

THE EDGE STATES OF EPITAXIAL GRAPHENE ON SIC

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THE EDGE STATES OF EPITAXIAL GRAPHENE ON SIC

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Although the world is full of suffering, it is also full of overcoming of it.

Helen Keller

To my parents

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LIST OF ACRONYMS

E_F Fermi Energy

AC Armchair

aC Amorphous carbon

AF antiferromagnetic

AFM Atomic force microscopy

ALD Atomic layer deposition

ARPES Angle-resolved photoemission spectroscopy

BOE Buffered oxide etch

C-AFM Contact AFM

CCS Confinement Controlled Sublimation

CMP Chemical Mechanical Polishing

CVD Chemical vapor deposition

DOS density of states

EBL E-beam lithography

FM ferromagnetic

FWHM Full-Width at Half-Maximum

GNR Graphene Nanoribbon

h-BN Hexagonal boron nitride

HOPG Highly-oriented pyrolytic graphite

ICP Inductive-coupling plasma

IPA Isopropyl alcohol

LDA Local Density Approximation

LFM Lateral force microscope

MIBK Methyl isobutyl keton

MOSFET Metal-oxide-semiconductor field-effect transistor

NC-AFM Non-contact AFM

rGO reduced graphene oxide

RIE Reactive ion etch

SdH Shubnikov-de Haas

SEM Scanning electron microscopy

STM Scanning Tunneling Microscopy

SiC Silicon carbide

STS Scanning Tunneling Spectroscopy

SWGFR Sidewall graphene nanoribbons

TEM Transmission electron microscopy

TICNN Tianjin International Center for Nanoparticles and Nanosystems

TMA Trimethylaluminum

UHV ultra-high vacuum

WL Weak localization

XPS X-ray photoelectron spectroscopy

ZZ Zigzag

SUMMARY

Exceptional ballistic transport was observed in sidewall epitaxial graphene nanoribbons on SiC (SWGNRs) at room temperature[1]. These objects are of fundamental interest as they provide a direct access to charge neutral graphene with excellent transport properties. In this thesis, beyond sidewalls, we fabricate epitaxial graphene devices on different crystal faces on SiC, including the Si-face and non-polar facets. We introduce novel fabrication process flows that have high temperature annealing and Al_2O_3 as a protective layer to reduce the edge roughness of ribbons and the contamination from resist residue. Then we discuss transport measurement results of graphene nanoribbons on Si-face as well as on non-polar SiC facets, which might reveal a ballistic edge state channel 0_+ with mean free path on the order of μm and another edge state channel 0_- activated by temperature. These special epitaxial graphene edge states are interesting from a fundamental physics standpoint and may find applications in future graphene electronic devices.

CHAPTER 1

INTRODUCTION AND BACKGROUND

Nowadays, integrated circuits exist in all aspects in our life, from a simple Arduino microcontroller to cutting-edge research hardware engineering such as autonomous vehicles and augmented reality/virtual reality headsets. With the development of electronic technology and computer algorithms, there is a need for higher performance and portability of these electronic devices. Therefore, scaling down transistor size has been an imperative for the past several decades following Moore's Law, which predicts that the number of transistors on a microprocessor chip will double every two years or so [2]. To maintain this spectacular trend, industry has explored and successfully applied technology breakthroughs, such as high- κ material to minimize gate dielectric thickness, and metal gates to reduce depletion capacitance [3]. More importantly, the structural evolution of Metal-oxide-semiconductor field-effect transistor (MOSFET) channel has switched from 2D planar to vertical 3D shape, as shown in Figure 1.1. This design increases gate controllability over the channel charge and accommodates more transistor devices under the same length scale [4]. However, this novel structure will finally come to an end in the near future after launching chip products that have minimum feature size 5nm and keeping push to 3nm, and even heading to 2nm node by manufacturing companies like TSMC and Samsung [5]. Therefore developing a new material with appropriate electrical properties to succeed Si is necessary to extend the Moore's Law.

Graphene is the first 2D material ever developed and immediately became one of the most promising candidates for next generation electronic devices[7]. It has outstanding electrical properties with high charge mobility up to $300\,000\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$ [8] and therefore, is suitable for the demand for faster electronics and can address future technology needs. Especially, epitaxial graphene on Silicon carbide (SiC), or epigraphene, is the most promis-

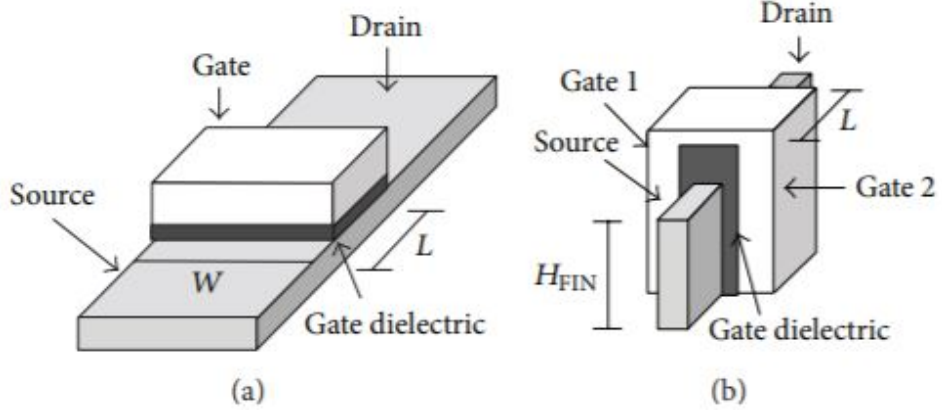


Figure 1.1: Structure Comparison between (a) Planar MOSFET and (b) FinFet. Figure from [6]

ing platform because it doesn't require transfer from one substrate to another. The SiC substrate is a commercially available single crystal wafer that is a well known large bandgap semiconductor. We can directly apply conventional lithography fabrication processes right after graphene growth. In order to utilize such advantages, we need to understand the transport phenomena thoroughly. This thesis explores if the graphene edge states that have exceptional long mean free path on epigraphene sidewall nanoribbons [1] can also exist for graphene grown on different SiC facets.

1.1 Graphene

Graphene is a two-dimensional honeycomb lattice consisting of sp^2 hybridized carbon atoms, and its hexagonal crystal structure is shown in Figure 1.2a. The structure can be considered as a triangular lattice with a basis of two atoms per unit cell. The lattice basis vectors are

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

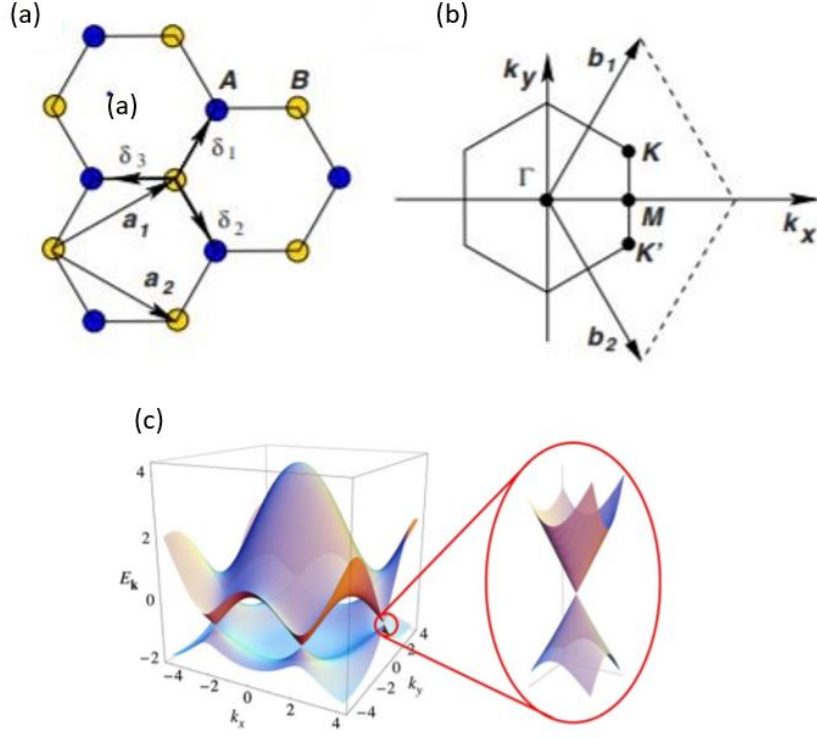


Figure 1.2: Graphene honeycomb lattice structure **a** Two unit vectors a_1 and a_2 **b** Reciprocal space and Brillouin zone. Dirac cones are on points $\mathbf{K}$ and $\mathbf{K}'$. **c** Electronic dispersion in the honeycomb lattice using the tight binding calculation. Zoom-in the Dirac point showing the linear dispersion relation. Figure from [9]

