $(\sqrt{3} \times \sqrt{3})R30^\circ$, (c) $(6\sqrt{3} \times 6\sqrt{3})R30^\circ$ surface reconstructions, (d) Si-face EG formation and (e) graphite. The reciprocal lattice vectors of the SiC (S_1 ; S_2) and graphene (G_1 ; G_2) lattices are indicated. The LEED patterns in (a) and (b) are adapted from Ref. 81. The LEED in (c), (d) and (e) are adapted from Ref. 79.

ever, the π -band is distorted due to a strong bonding with the underlying SiC and thus, the buffer layer shows nonmetallic behavior and different electronic properties compared to graphene [79]. Only one-third of the C-atoms of the buffer layer are covalently bonded to the Si-atoms of the SiC surface underneath, resulting in a significant degree of sp^3 hybridization of the buffer layer. Furthermore, the atomic configuration of the buffer layer leads to a high density of charged Si-atom dangling bonds at the SiC interface, which introduces a high electron doping into the graphene [79, 80].

2.4 Graphene on C-face SiC (000 $\bar{1}$) in UHV

C-face SiC surface shows a completely different surface reconstruction compared to Si-face SiC, as shown in Fig. 2.5. Heating the Si-rich $(2 \times 2)_{\text{Si}}$ (Fig. 2.4(a)) up to a temperature of 1050°C results in the formation of a C-rich $(3 \times 3)_{\text{C}}$ SiC (Fig. 2.3(b)), upon further annealing, the C-rich $(3 \times 3)_{\text{C}}$ SiC transforms in to a C-rich $(2 \times 2)_{\text{C}}$

Figure 2.5: LEED patterns C-face SiC $(000\bar{1})$ upon annealing of in UHV: (a) $(2 \times 2)_{\text{Si}}$, (b) $(3 \times 3)_{\text{Si}}$, (c) $(2 \times 2)_{\text{C}}$ surface reconstructions, (d) C-face graphene formation on $(2 \times 2)_{\text{C}}$ coexisting with $(3 \times 3)_{\text{C}}$ (e) FL C-face graphene. The reciprocal lattice vectors of the SiC (S_1 ; S_2) and graphene (G_1 ; G_2) lattices are indicated. The LEED patterns are adapted from Refs. 79 and 81.

phase (Fig. 2.5(c)). By further increasing the annealing temperature up to 1150°C, C-face graphene is formed (Fig. 2.4(d)) suggesting the growth rate of C-face graphene is much higher compared to Si-face EG. Furthermore, it was found that the $(2 \times 2)_{\text{C}}$ reconstruction coexists with $(3 \times 3)_{\text{C}}$ before graphene formation [79, 82] and C-face graphene grows on top of C-rich $(2 \times 2)_{\text{C}}$ or $(3 \times 3)_{\text{C}}$. The ratio between the two reconstructions depends on the growth temperature, surface preparation, heating furnaces, etc.

Further heating results in the formation of few layers (FL) C-face graphene. Unlike Si-face SiC (0001) that shows single $(1 \times 1)_{\text{graphene}}$, FL C-face LEED pattern shows multiple $(1 \times 1)_{\text{graphene}}$ diffraction spots and a diffusive ring-like diffraction pattern with a strong intensity modulation (Fig. 2.5(d) and (e)). These diffraction patterns were attributed to the rotation of adjacent graphene layers in the stack, exhibiting preferential rotational angles. FL C-face graphene shows a Dirac-like band structure similarly to single layer graphene [79]. This observation indicates that the adjacent layers in FL C-face graphene stack are electronically decoupled and behave as a stack of non-interacting graphene layers. Furthermore, it was shown that C-face graphene interacts weakly with the underlying SiC substrate and a buffer layer is absent, in contrast to Si-face EG [79].

Figure 2.6: (a) AFM image of Si-face SiC (0001) after hydrogen etching. (b) and (c) AFM and LEEM images of Si-face EG grown by UHV-sublimation. (d) AFM and (e) LEEM images of Si-face EG grown by low-temperature sublimation in argon atmosphere, receptively. (f) A zoomed LEEM image of Si-face EG grown by low-temperature sublimation in argon atmosphere. The LEEM image shows the formation of bilayer and trilayer Si-face EG around the step edges. Images are reprinted with permission from Ref. 51.

2.5 Low-temperature EG on Si-face SiC (0001)

Emtsev *et. al.* [51] have demonstrated uniform large-area monolayer (ML) Si-face EG by sublimation in argon atmosphere (Fig. 2.6(e)), with pressure of 1000 mbar and a growth temperature of about 1650°C. The presence of a dense argon gas slows down the Si atoms evaporation by acting as a diffusion barrier and shifting the Si atoms desorption to a significantly high temperature (up to 1500°C). This opens the temperature window where the SiC surface undergoes a surface restructuring before graphene is formed, leading to a major improvement of the Si-face EG surface morphology, as shown in Fig. 2.6(d). Furthermore, the high-temperature increases the diffusion rate of the carbon atoms, which improves EG crystalline quality.

LEEM investigations (Fig. 2.6(f)) show that using this method uniform ML graphene can be formed along the SiC terraces. However, bilayer and trilayer

graphene are formed close to the step edges. Often for low-temperature sublimation in argon, prior to graphene growth, the SiC surface is treated in hydrogen at relatively high-temperatures to remove the mechanically polishing process damage. Such so-called hydrogen etching results into a significant step bunching, as well as a change of the initial SiC from relatively flat surface (with atomic terrace steps height) to well-defined terraces perpendicular to the [0001] direction (with relatively higher terrace step height) [83, 84] (Fig. 2.6(a)). Additionally, during the initial stage of graphene growth, another significant step bunching occurs where a higher macro-terrace steps height with larger terraces in between are formed [85] (Fig. 2.6(d)). It was found that Si-face EG nucleates and exhibits much higher growth rate at the macro-steps compared to the terraces [86–88]. Si-face EG grown by low-temperature sublimation in argon forms on top of the buffer layer and exhibits high electron doping, similarly to the case of Si-face EG grown by UHV-sublimation [51].

Si-face EG grown by low-temperature sublimation in argon shows a higher carrier mobility of $900 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ at 300 K compared to Si-face grown in UHV with a mobility of $300 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ at 300 K. Similarly, Tedesco *et. al.* also reported the improvement of carrier mobility of Si-face EG grown in argon compared to those grown in an intermediate vacuum [89], as shown in Fig. 2.7.

2.6 Low-temperature graphene on C-face SiC(000 $\bar{1}$)

Confinement controlled sublimation (CCS) is another approach used to improve the uniformity of EG by confining SiC substrate in an enclosure (in argon or vacuum) with an orifice on top, which limits the Si escape and increases the Si vapor pressure at the SiC surface. This keeps the process close to the thermodynamic equilibrium. The high Si pressure at the SiC surface allows to grow graphene in an intermediate vacuum (10^{-7} to 10^{-4} mbar) or in moderate argon pressure [53]. The graphene growth temperature in CCS ranges from 1300 to 1600°C.

In contrast to Si-face EG, C-face graphene was found to form typically multilayer or FL graphene (Fig. 2.8(a)). Fig. 2.8(b) shows atomic force microscopy (AFM) topographic image of CCS grown multilayer graphene, revealing well-defined SiC terraces unlike C-face graphene grown in vacuum. Moreover, C-face graphene grown by CCS exhibits wrinkles (white lines in Fig. 2.8(b)), which may originate from compressive thermal strain generated by the different thermal expansion coefficients of SiC and graphene [90]. Similar to the case of UHV, C-face graphene grown by CCS shows multiple $(1 \times 1)_{\text{graphene}}$ spots. One set of $(1 \times 1)_{\text{graphene}}$ spots rotated by 30° (R30) with respect to the (1×1) diffraction spots of the SiC. There

Figure 2.7: Hall effect mobility versus sheet carrier density measured at 300 K for C-face and Si-face grown in vacuum and in argon. The dashed lines are linear fits to the data for C- and Si-face samples. Reproduced with permission from Ref. 89.

is also a diffusive ring located at $0 \pm 2.2^\circ (R^{2\pm})$ with respect to the SiC diffraction spots (see Fig. 2.8(c)). Multilayer C-face graphene grown by CCS was shown to have a Dirac-like band structure, (see Fig. 2.8(d)) [91] but also *AB*-stacking bi-layer and multilayer arrangement [41, 92, 93]. The presence of a Dirac-like band structure indicates that the individual layers in the FL C-face graphene stack are electronically decoupled and the stack behaves as a single layer graphene. The origin of the decoupling was attributed to the rotation disorder between the adjacent graphene layers [15]. The decoupling of FL C-face graphene was further confirmed by infrared transmission in magnetic field that showed a square-root dependance of the LL-transitions energies on magnetic field [97, 98]. It was found that the first graphene layers close to the SiC (000 $\bar{1}$) substrate possess a high-electron doping ($\sim 9.2 \times 10^{12} \text{ cm}^{-2}$), the top graphene layers are gradually doped until reaching the undoped graphene layers on the top [96, 99]. The doping of the graphene layer close to the SiC (000 $\bar{1}$) was attributed to a charge transfer from the interface and the SiC (000 $\bar{1}$) substrate. C-face graphene grown by CCS

Figure 2.8: (a) Thickness map of CCS FL C-face graphene extracted from LEEM measurement. The field of view is $10\ \mu\text{m}$. Reprinted with permission from Ref. 94. (b) AFM images of CCS grown multilayer C-face graphene ($10 \sim 12$ ML). Reprinted with permission from Ref. 95. (c) LEED patterns of CCS multilayer C-face graphene (~ 10 ML) acquired at 72.2 eV, showing the graphene and SiC spots and the diffuse arcs labeled as the R^{2+} and R^{2-} rods. Reprinted with permission from Ref. 95. (d) ARPES measured from the top 3 layers of a 10-layer CCS grown multilayer graphene C-face graphene film. Adapted from Ref. 96. (e) Inter-LL-transitions energies versus the square-root of the magnetic field. The solid symbols are data obtained for the CCS FL C-face graphene sample tilted with respect to the direction of B by an angle of 50° . The dashed lines represent calculated transition energies for single layer graphene with Fermi velocities $v_f = 1.03 \times 10^6\ \text{ms}^{-1}$ [97].

method shows a high carrier mobility at room temperature, in the range of 5000 to $15000\ \text{cm}^2\text{V}^{-1}\text{s}^{-1}$ [53, 100–102]. This was attributed to the high-quality of graphene, the decoupling of the adjacent graphene layers and the weak interaction between C-face graphene and SiC. Despite that, half-integer QHE was not observed for FL C-face graphene. On the other hand, For monolayer C-face graphene grown by CCS, half-integer QHE was observed and a very high carrier mobility of $15000\ \text{cm}^2\text{V}^{-1}\text{s}^{-1}$ and an electron density of $1.27 \times 10^{12}\ \text{cm}^{-2}$ was found [103].