where a is the length between two neighboring carbon atoms and equal to $0.142nm$. Therefore, the reciprocal-lattice vectors are given by

$$\vec{b}_1 = \frac{2\pi}{3a}(1, \sqrt{3}), \vec{b}_2 = \frac{2\pi}{3a}(1, -\sqrt{3}), \quad (1.2)$$

as shown in Figure 1.2**b**. Important physics of graphene is at the corners of the graphene Brillouin zone $\mathbf{K}$ and $\mathbf{K}'$. At these two points, by a simple tight-binding approximation calculation, the energy dispersion relation is given by [10]

$$E_{\pm}(\mathbf{k}) = \pm t \sqrt{3 + 2 \cos \sqrt{3} k_y a + 4 \cos \frac{\sqrt{3}}{2} k_y a \cos \frac{3}{2} k_x a}, \quad (1.3)$$

where t is the nearest-neighbor hopping energy and approximately equal to $2.8eV$. Close to the $\mathbf{K}$ (or $\mathbf{K}'$) point, after fully expanding the Equation 1.3, as $\mathbf{k}=\mathbf{K}+\mathbf{q}$ and $\mathbf{q} \ll \mathbf{K}$, we can get

$$E_{\pm}(\mathbf{q}) \approx \pm v_F |\mathbf{q}|, \quad (1.4)$$

where $\mathbf{q}$ is the momentum measured relatively to the Dirac points and v_F is the Fermi velocity with a value $1 \times 10^6 m/s$. The valence band and the conduction band touch each other at zero energy at the Dirac point, and both bands have a linear dispersion relation, as can be visualized in Figure 1.2c. This striking linear dispersion relation result indicates that the Fermi velocity is a constant that doesn't depend on energy or momentum, which matches the behavior of zero-mass photons. This special property also gives rise of anomalous quantum Hall effect that contains a single Landau Level $n = 0$ and $E_0 = 0$ and plateaus in the Hall resistance at half integer values $R_H = \frac{h}{e^2} \frac{1}{4n+2}$, indicating of a Berry phase of π .

1.1.1 Graphene Production Methods

There are several methods to produce graphene in the literature. Mechanical exfoliation graphene split from Highly-oriented pyrolytic graphite (HOPG) is one of the most common methods to prepare pristine single layer and magic angle twisted bilayer graphene samples in laboratories[11][12]. Exfoliating from graphite using scotch tape can produce small graphene flakes, which are then transferred to an insulating substrate such as Si or boron nitride for further characterization. However, this production method is not industry scalable due to small sizes, low efficiency, time consuming and uncontrolled interface. Chemical vapor deposition (CVD) graphene can produce wafer scale and multigrain monolayer graphene samples. The CVD furnace is filled with gas CH_4 flown on a heated catalytic substrate (e.g Cu or Ni) and carbon atoms from the gas decomposition will stick on the substrate and merge to form large area graphene [13]. However, this method needs to transfer to an insulating substrate to fabricate electrical devices. This transfer process introduces defects and contamination that degrades quality of graphene[14]. Also, reduced

graphene oxide (rGO) has also been tested for scalable production [15][16] but it exhibits large density of defects and is not suitable for nanoelectronics applications[17].

1.1.2 Epigraphene Growth on SiC

SiC is a large bandgap semiconductor material and has been widely used in high power electronics due to its high-breakdown voltage, high-operating electric field, high-operating temperature[18]. SiC polytypes used for epigraphene growth in this thesis are hexagonal 4H and 6H-SiC (with bandgap of 3.3 eV and 3.0 eV respectively), which have different stacking sequences of Si and C atoms, shown in Figure 1.3. SiC wafers can be made either semi-insulating by pinning the Fermi level in the gap or conductive by nitrogen doping the substrates.

High purity single crystal SiC wafers are commercially available from companies such as Wolfspeed and II-VI Incorporated. Optically polished commercial wafer surface is not smooth enough to perform epigraphene growth and hence, hydrogen etching is required to flatten the surface. However, Chemical Mechanical Polishing (CMP) SiC wafers surface have sub-nm roughness so that epigraphene can be grown directly. It was also shown that epigraphene grown on hydrogen etched SiC has larger overall resistance and resistance anisotropy between parallel and perpendicular orientation relative to step edge direction, compared with graphene on Ar annealed SiC substrates [20].

Epigraphene growth results depend on the SiC crystal facets. For both 4H and 6H-SiC wafers, there are two polar facets: Si terminated face or Si-face, ie. SiC (0001), and C terminated face or C-face, ie. SiC (000 $\bar{1}$). Growth results on these two facets differ a lot, as shown in Figure 1.4.

Si-face epigraphene Growth

On the Si-face, the first carbon layer bonds to the substrate, which alters the electronics properties. It is called buffer layer due to its dissimilar properties to graphene. It is non-

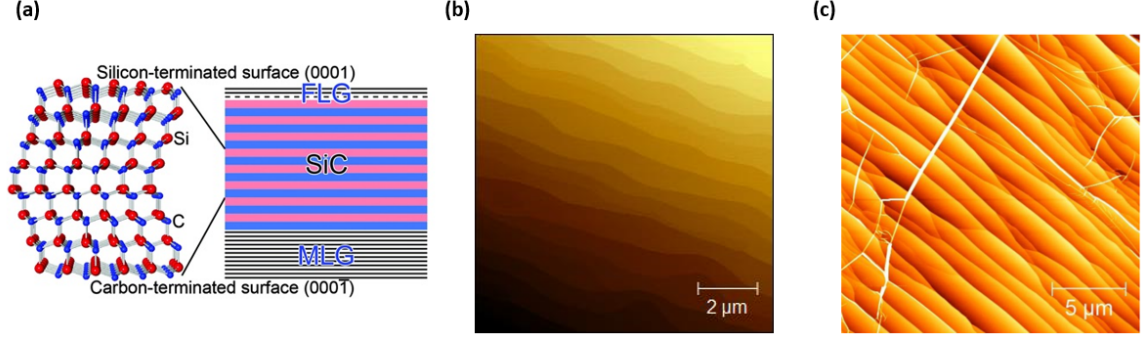


Figure 1.4: (a) Schematic diagrams of epigraphene growth on two different polar facets show distinctive structural properties. (b) Topography of epigraphene on Si-face. (c) Topography of epigraphene on C-face. Figure from [21].

which has much less substrate interaction. Therefore, it exhibits much more conductive behavior than the buffer layer and dominates the electrical transport. This graphene layer is negatively charged with carrier density around 10^{13}cm^{-2} measured at room temperature in UHV[29]. The origin of the doping was interpreted to be due to surface states at the SiC interface and to the buffer layer states [30]. In contrast, when there is no buffer layer (for example buffer layer has been converted to a graphene layer by intercalation), the graphene layer is p-doped, which is due to the SiC spontaneous polarization[30]. The graphene layer, with or without the buffer layer underneath, exhibits the anomalous quantum Hall effect with a Berry's phase of π , indicating a monolayer graphene transport system instead of bilayer graphene[31]. This demonstrates that the buffer layer is indeed not conducting. Further growth leads to more layers and their stacking order is Bernal[32].

Monolayer Si-face graphene growth is relatively uniform on atomically flat terraces, as shown in Figure 1.4b. Steps heights are around 0.5nm to 2nm and there might be bilayer patches starting at the steps edges[33][24]. Monolayer and bilayer regions are easily distinguished with Atomic force microscopy (AFM) and Raman spectroscopy, as discussed in Chapter 2. Si-face epigraphene has been used to develop as quantum resistance standard devices [31] and high frequency transistors[34].

C-face epigraphene Growth

On the carbon-terminated face of SiC, epigraphene shows different structural and electrical properties than Si-face. C-face graphene growth doesn't have a non-conducting buffer layer in contrast to Si-face graphene, and conventional growth method usually yields five to ten layers of graphene, as can be seen in Figure 1.4a. The main specificity of C-face graphene is the electronic decoupling between the layers. Multilayer graphene on the C-face has a rotational stacking preserving the A and B sub-lattice symmetry, which means about 30° rotation between layers so that each layer behaves as if it were an isolated graphene layer[35][36]. This preserves the electrical properties of graphene: high mobility as high as $50\,000\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$ [37][38] and charge neutrality[39]. Atomic force microscopy (AFM) image shown in Figure 1.4c shows the typical pleat structure of the C-face epigraphene layer. Pleats, $5 - 10\text{ nm}$ high, are typical on C-face graphene. They result from the different thermal expansion of the silicon carbide and graphene and the very weak coupling of the graphene to the substrate[37]. Monolayer C-face graphene shows strong potential for RF transistors with reports of a maximum oscillation frequency of 70 GHz [40].

Non-polar epigraphene

We also grow graphene on other SiC facets, with a similar facet orientation as sidewall graphene nanoribbon, which will be discussed later. As shown in Figure 1.5a, the $\text{SiC}(1\bar{1}0n)$ ($n > 1$) facet is referred to as the Armchair (AC) facet while the $\text{SiC}(11\bar{2}n)$ the Zigzag (ZZ) facet. In this thesis, we use the same facet as sidewall graphene nanoribbon which has a facet angle around 37° corresponding to $n \approx 5$ on the AC facet. Bare non-polar SiC substrates were cut and polished from commercially electronics grade 4H-SiC by Tianjin International Center for Nanoparticles and Nanosystems (TICNN). Large 2" wafers has been were produced as shown in Figure 1.5.

Graphene growth uses the Confinement Controlled Sublimation (CCS) method[37]. Growth results on non-polar facets are very different from polar facets. With very carefully

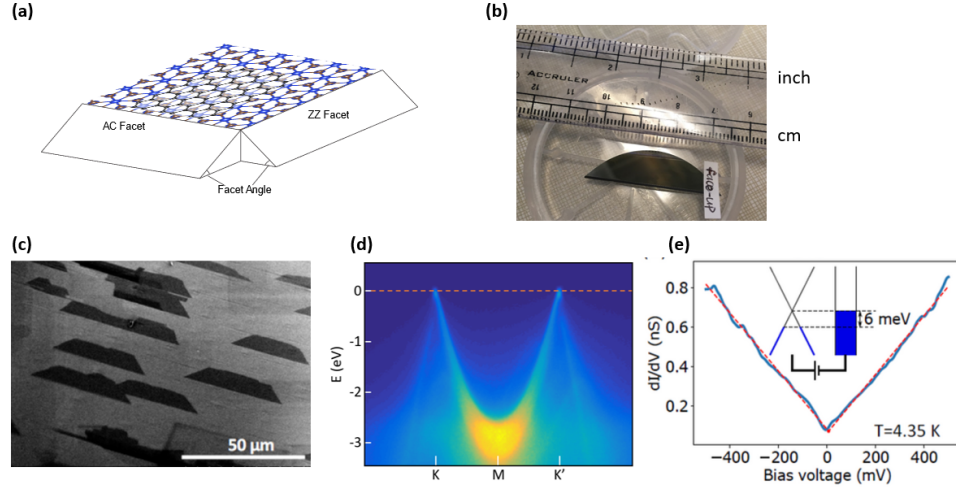


Figure 1.5: Graphene on SiC non-polar facet **(a)** Schematic diagram of non-polar facet relative to Si-face **(b)** Photo of 4H-SiC $1\bar{1}15$ non-polar facet wafer, cut and polish by TICNN **(c)** SEM image of a starting phase of graphene growth on 4H-SiC AC facet **(d)** ARPES image of the graphene on the 4H-SiC AC facet, performed by V. Prudkovskiy and C. Berger in collaboration with A. Tejeda and the Soleil Synchrotron Cassiopee beam. The red line shows the Fermi level. The graphene is indeed charge neutral. **(e)** The STS result indicates a charge neutral graphene film, performed by D. Wander and A. De Cecco in the group of C. Winkelmann, CNRS-Grenoble.

confined growth conditions, we can obtain patches of single layer graphene up to several tens of μm s, as seen in the SEM image in Figure 1.5c. These trapezoidal patches gradually emerge into a continuous film as growth time increases. Angle-resolved photoemission spectroscopy (ARPES) measurement shown in Figure 1.5d indicates iconic graphene Dirac cones, verifying the epitaxial alignment of the graphene with the SiC crystal lattice [41]. The Fermi level E_F is at the Dirac point, demonstrating that this graphene is intrinsically charge neutral as confirmed in Scanning Tunneling Spectroscopy (STS) in Figure 1.5e. More details about growth and characterization of epigraphene on non-polar facets can be found in [42].

1.2 Graphene Nanoribbons

Graphene lacks a bandgap at the Fermi level, which is a defining concept for semiconductor materials and essential for digital electronics. One common approach is to create a bandgap through confinement, such as Graphene Nanoribbon (GNR)[43].

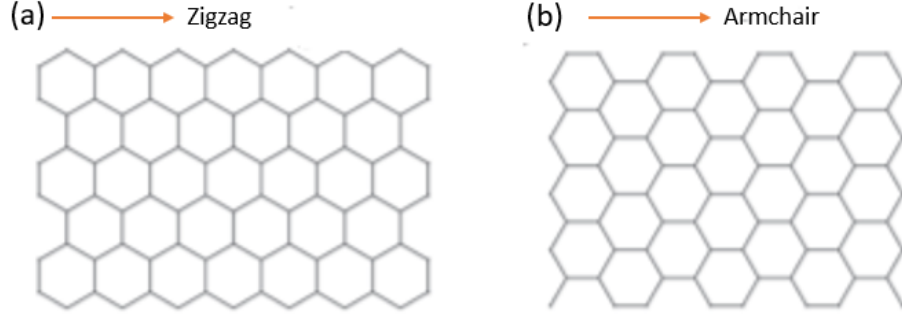


Figure 1.6: Schematic representation of (a) zigzag graphene nanoribbon and (b) armchair graphene nanoribbon.

GNRs are quasi one-dimensional graphene with lateral quantum confinement. This confinement causes quantization of transverse mode of electron momentum, which leads to one-dimensional sub-bands and bandgap opening for certain edge orientations. For a graphene ribbon with width W , the boundaries impose a constraint on the transverse motion so that k_y is quantized $k_y = \frac{n\pi}{W}$ with n is an integer. Therefore the n th electronic subband energy is roughly given by (ignoring the edge boundary conditions)

$$E_n = \hbar v_0 \sqrt{(k_x^2 + k_y^2)} = \sqrt{(E_x^2 + n^2 \Delta E^2)} \quad (1.5)$$

where ΔE is the spacing between adjacent subbands and equal to $\pi \hbar v_0 / W \sim (2\text{eV} \cdot \text{nm}) / W$ and W is in units of nanometer. Two main geometries of GNRs can be distinguished, the AC and the ZZ type, shown in Figure 1.6. The AC edge has alternating edge atoms from both sublattices. In contrast, edge atoms of the ZZ edge are from the same sublattice. Other directions of nanoribbons have a mixture of AC and ZZ edges. These are called chiral graphene nanoribbons. The electronic properties of these two types of ribbons

are very different and therefore, a brief review is presented here.

Depending on the value of m , the AC edges GNRs can be classified into three categories, namely, $m = 3p$, $3p + 1$ and $3p + 2$ (p is a positive integer) with different electronic properties. The ribbons with case $m = 3p + 2$ don't have a bandgap and shows metallic behavior, while the other two cases show semiconducting behavior within the tight-binding model calculation, shown in Figure 1.7a. On the other hand, the first-principles calculations within the Local Density Approximation (LDA) for very narrow ribbons show semiconducting behavior with a direct band gap for all the three types of AC-GNRs[44]. The energy band gap is roughly inversely proportional to the ribbon width, as displayed in Figure 1.7b,c. Nevertheless, the AC-GNRs with $m = 3p + 2$ show the smallest gap in all approximations, compared to the other two cases. The discrepancy between tight-binding model and first principle calculations can be explained by the different treatment of edge passivation by foreign atoms such as hydrogen[44].