C-face graphene also can be grown by sublimation in argon environment in CVD-type reactor. Typical growth temperatures are in the range of $1500\text{--}1600^\circ\text{C}$ and typical argon pressures range from 50 to 1000 mbar [104]. Similar to the CCS growth method, C-face graphene in this case consists also of small domains with different thicknesses. The surface defects of SiC were found to play an impor-

Figure 2.9: (a) Growth mode of C-face graphene as a function of growth temperature and argon growth pressure. Zero argon pressure corresponds to an *in-vacuum* growth at 10^{-5} mbar. Reprinted with permission from Ref. 104. (b) Electron channeling contrast imaging microscopy image showing the nucleation of C-face graphene at a threading screw dislocation, indicated with the white circle. Reprinted with permission from Ref. 105. (c) Typical AFM images of C-face graphene grown by low-temperature sublimation. Reprinted with permission from Ref. 89.

tant role in the growth in this case. Fig. 2.9(a) shows a histogram of the growth mode of C-face graphene as a function of growth temperature and argon growth pressure [104]. It is seen that graphene islands are typically formed before the entire SiC is covered with graphene, indicating that the C-face graphene grows in a three-dimensional mode. Hite *et. al.* showed that graphene nucleates around threading screw dislocation defects forming thick islands (see Fig. 2.9(b)). As the sublimation process proceeds, graphene islands coalesce, which results in non homogeneous FL or multilayer C-face graphene with a rough surface morphology [106] (Fig. 2.9(c)). Camara *et. al.* have investigated the stacking order of FL C-face graphene grown around the screw dislocations in intermediate vacuum regime and found that graphene is composed of AB-stacked multilayer (i.e. graphite) [107].

The transport properties of C-face graphene grown by low-temperature sublimation in argon were investigated by infrared transmission in magnetic field [108] and mid-infrared optical Hall effect [109]. These investigations showed inter-LL-transitions energies with square-root and sub-linear dependance on the magnetic field (Fig. 2.7, [109]). The quasi-linear dependance indicates that C-face graphene contains *AB*-stacked bi- and tri-layer graphene. The electric magneto-transport measurements showed further that C-face graphene grown by low-temperature sublimation in argon exhibits a higher carrier mobility (3000—5000 cm²V⁻¹s⁻¹ at room temperature and hole doping [89]) compared to graphene grown by sublimation in vacuum, as shown in Fig. 2.7.

Figure 2.10: Inter-Landau-level transition energies in multilayer (10-20 MLs) C-face graphene on 6H-SiC grown at 1400°C in argon atmosphere determined from optical Hall effect measurements at 1.5 K. Solid lines denote single-layer graphene [(a) black solid lines and dots], bilayer graphene [(b) blue solid lines and dots], and trilayer graphene [(b) red dashed lines and dots] dependencies on the magnetic field. Reprinted with permission from Ref. 109.

The interface properties of C-face graphene grown by low-temperature in argon pressure are not well understood. Luxmi *et. al.* observed the formation of diffraction spots with $(\sqrt{3} \times \sqrt{3})\text{R}30^\circ$ instead of the (1×1) SiC spots for C-face graphene grown at 1600°C and argon pressure of 1000 mbar [110]. They explained this observation by the presence of a silicate layer (Si_2O_3) at the interface between C-face graphene and SiC. It was found that the silicate layer suppresses the growth of uniform C-face graphene. The origin of the interface layer was attributed to unintentional oxidation of the C-face SiC during the annealing process in argon, due to the presence of oxygen species in the growth reactor. The silicate layer was reported to form at a temperature of $\approx 1200^\circ\text{C}$ and to remain stable up to 1640°C . Transmission electron microscopy studies showed that C-face graphene can either form on top of an amorphous interface layer composed of Si and C atoms [111–113], or grow directly on the C-face SiC without an interface layer [114, 115].

Figure 2.11: (a) The Si/C ratio in the vapor phase as a function of annealing temperature of SiC in C-rich (solid line) and Si-rich environment (dashed-line) (reproduced with permission from Ref. 116). (b) LEEM images taken from monolayer Si-face EG grown on 0.03° 6H-SiC (0001), the field of view is $50\ \mu\text{m}$. The graphene sample was a temperature of 2000°C at an ambient argon pressure of 1000 mbar. Adapted from Ref. 117.

2.7 High-temperature EG on Si-face SiC(0001)

A novel growth method was developed by Yakimova *et. al.* [52, 118] for large-area homogenous Si-face EG by using a high-temperature sublimation in argon atmosphere. This method uses high growth temperatures from 1800°C to 2000°C . The growth of Si-face EG is performed inside a high purity dense graphite crucible with excellent isothermal conditions to ensure uniform temperature distributions. The crucible is placed in radio frequency inductively heated furnace. The high-temperature and the growth inside a high purity graphite crucible present significant advantages for achieving large-area of uniform and high-quality Si-face EG. Fig. 2.11 (a) shows the Si/C ratio in the vapor phase as a function of annealing temperature of SiC in C-rich (solid line) and Si-rich environments (dashed line). The growth at high-temperature and the C-rich environment leads to the decrease of the Si/C ratio, consequently more carbon atoms are available for the growth of Si-face EG. Contrary to the low-temperature sublimation, in which hydrogen etching is performed to prepare uniform SiC terraces before graphene growth, high-temperature sublimation uses in-situ sublimation etching in argon for: i) controlling the surface restructuring (step bunching), and ii) obtaining regular terrace structures and controlled terraces step height before the graphene formation. This procedure is achieved by optimization of the growth process parameters and substrate misorientation (off-cut angle). Large-area of continuous monolayer Si-face EG without any bilayer neither multilayer inclusions at the terraces steps

Figure 2.12: (a) Temperature distribution inside the growth reactor and the crucible. Adapted from **Paper VII**. (b) Image of the growth reactor used for the growth of Si-face EG samples (Courtesy of Prof. Rositsa Yakimova).

have been demonstrated on nominally on-axis 6H-SiC (0001) with an off-cut 0.03° over an area of $\sim 2000 \mu\text{m}^2$ (Fig. 2.11 (b)) [117]. These monolayers grew on $6 \mu\text{m}$ wide terraces and 1-1.5 nm terraces step height (Fig. 2.11 (b)). Si-face EG grown by high-temperature sublimation also exhibits a buffer layer [52] and similar structural properties as Si-face EG grown by low-temperature sublimation in argon or UHV-sublimation [52]. Thus, Si-face EG has universal structural properties (buffer layer and electron doping) independently of the growth conditions. The Si-face EG grown by high-temperature sublimation in argon shows a high crystalline quality, in addition to good uniformity across the terraces steps, the observation of half-integer QHE, as well as a high mobility $\sim 2400 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ at room temperature for typical electron doping in the range 5×10^{11} to $1 \times 10^{12} \text{ cm}^{-2}$ (at room temperature) [62].

In this thesis, we have developed a new crucible to achieve large-area of uniform Si-face EG over 2 inch SiC substrates. To ensure uniform temperatures distribution, we have modeled the heat transfer in the growth system and temperature distribution of the crucible using virtual reactor software from Soft-Impact, Ltd. Fig. 2.12(a) shows the design and the thermal distribution of the crucible with a uniform temperatures distribution (**Paper VII**). The free charge carrier mobility parameters in Si-face EG grown with the new crucible were determined to be in the range $1500\text{--}2500 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ (**Papers VI and VII**).