The periodic ZZ-GNRs, unlike AC-GNRs, show interesting localized electronic states at the edges, known as edge states. These edge states are extended along the zigzag edges and decay exponentially towards the ribbon centre[45][46][47]. ZZ-GNRs exhibit interesting electronic properties with possibilities of fine tuning their electronic structure and band gap by structural or chemical modifications. In the case of the nonmagnetic approximation, the valence band and the conduction band converges and touch exactly at the E_F , as shown in Figure 1.8. This flat band remains degenerate and does not have dispersion relation up to the Brillouin zone boundary. The flat band structure results in a high density of states at E_F that doesn't exist in 2D graphene sheet, which leads to a potential instability [48][49]. This instability of nonmagnetic ZZ-GNRs can be resolved by electronic spin polarization [47]. As a result, the ground state of a ZZ-GNR has a parallel spin alignment localized along each edge but has opposite direction between the 2 edges. Therefore it is called an antiferromagnetic (AF) ZZ-GNR and its spin density is plotted in Figure 1.9a. The nearest neighbor shows an opposite spin alignment and the spin density gradually decays towards

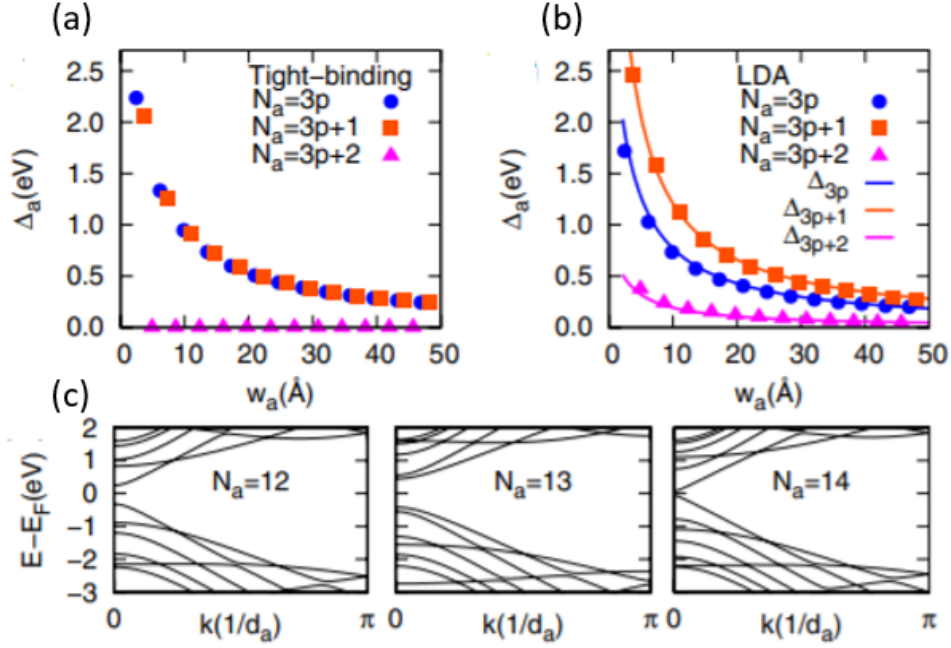


Figure 1.7: AC graphene nanoribbon energy band gap versus width in (a) tight-binding calculation (b) first principle calculation. (c) First-principles band structures of AC graphene nanoribbon with $N_a=12, 13$, and 14 , respectively. Figure from [44].

the center of the ribbon.

The AF ZZ-GNRs has the previous flat bands split up and exhibit a direct band gap Δ_z^0 at $k = 2\pi/3$, which varies inversely with the ribbon width, as can be seen in Figure 1.9b,c.

Finally we need to consider the ferromagnetic (FM) ZZ-GNR case. The undoped ZZ-GNRs with hydrogen-passivated edges show that the AF ground state is more stable than the FM state by a small margin, of the order of meV[51]. Therefore, the electron-electron interactions can overcome such a small gap to make the ground state of ZZ-GNRs ferromagnetic[52]. The corresponding spin density is shown in Figure 1.9d. The spins at the two edges of the ribbon are aligned in parallel. But the nearest neighbor still exhibits the opposite spin alignment. Like in the case in AF ZZ-GNRs, FM ZZ-GNR spin density decays away from the edges with a smaller penetration depth[50]. The band structure of a FM ZZ-GNR can be found in Figure 1.9e, along with local density of states. No band gap is

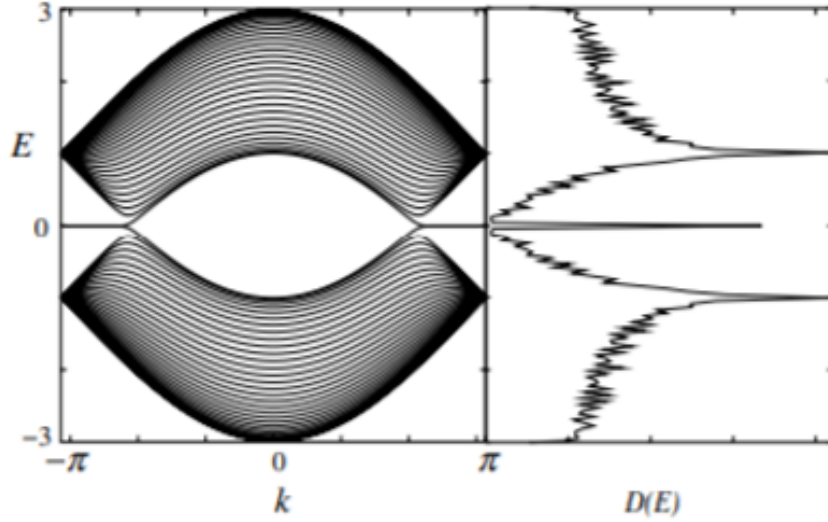


Figure 1.8: ZZ graphene nanoribbon energy band diagram and density of states from tight-binding calculation. Excerpt from [45].

presented in this case and therefore, the ribbon is metallic.

For ZZ-GNRs, magnetic effects on the bulk bands are very small[49]. With increasing ribbon width, the bulk bands approach each other and finally recover the conventional graphene 2D band structure. But the edge magnetism is not affected and remains spin-polarized even for a wide ribbon.

The band structure and edge states shown in Figure 1.9 are generic for all graphene ribbons with chiral edges, excluding only perfect armchair ribbons, as predicted by Akhmerov et.al. [53]. Also, edge states in chiral graphene nanoribbons have been observed in STM experiments [54][55]. Therefore, the band structure and density of states shown in Figure 1.8 are generic and good starting points for understanding the electrical transport behaviors in this thesis.

Several methods have been developed to fabricate graphene nanoribbon devices. Those can be realized by lithographically etching from planar graphene using e-beam resist[56] or nanowires as hard masks [57]. However, edge roughness can significantly affect electric transport. In particular, graphene nanoribbons etched from exfoliated graphene show

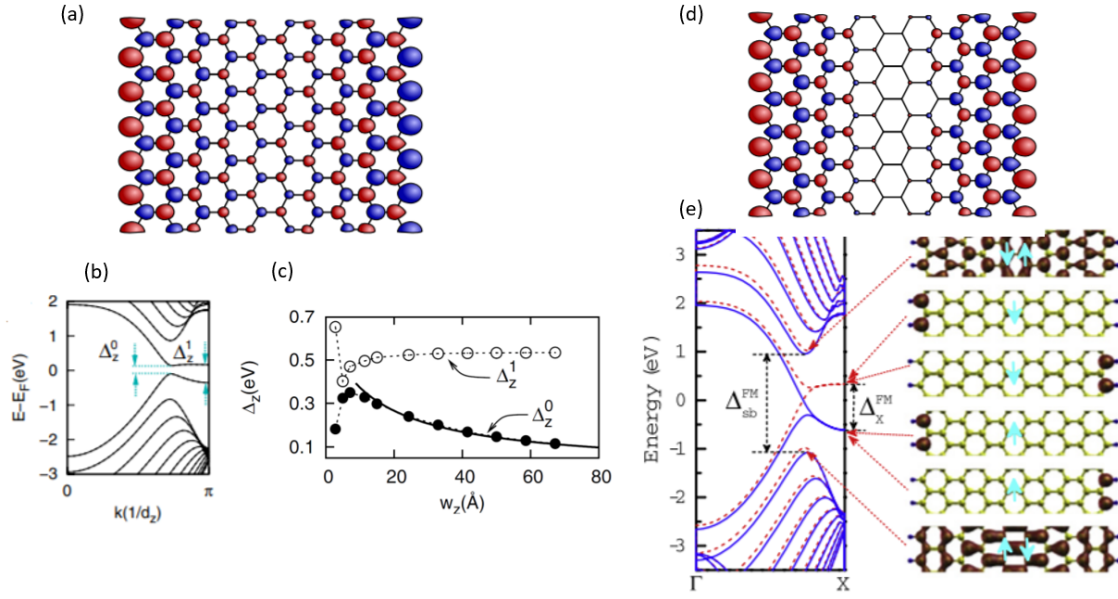


Figure 1.9: **(a)** Spin density plot of AF ZZ-GNR. Red (blue) color indicates spin up(down). Size of the circles is proportional to the spin density. **(b)** Energy band diagram of AF ZZ-GNR. **(c)** The variation of Δ_z^0 and Δ_z^1 with respect to ribbon width. Excerpt from [44]. **(d)** Spin density plot of FM ZZ-GNR **(e)** Band structure of FM ZZ-GN, where the local density of states of various states are shown alongside and the spin polarizations of these states are indicated by arrows. Figure from [50].