2.8 High-temperature graphene on C-face SiC(000 $\bar{1}$)

In similarity to the other sublimation methods, the growth of uniform large-area C-face graphene by high-temperature sublimation in argon is also very challenging. The C-face graphene obtained by this growth method consists of relatively small domains with a size of a few microns. Johansson *et. al.* have investigated the stacking of FL C-face graphene grown by high-temperature sublimation in argon using selected area LEED (micro-LEED). They found that FL C-face graphene shows no rotational disorder between the adjacent graphene layers in the stack, i.e. graphene layers exhibit $(1 \times 1)_{\text{graphene}}$ diffraction spots similar to Si-face EG (Fig. 2.13(b) and (c)), and that the rotation of different domains does not occur between adjacent layers in the stack but rather in-plane within the same graphene sheet (Fig. 2.13(d)) [119, 120]. Recently, the authors reported that FL C-face graphene is *AB*-stacked (Fig. 2.13(f)) and the single π -band observed in ARPES experiments is a superposition of several multiple bands associated with two, three or more *AB*-stacked layers (Fig. 2.13(e)), in contrast to the results reported for C-face graphene grown by other sublimation techniques [120]. Johansson *et. al.* could not identify any interface between C-face graphene and SiC [119, 121]. On the contrary, in this thesis, we have identified an amorphous interface layer between C-face graphene and 4H-SiC(000 $\bar{1}$) in relation with polishing defects using high-resolution transmission electron microscopy and spectroscopic ellipsometry. We have found that the interface layer is composed of Si, C and O atoms. We also have found that the interface layer thickness increases with increasing the growth temperature [122]. Our results were later confirmed by Nicotra *et. al.*. In **paper II**, we have identified a SiO_x layer between graphene and 4H-SiC(000 $\bar{1}$) without polishing defects using selected area X-ray photoelectron spectroscopy and we have shown that its chemical composition changes towards SiO₂ and its thickness increases with aging in ambient conditions. The interface SiO_x layer also causes the formation of non-ideal Schottky contact between the ML C-face graphene and SiC. In this thesis, we investigated the interaction between the individual layers in FL C-face graphene stack using mid-infrared optical Hall effect and the stacking order of FL C-face graphene using micro-LEED. We found that C-face graphene consists of decoupled non-interacting sheets independently of the substrate polytype. We further determined that FL C-face graphene does not show any rotational disorder. However, the presence of polishing defects on the substrate surface may cause the formation of *AB*-stacked inclusions. This may provide a possible explanation for the finding of *AB*-stacked FLG reported by Johansson *et. al.* [120].

Figure 2.13: (a) LEEM image of FL C-face graphene on SiC(000 $\bar{1}$) field of view 10 μm . The area 1 and 2 correspond to 6 ML of graphene. (b) and (c) Micro-LEED diffraction patterns collected using a probing area of 400 nm from the area 1 and 2, respectively. (d) Micro-LEED pattern of collected using a probing area of 5 μm^2 , the sampling area includes area 1 and 2. (e) Micro-ARPES of C-face graphene showing a Dirac-like band structure. (f) Nano-ARPES of different C-face graphene domains showing that the band structure is composed of multiple π -bands. (a), (b), (c) and (d) adapted with permission from Ref. 119. Copyrighted by the American Physical Society. (e) and (f) are reprinted with permission from Ref. 120.

2.9 Si- and C-face graphene on 3C-SiC(111)

Si-face EG grown on 3C-SiC(111) exhibits similar structural properties as Si-face EG on 4H- and 6H-SiC (0001), i.e. graphene grows on top of a buffer layer (Fig. 2.14(c)) [123–125] and is characterized by an excess of electron doping. Si-face EG and C-face graphene can be grown on 3C-SiC(111) on hexagonal SiC(0001) substrate. In this case, 3C-SiC(111)/4H-or 6H-SiC(0001) epilayers show an adequate crystalline quality. Si-face EG was grown by low- and high-temperature sublimation techniques, where a high-crystalline quality and at least $\sim 2000 \mu\text{m}^2$ large-area of homogenous graphene were achieved (Fig. 2.14(a)) [56, 123, 126]. Yazdi *et al.* compared the Si-face EG formation on 4H-SiC(0001), 6H-SiC(0001) and 3C-SiC(111) under the same growth conditions using high-temperature sublimation. They found that Si-face EG on 3C-SiC(111) exhibits a better thickness uni-

Figure 2.14: LEEM images from selected sample areas for Si-face EG (a) and (b) C-face graphene on 3C-SiC(111)/6H-SiC (field of view $50\ \mu\text{m}$). Domains with 1, 2 and few layer (FL graphene: 3 and 4 monolayers) graphene are indicated on the LEEM images. Micro-LEED pattern from a monolayer area of the Si-face (c) and C-face (d) taken at 40 and 44 eV, respectively. Reprinted with permission from Ref. 123.

formity compared to 4H-SiC(0001), 6H-SiC(0001) over an area of $\sim 2000\ \mu\text{m}^2$ [56]. Darakcheiva *et. al.* compared the Si-face EG and C-face graphene formation on 3C-SiC(111)/6H-SiC(0001) grown by high-temperature sublimation in argon [123]. On Si-face EG a large-area of homogenous monolayer graphene up to $\sim 2 \times 2\ \text{mm}^2$ can be achieved. However, the C-face graphene consists of small domains with uniform thickness (Fig. 2.14(b)). The micro-LEED investigations showed that C-face graphene in this case forms without a buffer layer (Fig. 2.14(d)). The structural properties, stacking order, interaction between the individual layers, as well as the free charge carrier properties in FL C-face graphene on 3C-SiC(111) are not well understood. Si-face EG can be also grown on 3C-SiC(111) epilayer on Si substrate, 3C-SiC(111)/Si(111). This approach facilitates the integration of EG in conventional Si technology but Si-face EG in this case is non-uniform over large-area and has a low crystalline quality [125, 127, 128].

Figure 2.15: (a) $30 \times 30 \mu\text{m}^2$ thickness map of Si-face EG on 4H-SiC(0001) with 98% of monolayer graphene coverage. (b) $30 \times 30 \mu\text{m}^2$ AFM image of Si-face EG on 4H-SiC(0001). Adapted from **Paper VII**.

2.10 Samples studied in the thesis

In this thesis, I have investigated Si-face EG and C-face graphene grown on 4H-SiC (0001) and 3C-SiC (111). The graphene samples were grown by high-temperature sublimation in custom build reactors at the sublimation laboratory at IFM. The C-face graphene samples were provided by Prof. Rositsa Yakimova. The Si-face EG sample were grown in a newly designed crucible as shown in Fig. 2.12(a). Figures. 2.15(a) and (b) show a typical thickness map and an AFM image, respectively of Si-face EG on 4H-SiC(0001) grown in our new crucible (Fig. 2.12(b)). The reflectance map shows uniform monolayer graphene (98%) over $900 \mu\text{m}^2$. The AFM shows uniform surface morphology with an average terrace step height of 0.5 nm. The 4H-SiC substrates used in this thesis are from Cree Inc. The Si-face 4H-SiC(0001) are chemically mechanically polished (CMP) epi-ready surfaces with an on-axis orientation. We have used mechanically polished (MP) and CMP polished epi-ready surfaces on-axis C-face 4H-SiC(000 $\bar{1}$) substrates. 3C-SiC(111) substrates are not commercially available. Thick 3C-SiC(111) films were grown by sublimation on 6H-SiC(0001) in house within the NetFISiC project. The as-grown 3C-SiC(111) quasi-substrates were CMP processed by NOVASiC.

Chapter 3

Experimental techniques

3.1 Raman scattering Spectroscopy

Raman spectroscopy describes the inelastic scattering of light by the Raman active optical phonons of a crystal. Raman scattering consists of the following processes: *i*) a phonon with frequency ω_i and a wavevector $\vec{k}_i$ interacts with a crystal and an optical transition occurs by exciting an electron-hole pair from the valence to the conduction band, *ii*) the excited electron interacts with Raman-optical active phonon with a frequency ω_0 and a wavevector $\vec{q}$ either by gaining (or losing) energy $\hbar\omega_0$, therefore becoming in a virtual state, *iii*) the electron recombines at the valence band by emitting a photon with $\omega_s = \omega_0 + \omega_i$ and $\vec{K}_s = \vec{q} + \vec{k}_i$ (so called *Stokes*) or with $\omega_s = \omega_0 - \omega_i$ and $\vec{K}_s = \vec{q} - \vec{k}_i$ (so called *anti-Stokes*). The first-order Raman process corresponds to an optical phonon with $\vec{q} \sim 0$ and the second-order Raman process involves two optical phonons where their energy and momentum are conserved. The difference between emitted photon frequency and the incident light frequency corresponds to the Raman shift. The Raman spectrum of graphene is typically measured in *Stokes* configuration and exhibits three main Raman peaks: G, D and 2D peaks (Fig. 1.6).

The G peak, located at 1582 cm^{-1} , corresponds to the E_{2g} vibrational mode and it is a first-order Raman scattering process. The D and 2D peaks are associated with $\mathbf{K}/\mathbf{K}'$ intervalley double resonance Raman scattering processes and involve two TO phonons. The D mode is Raman inactive and requires a defect to be activated. The D peak is caused by an intravalley double resonant Raman scattering process and it appears for graphene layers with significant amount of defects [20, 129, 130]. The D and 2D peak positions are blueshifted with increasing the laser energy. The G (ω_{G0}) and 2D (ω_{2D0}) peak positions for freestanding graphene (undoped and unstained graphene) are 1582 cm^{-1} and 2670 cm^{-1} , respectively for an excitation wavelength of 532 nm.

Figure 3.1: Raman spectra of pristine (top) and defected (bottom) graphene, showing the main Raman D, G and 2D peaks. Reprinted with permission from Ref. 130.

3.1.1 The effects of doping

Electron and hole doping has a major effect on the Raman spectra of graphene and it has been investigated on gated exfoliated graphene [131]. Figs. 3.1.1(a) and (b) show the position ω_G and the full width at half maximum (FWHM(G)) of the G peak as a function of electron and hole doping, respectively. Both electron and hole doping blueshift the G peak position with respect to those of undoped graphene by $\delta\omega_G^e/\delta E_F = 30 \text{ cm}^{-1} \text{ eV}^{-1}$ and $\delta\omega_G^h/\delta E_F = 42 \text{ cm}^{-1} \text{ eV}^{-1}$ for electron and hole doping, respectively [131, 132]. The FWHM(G) decreases for both electron and hole doping and saturates for a Fermi energy higher than half of the photon energy. The 2D peak position and FWHM(2D) exhibit different behaviors compared to the G peak. The ω_{2D} shows a quasi-linear shift to higher frequency for hole doping by $\delta\omega_{2D}^h/\delta E_F = 32 \text{ cm}^{-1} \text{ eV}^{-1}$, while for electron doping, the 2D position first shifts to higher energies for concentrations up to $2\text{--}3 \times 10^{-13} \text{ cm}^{-2}$, then drastically decreases [131, 133], as shown in Fig. 3.1.1(c). The FWHM(2D) increases with increasing the electron and hole concentrations. The increase of the FWHM(2D) with increasing doping was attributed to carrier interactions [134, 135]. The increases in doping leads to decrease of the ratio between 2D and G peak intensities, $I(2D)/I(G)$, and their integrated intensities, $A(2D)/A(G)$ [136] (Fig. 3.1.1(d)). These variations of Raman peak characteristics can be used to estimate the doping of graphene.