localized states, induced by the edge disorder affecting the conductive paths along the ribbons[58][59][60]. The charge transport is dominated by Arrhenius thermal activation at high temperature, while at low temperature, variable range hopping is observed between localized states, shown in Figure 1.10a[58]. Avouris et al. also carried out similar experiments to fabricate graphene nanoribbon devices with edge roughness mostly around 1–3nm and widths down to 10–15nm[61]. Conductance quantization at low temperature shown in Figure 1.10b were interpreted by subband formation in graphene nanoribbon. By employing silicon nanowires as etching masks in the lithography process, graphene nanoribbon can be produced down to 6nm. An 8nm graphene nanoribbon field-effect transistor showed an on/off ratio of about 160, which is several order of magnitude smaller than conventional lithography[57]. Other lithographic methods like Scanning Tunneling Microscopy (STM) lithography were also successfully used to produce GNRs with AC orientation. Neverthe-

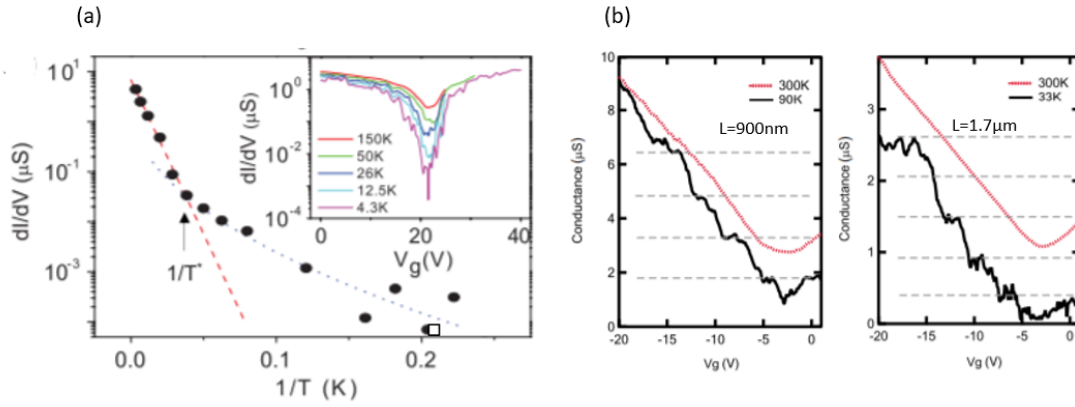


Figure 1.10: (a) Temperature dependence of the minimum conductance of graphene nanoribbon. The dashed and dotted lines are a fit to Arrhenius activated behavior and variable range hopping, respectively. Inset: dI/dV versus V_g at several temperatures. Figure from [58]. (b) Conductance measured as a function of gate voltage for 30-nm-wide graphene nanoribbon devices with different GNR lengths are 900 nm and $1.7\mu\text{m}$. Excerpt from [61].

less, the widths of GNRs obtained by this technique were scattered over a broad range, and most of the edges were extremely rough. Hence, fabricated devices showed unpredictable electrical transport performance.

”Bottom-up” techniques use surface-assisted coupling of precursor polymer to produce atomically precise graphene nanoribbons. Ribbon widths can be narrowed down to six atoms wide with precise edge termination [62]. This precise control of synthesis has allowed exploration of energy bandgap or topological band engineering through graphene nanoribbon heterojunctions structure or other outside source doping [63][64][65][66]. However, this method requires specific catalytic substrates (mostly gold) and subsequently transfer to other substrate for electric measurements. Field-effect transistors fabricated by bottom-up synthesis of graphene nanoribbons are heavily influenced by the environment. Large random conductance variations and hysteresis are observed [67].

1.2.1 Sidewall Graphene Nanoribbons

Unlike graphene nanoribbons mentioned in the previous section, sidewall graphene nanoribbons can be produced with a scalable process and their transport properties were shown not to be dominated by disorder[68][69]. In the CCS method, epigraphene growth is much faster on certain facets of SiC. Such facets can be produced as the sidewalls of trenches etched on SiC.

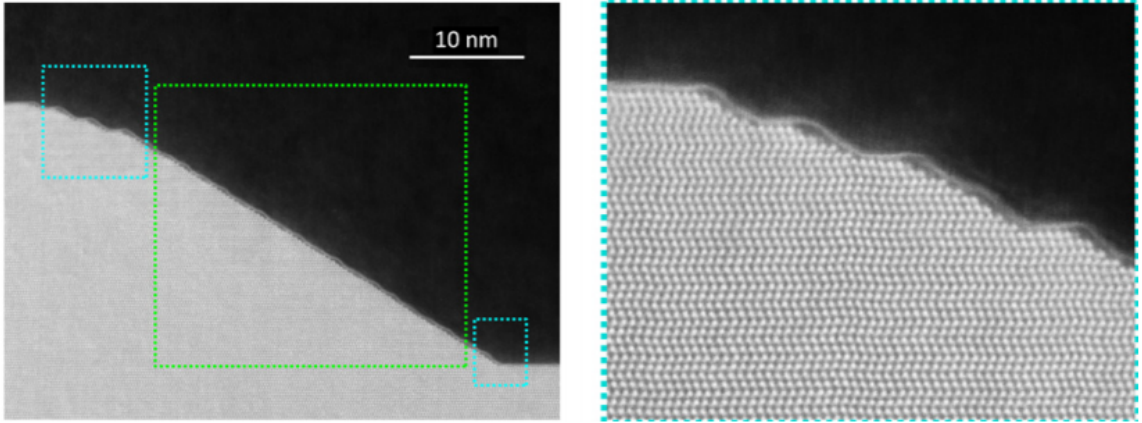


Figure 1.11: TEM image of SWGNR. Reprinted from [70].

Transmission electron microscopy (TEM) images of Sidewall graphene nanoribbons (SWGNR) shown in Figure 1.11 confirm that graphene grown on the sidewall can indeed be monolayer and freely stands on the sidewall that is stabilized at an angle 27° from the Si-face (horizontal in Figure 1.11)[70]. At the top and bottom of the steps, mini steps forms and the SWGNR merges into the buffer layer that extends on the plateaus. The buffer layer is strongly bonded to the substrate and was shown to have low electrical conductance compared to graphene[68]. Therefore the measurement of conductance is from graphene layer only.

SWGNR were first reported to have ballistic transport channels by Ming Ruan[69], and was continued by J.Baringhaus, who measured conductance with respect to ribbon length, as shown in Figure 1.12a[1]. With the help of built-in scanning electron microscopy, four nanoscopically sharp tungsten probes were placed directly on the SWGNR to avoid any

contamination from fabrication process[1]. All the linear fits of resistance versus length extrapolate to h/e^2 at $L=0$, implying a single channel showing spin and valley lifting of degeneracy. All ribbons have very small resistance versus length dependence, which indicates an exceptionally long mean free path of 4.2, 28, 16, 58 μm and greater than 100 μm for ribbon No.1-5, respectively (see section 1.2.2 for details). Those values are much larger than bulk subbands values on the order of a few nanometers.