Figure 3.2: (a) G peak position, (b) full width at half maximum of G peak, (c) 2D peak position and (d) ratio between 2D and G peak intensities, as a function of hole and electron doping in gated exfoliated graphene. Adapted from Ref. 131.

3.1.2 The effects of strain

Strain also can induce major changes in the Raman spectra of graphene. Tensile biaxial strain (ϵ) redshifts the G and 2D peak positions with respect to ω_{G0} , ω_{2D0} . The G(2D) peak position shift due to biaxial strain is described by [137]

$$\Delta\omega_{G(2D)}^b = -2\omega_{G(2D),0}\gamma_{G(2D)}\epsilon, \quad (3.1)$$

where $\gamma_{G(2D)}$ is the Grüneisen parameter of the G(2D) peak. Uniaxial strain shifts the G and 2D positions to lower frequencies with respect to ω_{G0} , ω_{2D0} . Uniaxial strain applied along either zigzag or armchair directions changes the crystal symmetry of graphene. In such case, distorted graphene belongs to the D_{2h} point

group and consequently, the E_{2g} degeneracy is lifted off and the G peak splits into G^+ and G^- peaks. In order to determine the direction, along which strain is applied, polarized Raman measurements are typically employed [137, 138].

3.1.3 The effects of number of layers and stacking

Ferrari *et. al.* showed that the number of graphene layers and their stacking can be determined for exfoliated graphene from the shape and FWHM of the 2D peak [129]. Fig. 3.1.4(a) shows the Raman spectra for exfoliated graphene in the vicinity of the 2D peak as a function of the number of graphene layers. Monolayer graphene has a symmetric 2D peak, which can be fitted using one Lorentzian peak, with a $\text{FWHM}(2D) \approx 25 \text{ cm}^{-1}$. However, AB-stacked bilayer graphene shows a broad and asymmetric peak, with a $\text{FWHM}(2D) \approx 55 \text{ cm}^{-1}$, which can be fitted using four Lorentzian peaks reflecting the parabolic band structure of bilayer graphene [20, 129].

3.1.4 Raman Spectroscopy of graphene on SiC

Si-face and C-face EG on SiC are doped and strained, consequently their ω_G and ω_{2D} are typically shifted from the strain-free position of undoped graphene (ω_{G0} , ω_{2D0}) [139]. Since these shifts are a combination of the effects caused by the strain and doping, the determination of doping type for EG is not feasible from Raman spectroscopy alone. If the doping type is known, the carrier concentration and strain can be estimated by solving a system of two equations with two unknown parameters [140]. In contrast to the case of exfoliated graphene, the determination of the number of layers in Si-face EG and C-face graphene by Raman spectroscopy is not a trivial task. Strain nonuniformity, defects, doping, and stacking order, are several factors that may change the shape of the 2D peak and the $\text{FWHM}(2D)$ in EG [141, 142]. The analysis of the 2D peak shape can be used to investigate the interaction between the individual layers in the FL C-face graphene stack. For example, Fig. 3.1.4 shows the Raman spectra of monolayer graphene and FL C-face graphene on 4H-SiC(000 $\bar{1}$) grown using the crucible shown in Fig. 2.12. The monolayer and FL C-face graphene show a symmetric Lorentzian peak with $\text{FWHM}(2D)$ of about 34 and 24 cm^{-1} , respectively and indicate that the FL C-face graphene behave as a single layer graphene.

In this thesis, we have used three different Raman systems: Raman setup at IFM (see section 3.2), Raman setup at Laboratoire Charles Coulomb (University of Montpellier, France), and Renishaw system at the University of Nebraska-Lincoln (U.S.A.).

Figure 3.3: (a) Raman spectra in the vicinity of the 2D peak for different numbers of graphene layers. Reprinted with permission from Ref. 130. The Raman spectra are obtained from exfoliated graphene. (b) Raman spectra of monolayer (black solid line) and FL C-face graphene (red solid line) on 4H-SiC(0001) (Investigated in the thesis).

3.2 Reflectance

Reflectance can be used to determine the number of graphene layers and map their distribution over the sample surface. Upon reflection, the intensity of light is changed as a result of interaction with graphene. Thus, the intensity of the reflected light from the graphene sample $R(N)$ can be used to determine the number N of graphene layers using [143]

$$R(N) = R_{SiC}(1 + 0.017N), \quad (3.2)$$

where R_{SiC} is the reflectance of a bare SiC reference. The intensity of the reflected light increases linearly by 1.7% per graphene layer for up to 12 layers.

Fig. 3.4 shows the reflectance experimental setup used in this thesis. The setup is based on a similar optical configuration as a conventional micro-Raman system, where two beam splitters (BS1 and BS2) were added. BS1 splits the incident laser beam and directs the laser beam after reflection from the sample to BS2. The role of BS2 beam splitter is to divide the laser beam into two beams: one reflected the CCD camera used as a feedback loop to control the focus on the sample via a piezoelectric system, while the other is reflected on the power meter. The samples are mounted on a three-axis piezoelectric stage used for scanning the sample dur-

Figure 3.4: Schematic representation of the reflectance setup at LiU. Adapted from Ref. 143.

ing the acquisition, to perform the reflectance mapping and focusing of the laser spot. The focus of the laser beam over the sample is achieved via a $100\times$ objective. The FWHM of the laser spot is about 400 nm. A diode-pumped semiconductor laser with a wavelength of 532 nm (photon energy $E_L = 2.33$ eV) was used as an excitation source [143].

This system has the capability to perform reflectance and micro-Raman mapping simultaneously. This allows to assign a specific Raman spectrum to the respective number of layers and draw a conclusion about the properties of graphene, such as coupling/decoupling, doping, and strain in relation to the number of layers.

3.3 Scanning probe microscopy techniques

3.3.1 Atomic force microscopy

Atomic force microscopy (AFM) was used in this thesis to measure the morphology (topography) of the graphene samples. The AFM uses a cantilever equipped with a sharp tip. The tip interacts with the sample surface via different forces, such as: Van de Waals force, mechanical contact, etc, which cause the deflection or oscillation of the tip. A detection system including laser, photodetector and

piezoelectric crystal is used to detect and measure this interaction during a scan over the sample. The AFM measurements are typically performed in the contact, non-contact or tapping modes. In contact mode operation, the AFM tip is in a mechanical contact with the sample surface inducing a deflection of the cantilever due to the repulsive forces between the tip and the sample. Such deflection is used as a feedback signal to measure the surface topography [144]. The tapping-AFM mode (dynamic scan mode) is used to measure the surface topography of soft samples, such as graphene, to avoid the surface damage that can be caused by using the contact mode. In the tapping mode, the cantilever oscillates with a frequency close to the resonance frequency of the piezoelectric crystal, which depends on the tip and cantilever properties. During the surface scan, the oscillating tip taps the surface of the sample inducing a change of its oscillation amplitude. These changes are used to measure the surface topography. A feedback loop keeps the oscillation amplitude constant by adjusting the distance tip-sample in order to ensure constant tip-surface interaction during the scanning [144, 145]. In this thesis, the graphene surface morphology was investigated using the AFM tapping mode and with a Veeco DI3100 AFM equipment at IFM.

3.3.2 Conductive atomic force microscopy

Conductive atomic force microscopy (CAFM) allows simultaneous measurements of surface topography and the local electrical conductivity map of a surface. The conventional CAFM uses scanning contact-AFM mode to measure surface morphology, in which the local current maps are obtained by applying a DC bias between a conductive tip in contact mode and the sample backside. A low-noise linear current amplifier senses the resulting electrical current through the sample, as illustrated in Fig. 3.5(a). Apart from conductivity maps, the CAFM can also be used to measure local current-voltage ($I - V_{\text{tip}}$) curves at a specific position of the topographic or current map. However, the CAFM is not suitable for investigating graphene sample due to the high shear forces that can damage the graphene sheets. Instead, torsion resonance conductive atomic force microscopy (TR-CAFM) was used in this thesis to investigate the local electrical conductivity of graphene samples. TR-CAFM is based on the same principle as CAFM, but the tip is oscillating in a torsional or twisting mode in close proximity to the sample surface (0.3—3 nm) [146, 147]. Consequently, the current flows from the tip to the graphene sample backside via tunneling when a DC bias is applied. Fig. 3.5 (a) and (b) show typical topographic and current conductivity maps of FL C-face graphene on 4H-SiC(000 $\bar{1}$), respectively.

Figure 3.5: (a) Schematic representation of torsion resonance conductive atomic force microscopy. (b) TR-CAFM topography and (b) the corresponding current map of FL C-face graphene on 4H-SiC(0001). Adapted from **Paper II**.

In this thesis, TR-CAFM measurements were carried out using a Veeco DI3100 AFM with Nanoscope V controller and tunneling atomic force microscopy (TUNA®) application module. Platinum-coated Si tips with a typical apex radius of 10–20 nm were used. From selected positions of the current maps, local $I - V_{\text{tip}}$ measurements were carried out by scanning current spectroscopy where the conductive tip was in direct contact with graphene. The measurement were performed at CNR-Institute for Microelectronics and Microsystems (Italy).

3.3.3 Scanning Kelvin probe microscopy

Scanning Kelvin probe microscopy (SKPM) allows to simultaneously measure the surface topography and to probe the local contact potential difference (CPD) between a conducting tip and a sample. When the tip and sample are not connected, their vacuum level are aligned but their Fermi energies are different (Fig. 3.6(a)). However, when the tip is in close proximity to the sample surface, the work function difference between the tip (ϕ_{tip}) and the sample surface (ϕ_{sample}) cause a tunneling electron current flow. In this case, the Fermi energy of the tip and sample surface line-up and the system reaches an equilibrium state. Therefore, the sample and tip are charged, and have now different vacuum levels. As a result of charging of the tip and the sample, an electrostatic force is created and an apparent V_{CPD} is formed between the tip and sample surface [144], as illustrated in Fig. 3.6(b). V_{CPD} can be compensated when an external bias V_{DC} with the same magnitude and opposite sign to V_{CPD} is applied to the tip, and consequently the force between the tip and the sample will be canceled as seen in Fig. 3.6(c). In this thesis, we have used amplitude modulated SKPM, which is a two-pass technique: i) during the first pass, the surface topography is measured using tapping-AFM mode, ii) the second pass uses the saved surface topography to maintain the tip

Figure 3.6: Schematic diagram of the energy levels of: (a) the AFM-tip and the sample surface in noncontact mode, (b) the AFM-tip and the sample close in the proximity, (c) the AFM tip and the sample in close proximity when V_{DC} bias is applied to nullify V_{CPD} and consequently the electrostatic forces. E_{vacuum} denotes the vacuum level [144].

at certain constant lift height of 10-20 nm and the tip oscillation caused by the piezoelectric crystal is disabled. During the second pass an AC (V_{AC}) and DC (V_{DC}) biases are applied to the tip. The frequency of the AC bias is similar to the resonance frequency of the tip-cantilever (ω). The electrostatic forces between the non-contacting tip and the sample surface are very small [148]. The V_{AC} is used to increase the sensitivity while the V_{DC} is used to nullify the tip-sample forces. The electrostatic forces between tip-sample can be expressed as [144]

$$F(z, t) = -\frac{1}{2}C (\Delta V)^2, \quad (3.3)$$

where

$$V = V_{\text{CPD}} - V_{\text{DC}} + V_{\text{AC}} \sin(\omega t). \quad (3.4)$$

Inserting Eqn. 3.4 into the Eqn. 3.3 gives

$$\begin{aligned} F(z, t) = & -\frac{1}{2} \frac{dC}{dz} (V_{\text{CPD}} - V_{\text{DC}})^2 \\ & - \frac{dC}{dz} (V_{\text{CPD}} - V_{\text{DC}}) \times V_{\text{AC}} \sin(\omega t) \\ & + \frac{1}{4} \frac{dC}{dz} (V_{\text{AC}}^2 \cos(2\omega t) - 1). \end{aligned} \quad (3.5)$$

The V_{CPD} value can be measured by using a feedback loop that nullifies $F(z, t)$ by adjusting V_{DC} . The local work function of graphene W_{G} is related to V_{CPD} by

$$W_{\text{G}} = \phi_{\text{tip}} - eV_{\text{CPD}}, \quad (3.6)$$

Figure 3.7: Schematic representation of the ELMITEC-LEEM III instrument. Adapted from Ref. 149.

where ϕ_{tip} and e are the work function of the tip and the elementary charge, respectively. The absolute local work function of graphene is difficult to quantify due to the change of ϕ_{tip} during the SKPM scans caused by attachment of adsorbates present at graphene surface and the tip, variation of ambient humidity, tip deformation etc. However, one can investigate the local variations of the work function which can be expressed independently of ϕ_{tip} .

In this thesis, SKPM was performed at room temperature and ambient conditions using a Veeco DI 3100 scanning probe microscope equipped with Nanoscope IV controller. Conductive Pt/Ir-coated Si tips (Nanosensors PPP-EFM-20) with resonance frequencies between 45 and 115 kHz was used [148].

3.4 Surface techniques

3.4.1 Low-energy electron microscopy

Low-energy-electron microscopy (LEEM) uses low-energy elastically backscattered electrons for surface imaging. Fig. 3.7 shows a schematic illustration of the used LEEM instrument with a resolution ~ 5 nm used in this thesis. In LEEM measurements, the electrons are emitted by an electron gun with high energy and guided to the sample via the illumination column. A beam separator bends the electrons to the sample through an objective lens. As they approach the sample, the electrons are decelerated by a negative potential held between the electron gun

Figure 3.8: (a) LEEM image of FL C-face graphene on 3C-SiC(111) acquired at an electron energy of 2.8 eV and with a field of view of $30\ \mu\text{m}$, (b) electron reflectivity $I - V$ spectrum extracted from the area indicated by a circle in (a). Adapted from **Paper III**.

and the sample, reaching a low energy in the range of 0–100 eV. The energy of the incident electron can be adjusted by changing the potential (bias voltage) between the gun and the sample. The backscattered electrons are then reaccelerated through the same objective lens and deflected by a beam separator to the imaging column. The objective lenses and the imaging column induce a magnification of the probed area. The LEEM instrument can be used also in a diffraction mode. In this case, the elastically backscattered electrons form low energy diffraction patterns of the sample surface at the backfocal plane of the objective lens. If an illumination aperture is introduced to the objective lens, a selected area-low energy diffraction (micro-LEED) can be performed on the sample [150, 151].

The surface morphology and the crystallographic structure of the sample surface induce a phase contrast in the LEEM image. Electron reflectivity curves ($I - V$) are used to extract the number of graphene layers. Fig 3.8(a) presents a LEEM image of FL C-face graphene on 3C-SiC(111), and the corresponding electron reflectivity spectrum from selected area indicated by the circle in Fig 3.8(b). The electron reflectivity spectra are characterized by the presence of minima that are due to the constructive and destructive interference caused by the electron waves reflected from the different graphene layers [152]. The number of graphene layers can be determined by counting the number of minima in the reflectivity spectrum, e.g., the area indicated by a circle in Fig 3.8(b) exhibits an $I - V$ curve with four minima which correspond to four graphene layers.

Figure 3.9: (a) Schematic representation of a LEED experiment. (b) Ewald sphere construction in two dimensions.

In this thesis, LEEM measurements were performed in ultra-high vacuum (UHV) conditions, in a ELMITEC-LEEM III instrument at the I311 beamline of the MAX-Lab synchrotron radiation facility in Lund (Sweden).

3.4.2 Low-energy electron diffraction

Low-energy electron diffraction (LEED) is a surface technique that can determine the crystallographic structure of a surface. In a LEED experiment, a low energy electron beam, with a wavevector $\vec{k}_i = 2\pi/\lambda_i$, is directed to a sample surface at normal incidence, then the electrons are backscattered: *i*) elastically with a wavevector $\vec{k}_s = 2\pi/\lambda_s$ and *ii*) inelastically (filtered out using energy-filtering grids). The elastically scattered electrons are then accelerated by a potential between the grids and a fluorescent screen. A schematic of a LEED experiment is shown in Fig. 3.9(a). In order to observe a diffraction (interference) pattern, the incident and the reflected beams must obey Laue equation

$$\vec{k}_0 - \vec{k}_1 = \vec{G}_{hk}, \quad (3.7)$$

where $\vec{G}_{hk}$ is the lattice vector of the sample surface. Since we only consider the elastically scattered electrons, then, $|\vec{k}_0| = |\vec{k}_1|$. The Ewald sphere is usually used to visualize the Laue equation (Fig 3.9(b)). This sphere is centered at the origin of the incident vector and represents all the possible vectors having the same magnitude and origin as $\vec{k}_i$. The intersections between the Ewald sphere with the reciprocal lattice rods indicate the different $\vec{k}_s$ vectors that satisfy the Laue equation and the direction of the diffraction spots [153, 154], as sketched in Fig. 3.9. The LEED experiments in this thesis were performed with the LEEM equipment introduced in section 3.4.1.

Figure 3.10: Schematic presentation of the XPS emission process.

3.4.3 X-ray photoelectron spectroscopy and microscopy

X-ray photoelectron spectroscopy (XPS) is a surface technique used to probe the chemical composition of a sample surface. XPS is based on the photoelectric effect. When a soft-X-ray photon with an energy ($E = h\nu$) excites the sample surface, an interaction occurs with an electron (with bonding energy E_B) located in the core-levels of an atom [155]. If the photon energy is higher than E_B , the energy of the photon is transferred to the electron, which leaves the sample surface with a certain kinetic energy

$$E_{\text{kin}} = h\nu - E_B - \phi_s, \quad (3.8)$$

where ϕ_s is the work function of the sample surface. The kinetic energies of the photoexcited electrons are recorded using a spectrometer. The sample and the spectrometer are electrically connected and as a result their Fermi energies are aligned, while their vacuum levels are different (see Fig. 3.10). Consequently, the kinetic energy of the electrons measured at the spectrometer (E_{kin1}) is different and can be expressed as

$$E_{\text{kin1}} = E_{\text{kin}} - (\phi_s - \phi_{\text{spec}}), \quad (3.9)$$

where ϕ_{spec} is the work function of the spectrometer. Replacing Eqn. 3.9 in Eqn. 3.8 gives

$$E_B = h\nu - E_{\text{kin1}} - \phi_{\text{spec}}. \quad (3.10)$$

The bonding energy can be measured if the energy of the photon and the work function of the spectrometer are known parameters. X-ray photoemission electron microscopy (XPEEM) can be used in several modes [156–158]: secondary electron XPEEM, selected area XPS (micro-XPS) and energy filtered XPEEM. Micro-XPS is based on XPS in microscopy mode, performed on a selected area on sample surface (or an area chosen from LEEM image). Energy filtered XPEEM is an imaging mode that uses the electrons emitted from the atomic core levels (XPS), where an energy filter is used to select certain E_{kin} . The image obtained from XPEEM provides information about the lateral chemical composition of sample surface. The XPS and XPEEM measurements reported in this thesis are performed using the synchrotron radiation facility at MAX IV.