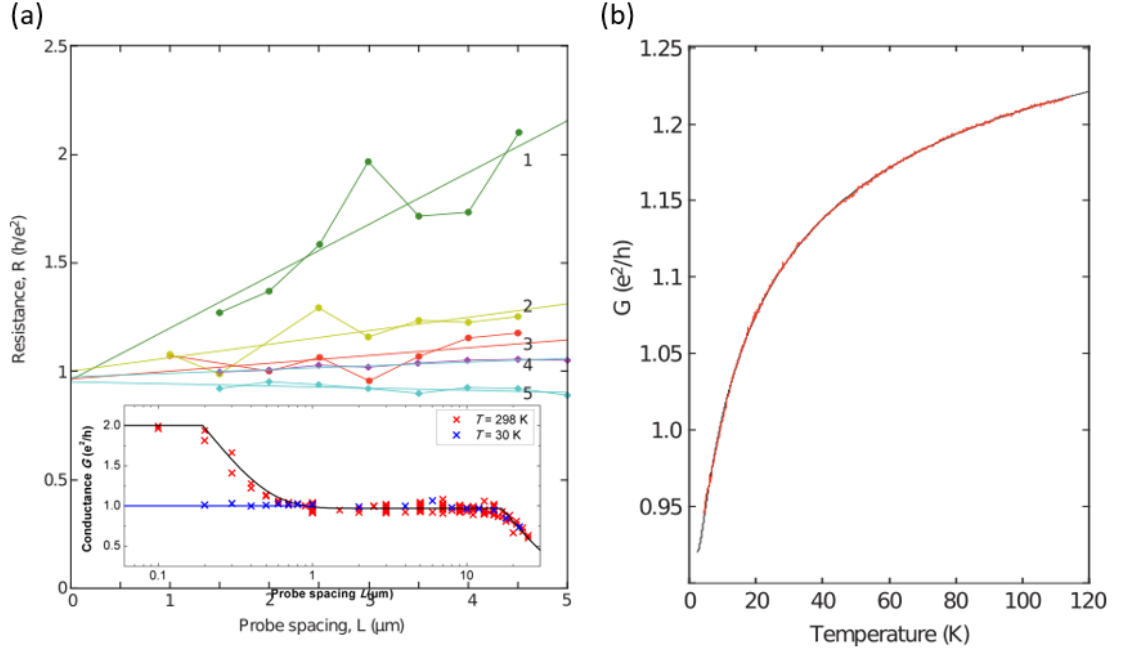


Figure 1.12: **(a)** Resistance versus probe spacing L for several ribbons. Linear fits extrapolate to h/e^2 . Inset: Non-linear conductance decrease at critical lengths. At a higher temperature, a second mode involves and contribute $1G_0$ below $1\mu\text{m}$ distance. **(b)** Conductance of a fixed-geometry SWGNR with respect to temperature. Figures from[1].

Figure 1.12a inset shows the length dependent conductance versus length measurements at two different temperatures. We can clearly see that there are two plateaus of conductance at room temperature, with values at G_0 and $2G_0$. The G_0 conductance plateau extends over some distance indicates scattering-free transport up to $20\mu\text{m}$. At short length scale less than $1\mu\text{m}$, another conduction channel activates and adds $1G_0$ to the conduction. The transition between these plateaus is not discrete, but has an exponential decay at room temperature. At low temperature, the conductance stays at $1G_0$. This reveals that one chan-

nel (0_-) is activated at room temperature but not at low temperature and dies out for length above $1\mu m$, while the another channel (0_+) can survive for a much longer length, up to $20\mu m$.

To confirm this temperature dependent transport channel, the four-points conductance versus temperature on a fix-geometry SWGNR of length $\approx 1\mu m$ is shown in Figure 1.12b. The data can be fitted with equation

$$G(T) = \alpha \frac{e^2}{h} \left[1 + 0.5 \exp \left\{ - \left(\frac{T^*}{T_{el} - T_0} \right)^{1/2} \right\} \right] \quad (1.6)$$

with fitting parameters $\alpha = 0.922$, $T^* = 21.5K$, and $T_0 = 2.2K$. The equation shows that one ballistic channel (0_+) of conductance $G = 1G_0$ that is temperature independent and another channel (0_-) contributes a thermal activated conductance. The characteristic activation temperature T^* is inversely dependent with the ribbon length, which implies this thermal activated channel is related with longitudinal mode (see Equation 1.5)[1].

Also, since Si-face of SiC substrate shows step bunching at high temperature, we can also grow graphene on these natural nanofacets (10-20 nm high) and build devices on selected ones.

One way to produce sidewalls is to anneal bare SiC wafers in an Ar atmosphere at high temperature, using the natural step bunching of SiC[71][69]. For that, six SiC wafers are stacked face-to-face together in a closed graphite Si-saturated crucible and the temperature is raised to $1700^\circ C$ in an Ar atmosphere. This stacking and Ar atmosphere suppresses Si sublimation and prevents any graphene growth during this annealing process. After annealing, the sample is placed in the graphite crucible with a small hole and heated to $1500^\circ C$ for graphene growth, similar to samples etched with trenches.

We also fabricated SWGNR devices with Amorphous carbon (aC) pads that are high temperature compatible material that allows us to further anneal to clean up the samples. Amorphous carbon pads are photolithography patterned and lift-off from the pre-annealed

chip and the SWGNRs are grown on natural steps, mentioned in the previous paragraph. Then the sample is annealed at 1000°C to clean up the surface and decrease the resistance of aC. Then we placed the sample in a probe station under vacuum. Lastly, the sample is annealed up to 260°C in vacuum and cooled back down to room temperature. A resistance versus length plot is shown in Figure 1.13, and each data point consists of a single device. The measurement shown in Figure 2.5 is the longest ballistic transport length (R

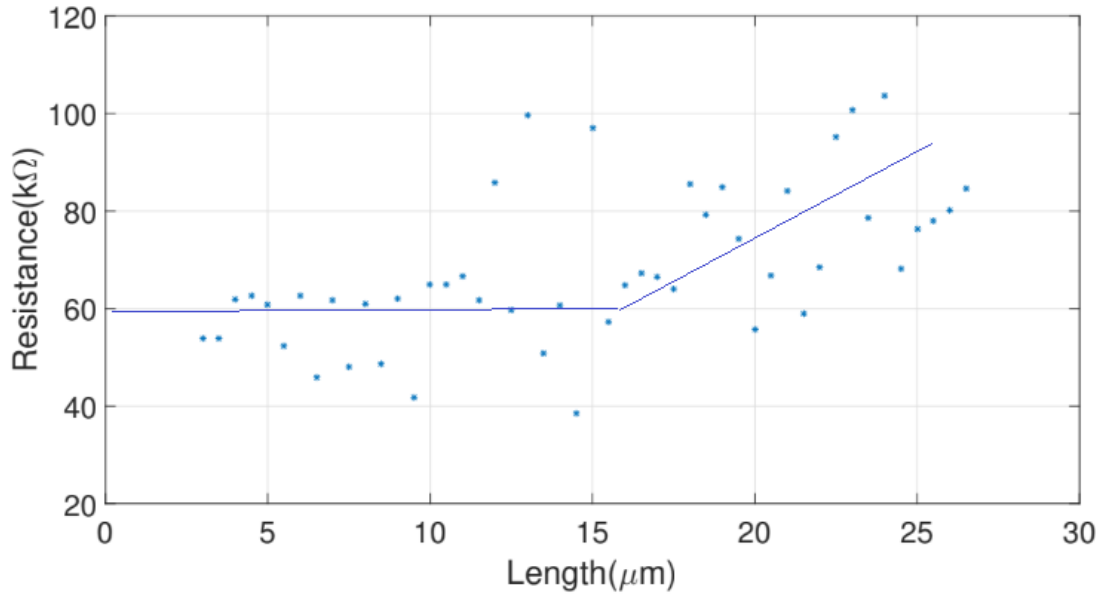


Figure 1.13: Two points resistance of SWGNR versus length, measured at room temperature in vacuum condition, figure from [72]

independent of length up to $\approx 10\mu\text{m}$) obtained in this study. The high resistance value can be accounted for the aC lead resistance, so that y is measurement is compatible with the one channel transport measurement in [1][69]. Samples with the post growth processing approach have also been measured, with mean free path around $2 - 3\mu\text{m}$. We attribute the improved mean free path for various reasons: clean processing, measuring in vacuum conditions, avoiding an etching step which decreases the contamination from organic e-beam resist, and also the improved ribbon growth methods that help confining the graphene to the sidewalls and giving narrow ribbon geometries. More detailed explanation and analysis of the contact resistance and transport measurement can be found in D. Deniz's thesis [72].

1.2.2 Ballistic Transport in Conductors

In this subsection, we are going through some basic concepts about ballistic transport. Before the quantum mechanics was developed, electron motion in a diffusive conductor was well described by the Drude model, which shows a linear relation between conductance and sample width over length ratio, with equation

$$G = \sigma \frac{W}{L} \quad (1.7)$$

where G is conductance, and σ is conductivity and equal to $n|e|\mu$ while n , e and μ are carrier density, electric charge and mobility, respectively[73]. The Drude model of electric conduction can explain most of the electrical behaviors of materials and leads to the classic Ohm's Law. However, in the experiments with high purity nanowires, conductance is quantized in units of $\frac{e^2}{h} = \frac{1}{25.8k\Omega}$. The resistance approaches $25.8 k\Omega/N$, rather than zero, where N is the number of conducting channels. This unusual resistance relates to the fermionic nature of electrons[74].