3.5 Spectroscopic ellipsometry

Spectroscopic ellipsometry (SE) measures the relative change of the polarization state of an incident beam upon reflection (or transmission) from a sample. The incident electromagnetic wave is polarized perpendicular (*s*) or parallel (*p*) to the plane of incidence (see Fig. 3.11). The wavevector k_{in} of the incoming electromagnetic plane wave and the sample normal define the angle of incidence ϕ_a and the plane of incidence. More precisely, standard SE measures two complex reflectance ratios defined in terms of the ellipsometric angles ψ and Δ . $\tan \psi$ and Δ represent the amplitude of the complex ratio and the relative phase changes of the *s* and *p* components of the electric field vectors, respectively.

3.5.1 Types of ellipsometry

3.5.1.1 Standard spectroscopic ellipsometry

Standard SE is used for optical isotropic materials, where the ellipsometric angles ψ and Δ do not depend on the polarization state of the incident incoming electromagnetic plane waves, in this case ψ and Δ are defined by

$$\rho = \frac{r_p}{r_s} = \tan \psi \exp(i\Delta), \quad (3.11)$$

where r_p and r_s represent the *p*- and *s*-polarized complex reflection coefficients.

3.5.1.2 Generalized spectroscopic ellipsometry

Generalized spectroscopic ellipsometry (GSE) is used for optical anisotropic materials, e.g. SiC, in which the conversion of *p*- into *s*-polarized light or vice versa

Figure 3.11: Schematic representation of a SE measurement in reflection mode: the amplitudes of the electric field of the incoming E_{in} and the reflected E_{out} plane wave can be decomposed into complex field amplitudes E_p^{in} , E_s^{in} , E_p^{out} and E_s^{out} .

occurs. The GSE parameters can be described by using the Jones reflection matrix r or the Mueller matrix formalism.

The Mueller matrix formalism describes the polarization state of the electromagnetic plane waves in terms of intensities. The Stokes parameters of the electromagnetic plane waves are described via the Mueller matrix, before and after sample interaction. In the s - and p -coordinate system, the individual Stokes parameters components can be defined by $S_1 = I_p + I_s$, $S_2 = I_p - I_s$, $S_3 = I_{+45} - I_{-45}$, and $S_4 = I_{\sigma_+} + I_{\sigma_-}$, where I_p , I_s , I_{+45} , I_{-45} , I_{σ_+} , and I_{σ_-} being the intensities for the p -, s -, $+45^\circ$, -45° , right- and left-handed circularly polarized light components, respectively. The Mueller matrix M is the transformation matrix for Stokes vectors [159–161]

$$\mathbf{S}^{out} = M \mathbf{S}^{in}, \quad (3.12)$$

where $\mathbf{S}^{out}$ and $\mathbf{S}^{in}$ denote the Stokes vectors of the electromagnetic plane wave before and after the transformation. The Mueller matrix is a dimensionless, real-valued 4×4 matrix

$$M = \begin{pmatrix} M_{11} & M_{12} & M_{13} & M_{14} \\ M_{21} & M_{22} & M_{23} & M_{24} \\ M_{31} & M_{32} & M_{33} & M_{34} \\ M_{41} & M_{42} & M_{43} & M_{44} \end{pmatrix}. \quad (3.13)$$

Figure 3.12: Optical Hall effect schematic representation: Free charge carriers induce a dielectric polarization following the electric field of an incident electromagnetic field, here for example parallel to the surface. The induced polarization $\mathbf{P}_{\text{FCC}}$ produces $\mathbf{P}_{\text{Hall}}$ due to the Lorentz force, oriented perpendicular to $\mathbf{B}$ and the incident electric field vector. $\mathbf{P}_{\text{FCC}} + \mathbf{P}_{\text{Hall}}$ are the source of the reflected light and contain a small circular polarization component, which provides information on the type of charge carrier, its density, mobility, and effective mass properties. Reprinted with permission from Ref. 164.

The Muller matrix elements can be decomposed in 4 sub-matrices, where the matrix elements of the two off-diagonal-blocks $\begin{bmatrix} M_{13} & M_{14} \\ M_{23} & M_{24} \end{bmatrix}$ and $\begin{bmatrix} M_{31} & M_{32} \\ M_{41} & M_{42} \end{bmatrix}$ are non-zero only if p - s -polarization mode-conversion appears. The matrix elements in the two on-diagonal-blocks $\begin{bmatrix} M_{11} & M_{12} \\ M_{21} & M_{22} \end{bmatrix}$ and $\begin{bmatrix} M_{33} & M_{34} \\ M_{43} & M_{44} \end{bmatrix}$ are typically non-zero and contain information about p - s -polarization mode-conserving processes [159].

3.5.2 Optical Hall effect

3.5.2.1 The Optical Hall effect

The optical Hall effect is the magnetic field-induced birefringence in the free charge carrier response when interacting with an electromagnetic wave (see Fig. 3.12) [162, 163]. When a sample is excited with an incident electromagnetic plane wave with an angular frequency (ω) and a linear polarization parallel to the sample, the free charge carriers oscillate in a straight line in the direction of the time-varying electric field ($\mathbf{P}_{\text{FCC}}$) (see Fig. 3.12).

Figure 3.13: Schematic representation of the cavity-enhanced optical Hall effect principle demonstrated for a III-nitride 2DEG heterostructure as an example. Reprinted with permission from Ref. 165.

In the presence of a static magnetic field ($\mathbf{B}$), the motion of the free charge carrier is dominated by the Lorentz force. The reflected electromagnetic plane wave in this case possesses a small fraction of circularly polarized light and causes polarization-state changes ($\mathbf{P}_{\text{FCC}} + \mathbf{P}_{\text{Hall}}$), which contain information on the type of charge carriers, their density, mobility, and effective mass properties (see Fig. 3.12) [164].

Mueller matrix formalism is employed to measure the changes in the polarization states induced by the OHE and the OHE data $\delta\mathbf{M}$ are defined as the difference between the Muller matrix elements measured under magnetic field $\pm\mathbf{B}$ ($\mathbf{M}_{\pm\mathbf{B}}$) and their corresponding GSE ($\mathbf{M}_0$)

$$\delta\mathbf{M} = \mathbf{M}_{\pm\mathbf{B}} - \mathbf{M}_0. \quad (3.14)$$

3.5.2.2 Cavity-enhanced and in-situ cavity-enhanced THz optical Hall effect

The cavity-enhanced terahertz optical Hall effect (THz-OHE) is a variety of the OHE technique. The cavity-enhanced OHE uses a tunable air gap between the sample and a metallic permanent magnet. The metal surface of the magnet reflects back the unused radiation emitted out the backside of the sample. As a result, the THz-OHE signal is enhanced (see Fig. 3.13). The physical cause of the enhancement is the radiation reflected back in by the magnet surface undergoing further polarization-state changes when passing the magneto-optic birefringent sample constituent [165, 166]. THz OHE allows performing an OHE measurements a room temperature and with relatively low-field permanent magnet.

In this thesis, in-situ THz-OHE is further used to measure the effect of ambient conditions on the free charge carrier parameters of epitaxial graphene. For in-

Figure 3.14: Schematic representation of the in-situ cavity-enhanced THz optical Hall effect. Adapted from **paper VI**.

situ cavity-enhanced OHE, a gas flow cell is mounted in the THz ellipsometer. The sample and the magnet are placed inside a gas flow cell (Fig. 3.14). The cell windows are made from homopolymer polypropylene with a thickness of 0.27 mm. The gas follow system is connected to the humidifier enabling precise control of the relative humidity levels. This technique allows the in-situ and the contactless measurements of the free charge carrier properties upon varying the relative humidity or gasses. In this thesis, the in-situ cavity-enhanced OHE has been used to investigate the effect of air and inert gasses on the free charge carrier parameters of epitaxial graphene.

3.5.3 Optical models

Spectroscopic ellipsometry is an indirect technique, therefore, a optical model is needed in order to extract the physical parameters of interest. The model is constructed using parametrized model dielectric functions (or tensor) (MDF) of each layer component. A regression analysis is performed via Levenberg-Marquardt algorithm allowing the model parameters to be varied until the model-calculated data are matched as close as possible to the experimental data. The mean squared error used to evaluate the difference between experimental and model generated data is minimized to achieve the best-match model.