The Landauer formula captures the basic features

$$G = \frac{2e^2}{h} \sum_{n=1}^M T_n, \quad (1.8)$$

where M is the total number of channels inside the conductor and each individual channel transmission probability is T_n [75]. If there are N incoherent scattering centers within the conductors, each having a transmission coefficient T_N , then the total transmission probability can be expressed as

$$T(N) = \frac{T_N}{N(1 - T_N) + T_N} = \frac{\lambda_o}{\lambda_o + L} \quad (1.9)$$

where $\lambda_o = \frac{T_N}{(1-T_N)\frac{N}{L}}$ [74]. Then we can combine Equation 1.8 and Equation 1.9 and obtain

$$R(L) = \frac{h}{2e^2 M} \frac{1}{T} = \frac{h}{2e^2 M} \left(1 + \frac{L}{\lambda_o}\right) \quad (1.10)$$

This relation reveals that the resistance of a ballistic conductor with additional scatters is expected to have a linear increase with length that extrapolates to $\frac{h}{2e^2 M}$ at $L = 0$ [74].

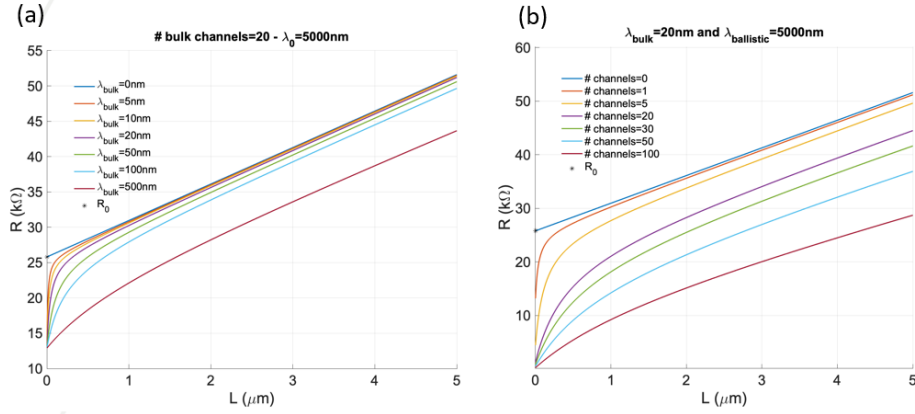


Figure 1.14: Simulation of resistance versus length with one ballistic channel with many diffusive channels. (a) A ballistic channel with mean free path $5\mu m$ along with 20 diffusive channels with various mean free path. (b) A ballistic channel with mean free path $5\mu m$ along with various number of diffusive channels with mean free path $5nm$.

When multiple channels are in parallel within a sample, the resistance of the conductor can be rewritten as

$$R = \frac{h}{e^2} \left(\sum_i \frac{\lambda_i}{\lambda_i + L} \right)^{-1}, \quad (1.11)$$

where λ_i is the mean free path in each channel. Assuming one of these channels has a relatively longer mean free path than the others, then the transport is dominated by this channel in the long length regime. Figure 1.14 a shows a simulation of resistance versus length for 21 channels in parallel simulating conductance of a ballistic state and 20 diffusive states. The ballistic channel has mean free path $\lambda_0 = 5\mu m$ and 20 diffusive channels has various mean free path from 0 to $500nm$. The resistance vs length profile shows that at very short length, diffusive channels play an important role. At long length scales, the slope of the resistance versus length plot with multiple diffusive channels is very close to the slope of a single ballistic channel. Moreover, the intercept at $L=0$ decreases as the mean free

path of the diffusive channels increases. As $\lambda_{bulk} = 500nm$ that is comparable with λ_0 , the intercept is around $15k\Omega$, still significantly larger than 0. Figure 1.14 **b** shows a simulation with one ballistic channel $\lambda_0 = 5\mu m$ and various number of diffusive channels with mean free path $\lambda_{bulk} = 20nm$. We can clearly see that the slopes at long length scale are similar in all cases. More diffusive channels induce a smaller intercept at $L=0$. In summary, from Figure 1.14, we can measure the slope of R versus L and calculate the mean free path of the ballistic channel as

$$\lambda_0 \approx \frac{R_0}{dR/dL} = \frac{25.8k\Omega}{dR/dL} \quad (1.12)$$

The intercept at $L=0$ of resistance versus length plot at any length will be slightly less than $25.8k\Omega$ in the case of ballistic plus diffusive channels, but clearly a nonzero value.

1.2.3 Electrical Transport in Graphene

Due to the linear dispersion relation of the valence band and conduction band near the Dirac point, in 2-dimensional monolayer graphene, the low energy electronic states are described by a massless Dirac equation. The Fermi wavevector is given simply by filling up the non-interacting momentum eigenstates up to $q = k_F$

$$n = g_s g_v \int_{|\mathbf{q}| \leq k_F} \frac{d\mathbf{q}}{(2\pi)^2} \rightarrow k_F = \sqrt{\frac{4\pi n}{g_s g_v}}, \quad (1.13)$$

where the valley and spin degeneracy $g_v = g_s = 2$ for monolayer graphene and n is the 2D carrier density in the system[76]. Therefore, the Fermi Energy (E_F) is given by

$$E_F = \hbar c^* k_F = \hbar c^* \sqrt{\pi n} \quad (1.14)$$

with $c^* = 10^6 m/s$ the Fermi velocity of graphene. As we apply a gate voltage on graphene samples to tune the Fermi level, the conductivity changes following $\sigma = n|e|\mu$. Experiments have shown that there is an extended range where mobility $\mu \equiv d\sigma/dn$ is a con-

stant[77][78][79]. It would be expected that for a graphene sample, the conductance plot versus gate voltage has a minimum conductivity at 0 when the Fermi energy lies exactly at the Dirac point (i.e., the charge neutrality point(CNP)). However, in experiments, the measured conductivity at the Dirac point is finite and varies strongly from sample to sample[77][79]. The discrepancy can be explained by disorder in graphene sheets that, in addition to adding sources of scattering, locally shifts the charge neutrality point[76] [80]. This leads immediately to a disorder-induced inhomogeneous density landscape with electron-hole puddles[81]. Regions of electron-rich and hole-rich puddles could explain graphene's non-zero minimum conductivity at zero average carrier density. Such puddles have been experimentally verified by scanning single-electron transistor[82].

As discussed in the previous section, in chiral graphene nanoribbons, there exists a $n=0$ flatband at $E=0$ shown in Figure 1.8. It is narrowly confined to the physical edges of the ribbon and therefore, also named edge state. This flatband is predicted to have a large density of states (DOS) peak, as shown in the right image of Figure 1.8. This DOS peak pins the Fermi level at $E=0$ by depleting charges near the edge when there is a gate voltage V_g applied to induce charge density. Therefore, with doped graphene, we can rewrite the Landauer equation Equation 1.8 into an edge conduction plus bulk conduction

$$G = G_{edge} + G_{bulk} = \frac{e^2}{h} T_{edge} + \sum_{n=1}^M \frac{e^2}{h} T_{bulk} \quad (1.15)$$

where M is the total number of subbands occupied below the Fermi level. Without considering interference effect, we can combine Equation 1.15 and Equation 1.9 to obtain

$$G = \frac{e^2}{h} \frac{1}{1 + L/\lambda_{edge}} + \sum_{n=1}^M \frac{e^2}{h} \frac{1}{1 + L/\lambda_{bulk}} \quad (1.16)$$

where λ_{edge} and λ_{bulk} are respectively the mean free path of the edge state and bulk subbands. Therefore, if λ_{edge} is much larger than sample length L , the minimum conductance versus gate voltage would intercept at $\frac{e^2}{h}$ at CNP. By contrast, as in the last section, 2D

graphene without edge state theoretically has a minimum conductance at 0 when the Fermi level lies at CNP. Moreover, in a ballistic system, the conductance no longer scales proportionally to W/L . Applying a gate voltage only modifies the second term in the right-hand side of Equation 1.16. Therefore the conductance change due to gate voltage sweep measurement can help us to identify the ballistic edge states from the bulk states in experimental measurements.

1.3 Thesis Outline

I will cover the main experimental methods used in this thesis in Chapter 2. Chapter 3 will cover graphene nanoribbon on Si-face of SiC and Chapter 4 focuses on the graphene devices on SiC non-polar facets. Chapter 5 will be the conclusion of this thesis and some outlooks are presented. This thesis may show evidence that ballistic edge state transport may form not only on epigraphene nanoribbons on the Si-face, but also on non-polar facet of SiC. Thermal annealing is critical to restore edge states and obtain long mean free path up to μm range.

CHAPTER 2

EXPERIMENTAL METHODS

In this chapter, I will discuss the experimental methods used in this thesis. These methods can be categorized into several parts: graphene growth, graphene characterization, device fabrication and finally, electrical measurement.