3.5.3.1 Dielectric tensor

The interaction between an electromagnetic wave and a dielectric medium causes the displacement of bound carriers. In linear anisotropic materials, this displacement ($\mathbf{D}$) is a tensor that can be expressed as

$$\mathbf{D} = \varepsilon_0 \mathbf{E} + \mathbf{P} = \varepsilon_0 \mathbf{E} + \chi \mathbf{E} = \varepsilon_0 (\mathbf{I} + \chi) \mathbf{E} = \varepsilon_0 \boldsymbol{\varepsilon} \mathbf{E}, \quad (3.15)$$

ε_0 , $\mathbf{E}$, $\mathbf{P}$, and χ denote the electric vacuum permittivity, the electric field vector, the electric polarization vector and the electric susceptibility tensor of the medium, respectively. In the Cartesian coordinates (x, y, z) , the dielectric tensor can be deduced from ($\mathbf{D}$) and can be expressed as a function of χ using

$$\boldsymbol{\varepsilon} = \mathbf{I} + \chi = \mathbf{I} + \begin{pmatrix} \chi_{xx} & \chi_{xy} & \chi_{xz} \\ \chi_{yx} & \chi_{yy} & \chi_{yz} \\ \chi_{zx} & \chi_{zy} & \chi_{zz} \end{pmatrix}. \quad (3.16)$$

3.5.3.2 Visible to vacuum ultraviolet optical models

The visible to vacuum ultraviolet (VUV) MDF of epitaxial graphene is described using a sum of Lorentzian and Gaussian oscillators in order to account for the contribution of the critical point (CP) in the DF associated with the Van-Hove singularity at ~ 4.5 eV [167] such as $\varepsilon = 1 + \varepsilon_L + \varepsilon_G$ with

$$\varepsilon_L(E) = \frac{A_L \gamma_L}{E_L^2 - E^2 - i\gamma_L E}, \quad (3.17)$$

$$\Im(\varepsilon_G(E)) = A_G \left[e^{-\left(\frac{E-E_G}{\sigma}\right)^2} + e^{-\left(\frac{E+E_G}{\sigma}\right)^2} \right], \sigma = \frac{\gamma_G}{2\sqrt{\ln(2)}}, \quad (3.18)$$

where A_L , E_L , and γ_L are the amplitude, the center energy and the broadening of the Lorentzian oscillator, respectively and A_G , E_G , and γ_G are the amplitude, the center energy and the broadening of the Gaussian oscillator, respectively.

The optical model used in this thesis to describe the optical response of C-face graphene on 4H-SiC(000 $\bar{1}$) in the visible-VUV spectral range consist of: 4H-SiC substrate/interface layer/graphene/roughness layer (Fig. 3.15). The 4H-SiC substrates MDF are described by using a sum of harmonic oscillators [168]. The SiC-graphene interface is described by using a linear effective medium approximation (EMA) [160] with 50% graphene and 50% SiC. The graphene MDF is given above. The surface roughness is modeled by an EMA with 50% graphene and 50% air ($\varepsilon = 1$).

Figure 3.15: A schematic presentation of the optical model used to model the optical response of graphene in the visible-VUV spectral range. Adapted from **paper I**.

The interface layer accounts for the contributions of: (i) surface roughness and a possible slight off-axis cut of the substrate, (ii) step bunching at the SiC substrate surface, (iii) non-uniform sublimation of silicon from the SiC substrate, and (iv) possible existence of an interface/buffer layer with different structural properties from graphene.

3.5.3.3 Mid-infrared/terahertz optical models

Polar phonons contribution

In the mid-infrared spectral range (MIR) and at terahertz (THz) frequencies, the SiC model dielectric tensor has a contribution from its polar lattice vibrations. 4H-SiC is uniaxial and its dielectric tensor can be expressed as [169]

$$\epsilon = \begin{vmatrix} \epsilon_{\parallel} & 0 & 0 \\ 0 & \epsilon_{\parallel} & 0 \\ 0 & 0 & \epsilon_{\perp} \end{vmatrix}, \quad (3.19)$$

where

$$\epsilon_j = \epsilon_{\infty} \frac{\omega_{LO,j}^2 - \omega^2 - i\omega\gamma_j}{\omega_{TO,j}^2 - \omega^2 - i\omega\gamma_j}, \quad (3.20)$$

with $j = \perp, \parallel$, where ϵ_{∞} , ω_{LO} , γ_{LO} , ω_{TO} , γ_{TO} are the the high-frequency dielectric constant and the frequency and the broadening values of the longitudinal optical (LO) and the transverse optical (TO) phonon modes, respectively. In case of 3C-SiC(111) $\epsilon_{\perp} = \epsilon_{\parallel}$ [169].

Free charge carrier contribution

The dielectric tensor (ϵ) of a material without a magnetic field can be described

$$\epsilon_{B=0} = \mathbf{I} + \chi_{B=0} . \quad (3.21)$$

In the presence of magnetic field, The dielectric tensor can be expressed as [159, 164]

$$\epsilon_{OHE}(\pm \mathbf{B}) = \mathbf{I} + \chi_{B=0} + \chi_{\pm B} . \quad (3.22)$$

where $\chi_{\pm B}$ is the magnetic field induced electric susceptibility which can be expressed as χ_+ and χ_- , for left and right handed circularly polarized light, respectively. In this case, the OHE tensor can be expressed as [159, 163, 164]

$$\epsilon^{MO} = \mathbf{I} + \frac{1}{2} \begin{pmatrix} (\chi_+ + \chi_-) & \mp i(\chi_+ - \chi_-) & 0 \\ \pm i(\chi_+ - \chi_-) & (\chi_+ + \chi_-) & 0 \\ 0 & 0 & 0 \end{pmatrix} . \quad (3.23)$$

The motion of free charge carrier subjected to a magnetic field and electromagnetic radiation ($\mathbf{E}(t) = \mathbf{E} \exp(-i\omega t)$) can be described by Newtonian equation of motion [159, 163, 164]

$$\mathbf{m} \frac{d^2 \mathbf{r}}{dt^2} + \mathbf{m} \gamma \frac{d\mathbf{r}}{dt} + \mathbf{m} \omega_0^2 \mathbf{r} = q \mathbf{E} + q(\mathbf{v} \times \mathbf{B}) , \quad (3.24)$$

where $\mathbf{m}$, q , $\gamma = q/m\mu$, $\mathbf{r}$, $\mathbf{v} = \frac{d\mathbf{r}}{dt}$, ω_0 are the effective mass tensor, the electric charge, the plasma broadening parameter, the spacial coordinate of a free charge carrier, the drifting velocity of a free charge carrier and the resonant frequency of a bound carrier. μ is the mobility tensor. The drifting velocity of the free charge carrier is considered to be harmonic $\mathbf{v}(t) = \mathbf{v} \exp(-i\omega t)$ and the free charge carriers current density is

$$\mathbf{j} = Nq\mathbf{v} , \quad (3.25)$$

where N is the free charge carrier density parameter. Replacing Eqn. 3.25 and $\mathbf{v}(t)$ into the Eqn. 3.24 gives

$$\mathbf{E} = \frac{1}{Nq} \left[i \frac{\mathbf{m}}{q\omega} \left(\omega_0^2 - \omega^2 \mathbf{I} - i\omega\gamma \right) \mathbf{j} + (\mathbf{B} \times \mathbf{j}) \right] . \quad (3.26)$$

The dielectric tensor and the electric field are related to the conductivity tensor σ via $\epsilon = \mathbf{I} + \frac{\sigma}{i\epsilon_0\omega}$ and $\mathbf{E} = \sigma^{-1} \mathbf{j}$, respectively. The contribution χ^D to the dielectric tensor of free charge carriers subject to external magnetic field $\mathbf{B}$ can be expressed as [159, 163, 164]

$$\chi_{ik}^D = \frac{Nq^2}{\epsilon_0} \left[m_{ik}(\omega_{0,ik}^2 - \omega^2 - i\omega\gamma_{ik}) - i\omega\epsilon_{ijk}qB_j \right]^{-1} , \quad (3.27)$$

where ϵ_{ijk} and ϵ_0 are the Levi-Cevita symbol and the dielectric constant, respectively. The eigenfrequency tensor ω_0 of the system for free charge carriers is equal to zero. The contribution of free charge carriers to the dielectric tensor, χ_{ik}^D (Eqn. 3.27), for isotropic effective mass and conductivity tensors, and magnetic fields aligned along the z -axis, can be expressed as [164]

$$\chi^D = \chi_{B=0}^D + \chi_{\pm B}^D, \quad (3.28)$$

where $\chi_{B=0}^D$ is the Drude contribution to the dielectric tensor for $B = 0$

$$\chi_{B=0}^D = -\frac{\omega_p^2}{\omega(\omega + i\gamma)} \mathbf{I} = \chi^D \mathbf{I}, \quad (3.29)$$

and the isotropic plasma frequency is given by $\omega_p = \sqrt{\frac{Nq^2}{m\epsilon_0}}$.

The magneto-optic contribution $\chi_{\pm B}^D$ to the dielectric tensor for isotropic effective masses and conductivities can be expressed through susceptibility functions for right- and left-handed circularly polarized light [159, 163, 164]

$$\chi_{\pm} = \frac{\chi^D}{1 \mp \frac{\omega + i\gamma}{\omega_c}}, \quad (3.30)$$

and where the isotropic cyclotron frequency is $\omega_c = \frac{q|B|}{m}$.

Inter-LL-transitions contribution

In the MIR spectral range and in the presence of a static magnetic field, in addition to the free charge carrier and the polar lattice vibrations, the inter-LL-transition contribution to graphene dielectric tensor has to be considered. The inter-LL-transitions dielectric tensor is expressed using the magneto-optic polarizability functions χ_+ and χ_- for right and left-handed circularly polarized light, respectively [109, 159, 164],

$$\chi_{\pm} = \sum_k \frac{A_{\pm,k}}{\omega_{\pm,k}^2 - \omega^2 - i\omega\gamma_{\pm,k}}, \quad (3.31)$$

where $A_{\pm,k}$, $\omega_{\pm,k}$, and $\gamma_{\pm,k}$ are the amplitude, energy, and broadening parameters of the k_{th} transition, respectively, for (+) right- and (-) left-handed circular polarized light. These parameters depend on the magnetic field. In case of single layer graphene, the polarizabilities for left- and right-handed circularly polarized light are found to be equal ($\chi_+ = \chi_-$), and ϵ^{LL} is diagonal, while for inter-LL-transitions originating from coupled graphene (AB -stacked graphene layers) a $\chi_+ \neq \chi_-$ is determined, and ϵ^{LL} is a full-ranked tensor [109].

3.5.4 Instrumentation

Visible-VUV ellipsometer

Vacuum ultraviolet (VUV) SE measurements were performed in the photon energy range from 3.5 to 9 eV in nitrogen-purged environment using VUV-302 VASE ellipsometer from J. A. Woollam Co., Inc at the University of Nebraska-Lincoln (U.S.A). The ellipsometry measurements were performed at multiple angles of incidence in order to reduce the correlation between parameters.

Mid-infrared OHE instrument

The mid-infrared (MIR) OHE measurements were carried out at the University of Nebraska-Lincoln (U.S.A), using the MIR sub-system of the integrated optical Hall effect instrument. The integrated OHE instrument is based on a rotating analyzer ellipsometers design, allowing the measurement of the upper left 3×3 block of the Mueller matrix (M_{ij} , $i, j = 1, 2, 3$). The MIR sub-system employs a Bruker Vertex V70 FTIR-spectrometer, which covers the spectral range $600 - 8000 \text{ cm}^{-1}$. OHE measurements (with the superconducting magnet) can be carried out at a 45° angle of incidence of the MIR radiation onto the sample. The magnetic field can be varied between 0 and 8 T and is aligned parallel to the reflected beam, resulting in a magnetic field $B_\perp = B/\sqrt{2}$ parallel to the sample normal. The sample temperature can be varied between 1.5 and 300 K [159].

THz-OHE measurements

The THz cavity-enhanced and in-situ cavity-enhanced OHE (100-1040 GHz) measurements were carried out at the THz materials analysis center at Linköping University, using a newly build OHE instrument which has similar characteristic as the one used in the mid-infrared OHE [166, 170]. In this instrument, the measurement can be carried out at different angle of incidences from 28° to 90° . The sample is mounted on a neodymium permanent magnet where the magnetic field is perpendicular to the sample. The measurements were performed at room temperature [170].

Chapter 4

Summary of the results

The results presented in this thesis concern epitaxial graphene grown on the Si- and C-terminated surfaces of 4H-SiC{0001} and the C-terminated surfaces of 3C-SiC(111) substrates using high-temperature sublimation. We focus on the structural and electronic properties of epitaxial graphene and address several critical questions regarding the effects of substrate polytype and polarity on graphene thickness, stacking order, interaction with the substrate, free charge carrier properties, and interface structure. Our results contribute to the current understanding of the nature and limitations of epitaxial graphene on SiC. We also demonstrate novel THz ellipsometry methods for the contactless determination of free charge carrier properties of 2D materials. The major results can be summarized as follows:

C-face few layer graphene

Interface properties of few layer graphene on C-face 4H-SiC(000 $\bar{1}$)

We have reported for the first time the presence of an amorphous SiO_x interface layer for C-face graphene on 4H-SiC(000 $\bar{1}$) and propose a mechanism for its formation. We found that this interface layer forms both on 4H-SiC substrates with (**Paper I**) and without (**Paper II**) surface polishing defects. The thickness of the interface layer was found to increase with aging in ambient conditions. We also have demonstrated that the interface layer causes the formation of non-ideal Schottky contact behavior for electrical transport between monolayer graphene and SiC, which can limit the potential use of thin C-face graphene (1 to 2 monolayers) in electronic applications.

Decoupling and stacking order of C-face graphene on 4H-SiC(000 $\bar{1}$) and 3C-SiC(111)

We have shown that few layer C-face graphene grown on 4H-SiC (paper II) and 3C-SiC (paper III) consists of decoupled graphene sheets that behave effectively as a single layer graphene with linearly dispersing bands (Dirac cones) at the graphene

K point. This fact, together with the high mobility parameters of $23500 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ to $33000 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ (at 1.5 K), indicate good prospects for implementing few layer C-face graphene (> 2 MLs) in future electronic devices. We also found that azimuth rotation between graphene domains may occur laterally not vertically, as generally believed (**Papers II and III**). In the presence of polishing defects on the substrate surface, C-face graphene may grow either as an AB-stacked or a decoupled stack of layers depending on growth temperature (**paper I**). This can provide possible explanation for the different stacking of C-face graphene, previously reported in the literature. Finally, we have established the thickness dependence of the MDF of graphene in the visible-VUV spectral range (**Paper I**).

Origin of Landau level splitting in C-face graphene on 4H-SiC(000 $\bar{1}$)

We have investigated the possible reasons for Landau level splitting and suggest that the most likely origin is the presence of vacancy defect in C-face graphene (**Paper IV**).

Si-face epitaxial monolayer to multiple layers graphene

Contactless access to free charge carriers

We have demonstrated for the first time a contactless THz ellipsometry method for reliable determination of free-charge carrier properties of epitaxial graphene with different number of graphene layers (**Paper V**).

Effect of environmental gases on free-charge carriers in Si-face graphene

A novel method for in-situ contactless characterization of free-charge carrier properties of epitaxial graphene under the influence of different gases is demonstrated for the first time (**paper VI**). The method is based on THz cavity-enhanced optical Hall effect. We have shown that exposure to an inert gas reverses the electron withdrawal caused by air. The doping trend is essentially repeatable when switching between inert gases and air. We found that the mobility variation as a function of sheet density obtained from the different doping cycles shows a linear dependence. This suggests that the dominant scattering mechanism related to ambient doping originates from charged impurities.

Design of an improved crucible and growth of Si-face graphene

We have designed a crucible with improved temperature homogeneity and used it to grow Si-face graphene on 4H-SiC(0001). The effect of buffer layer growth conditions on the thickness homogeneity and free charge carrier properties of Si-face graphene is established. We also demonstrate that at the optimized growth conditions, 99% monolayer graphene with uniform surface morphology, can be grown over area of $15 \times 10 \text{ mm}^2$ (**Paper VII**).

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List of Figures

1.1	Crystallographic structure of graphene	2
1.2	Electronic structure of graphene	3
1.3	Crystallographic and electronic structure <i>AB</i> -stacked bilayer graphene .	4
1.4	Band structure of monolayer graphene, <i>AB</i> -stacked bilayer graphene and twisted bilayer graphene	6
1.5	Crystal and electronic structure of graphite	7
1.6	Phonon dispersions for monolayer graphene	8
1.7	Optical properties and optical transmittance of graphene	9
1.8	Exfoliated graphene and magneto-transport measurements	11
1.9	Landau level energies as a function of magnetic field for monolayer and bilayer graphene	13
1.10	Schematic representation of LL-energies for graphene at a constant magnetic field showing the inter-, intra- and mixture-LL-transitions . .	14
2.1	Schematic summary of techniques used to fabricate large-area graphene	18
2.2	Stacking sequence of bilayer Si-C of the 3C-, 4H and 6H-SiC polytypes .	19
2.3	Schematic illustration of sublimation growth method and equilibrium partial pressures at different temperature for volatile Si species	20
2.4	LEED diffraction patterns showing the Si-face SiC (0001) surface recon- struction upon annealing	21
2.5	LEED diffraction patterns showing the C-face SiC (000 $\bar{1}$) surface recon- struction upon annealing	22
2.6	Comparison of the surface morphology and thickness uniformity of Si-face EG grown in UHV and in argon environment	23
2.7	Comparison of Hall effect mobility versus sheet carrier density Si-face EG and C-face graphene grown in UHV and in argon environment . . .	25
2.8	Thickness uniformity, surface morphology, LEED diffraction patterns, electronic band structure and inter-LL-transition of FL -C-face graphene grown by CCS	26

2.9	Histogram of the growth mode of C-face graphene as a function of growth temperature and argon growth pressure, graphene nucleation on screw dislocation, and morphology of FL C-face graphene in argon .	27
2.10	Inter-Landau-level transition energies in for multilayer C-face graphene grown in argon environment	28
2.11	Comparison of Si/C ratio in the vapor phase as a function of annealing temperature of SiC in C-rich and Si-rich environments. (b) LEEM image of Si-face EG grown by high-temperature sublimation	29
2.12	Temperature distributions inside the growth reactor and the crucible . .	30
2.13	LEEM image, LEED diffraction patterns, micro- and nano-ARPES of FL C-face graphene on SiC(000 $\bar{1}$) by high-temperature sublimation	32
2.14	Comparison uniformity and structural properties of Si-face EG and C-face graphene on 3C-SiC(111)	33
2.15	Reflectivity and AFM topography images of Si-face EG by high-temperature under the best conditions	34
3.1	Raman spectrum of graphene	36
3.2	Effect of electron and hole doping on the G and 2D peak	37
3.3	Raman spectra in the vicinity of 2D peak as a function of graphene number of layers for exfoliated and FL C-face graphene	39
3.4	Schematic representation of the reflectance setup	40
3.5	Schematic representation of torsion resonance conductive atomic force microscopy and example of maps	42
3.6	Schematic representation of scanning Kelvin probe microscopy	43
3.7	Schematic representation of the ELMITEC-LEEM III instrument	44
3.8	LEEM image of FL C-face graphene on 3C-SiC(111) and electron reflectivity spectra	45
3.9	Schematic representation of a LEED system	46
3.10	Schematic representation of the XPS emission process	47
3.11	Schematic representation of spectroscopic ellipsometry	49
3.12	Optical Hall effect schematic representation	50
3.13	Schematic representation of cavity-enhanced optical Hall effect	51
3.14	Schematic representation of in-situ cavity-enhanced THz optical Hall effect	52
3.15	Schematic representation of the optical model used to model the dielectric function of graphene in the visible VUV spectral range	54

Papers

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