2.1 Graphene Growth

Epigraphene is obtained by thermal decomposition of SiC. At high temperature at around 1500°C , Si atoms sublime from the SiC surface and leave carbon atoms behind that form graphene. Graphene growth on SiC was first realized by annealing SiC at high temperature in ultra-high vacuum (UHV) condition[83]. However, the Si sublimation rate is extremely fast, which causes growth hard to control. Moreover, in the out of equilibrium UHV sublimation process, graphene has a lot of defects that reduce the electronic mobility significantly. Therefore, we need to find an alternate way to limit the Si sublimation rate.

2.1.1 Confinement Controlled Sublimation Process

The CCS process can effectively limit the escape of Si by maintaining a high Si vapor pressure so that graphene growth proceeds close to thermodynamic equilibrium[37]. A schematic diagram of the experimental setup is shown in Figure 2.1. In this CCS process, a SiC chip is placed in a graphite crucible with a leak hole. This graphite crucible is in a quartz tube in ultrahigh vacuum and can be heated by an induction coil while a laser pyrometer records real time temperature and sends feedback to set the RF power of the induction coil.

As the temperature of the crucible is rising, Si starts to sublime from the SiC surface and this sublimated Si gas is confined in a graphite enclosure so that growth occurs in near

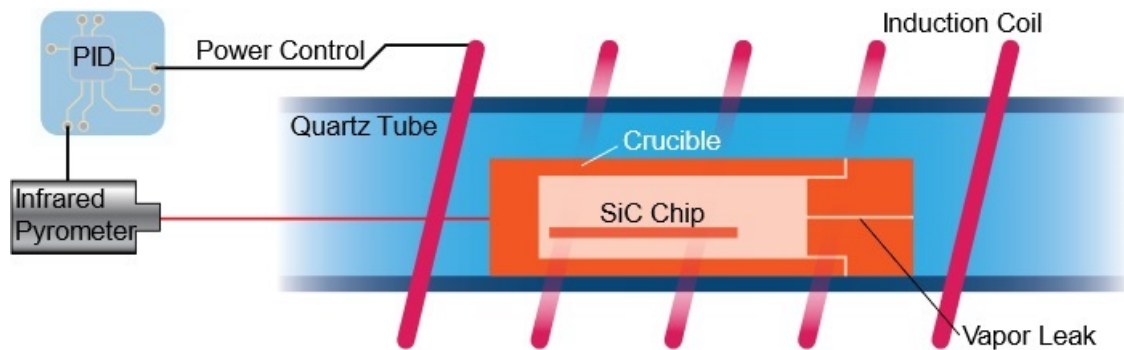


Figure 2.1: Schematics of epigraphene furnace. SiC chip is placed in a graphite crucible with a leak hole and whole thing is heated by an induction coil.

thermodynamic equilibrium. Growth rate is controlled by the leak hole size and the furnace pressure (around 10^{-6} mbar or in Ar atmosphere). Si sublimation rate is small enough to remove Si only from the first few layers of the SiC and leftover carbon on the surface form graphene with high structural quality.

Prior to growing graphene, it is necessary to prepare the bare SiC surface. First, blank CMP polished SiC wafer is diced into small chips with dimension $3.5 \times 4.5 \text{ mm}^2$. Each chip is sonicated in acetone and IPA for 15 minutes respectively to remove any dust and chemical residue. SiC chips will then go through a high temperature annealing around 1200°C in the CCS furnace to remove oxide and organic residues on the surface before graphitization.

2.1.2 Polymer-Assisted Growth

More than a simple Si atoms sublimation, a polymer coating can assist for graphene growth and has been tested successfully on Si-face of SiC[84]. In this process, the photoresist AZ-5214E, consisting of a long-chain polymer, is first diluted with IPA and then spin-coated on the Si-face of SiC. The polymer thickness is a key factor because too much polymer will leave residue after growth and too little won't provide full chip coverage. The optimal thickness is around $10 - 15 \text{ nm}$; the center of the coated SiC chip may have thinner

and edges have thicker resist coating. Then the sample is placed in a graphite crucible, stacked face-to-face to a same type SiC chip without resist on it. The Raman spectrum

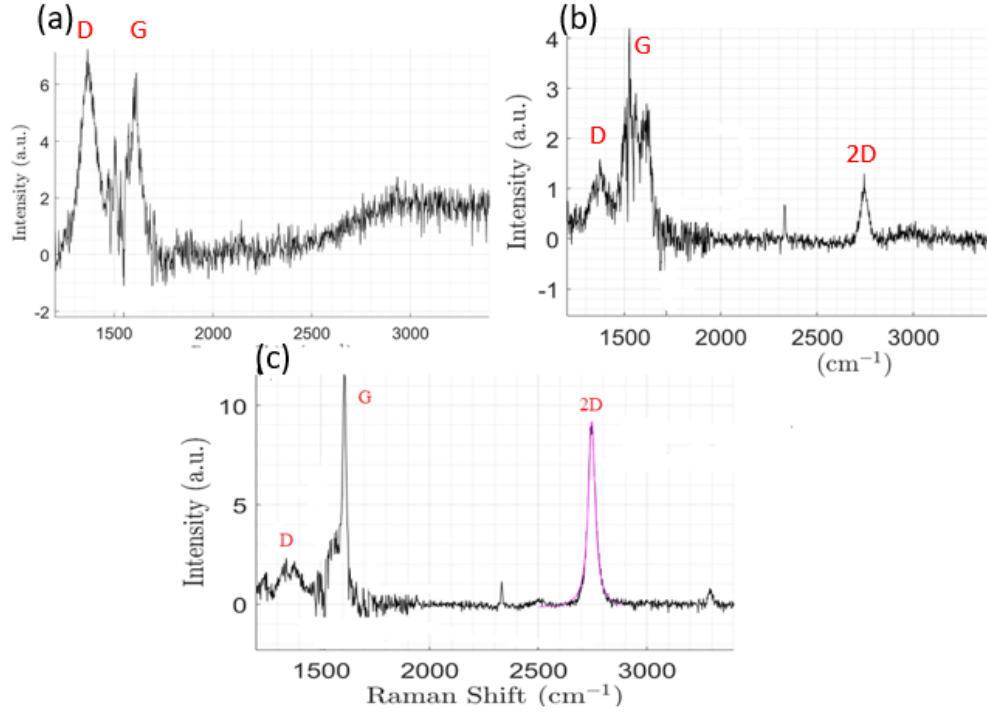


Figure 2.2: All these three Raman spectrum are after SiC background subtraction. Large noise is due to imperfect subtraction of the very large SiC peaks. (a) Raman spectrum of sample annealed under 900°C. High D-peak can be seen. (b) Raman spectrum of sample annealed under 1600°C. Ratio of $I(D)/I(G)$ is reduced and small 2D-peak starts to show up. (c) Raman spectrum of sample annealed under 1700°C. Sharp 2D-peak is observed along with small D-peak.

(more details in next section) in Figure 2.2 shows the evolution of samples annealed at several different temperatures. After annealing around 900°C, the polymer decomposes into volatile species and carbon atoms. A noncrystalline graphite network forms on the SiC surface, shown in the Figure 2.2a. After reaching 1600°C, these carbon networks are incorporated into the buffer layer, as shown in Figure 2.2b. The ratio of $I(D)/I(G)$ is significantly reduced and a small 2D-peak appears, indicating small area of graphene growth. Monolayer graphene fully grows by raising the temperature to 1700°C in an Ar

atmosphere. The Raman spectrum is shown in Figure 2.2c: it has a small D-peak and a narrow 2D-peak with full width at half maximum (FWHM) less than 40 cm^{-1} , which confirms that it is monolayer with relatively low defects[85]. Notice that a bare SiC chip without polymer coating doesn't have any graphene after this process, so we can attribute this grown graphene to the assistance of polymer. This polymer-assisted growth on Si-face successfully produces large area monolayer graphene without patches of bilayer or buffer layer.

We have fabricated Hall bar devices after growth using conventional E-beam lithography (EBL) and O_2 etch techniques and measure them at low temperature. The magnetoresistance exhibits Shubnikov-de Haas (SdH) oscillation and non-zero Berry phase, which confirms large mobility of single layer graphene. Some of those results are presented in Appendix A.

2.2 Characterization Methods

We mainly use Scanning electron microscopy (SEM), AFM and Raman spectroscopy to characterize the epigraphene samples.

2.2.1 Scanning Electron Microscope

SEM is one of the key techniques for surface characterization. Unlike optical microscope, it uses electrons instead of light to form an image. A beam of electrons is produced at the top of the microscope by an electron gun, based on either thermionic or field emission sources. Then the electron beam follows a vertical path through the microscope column, which is operated under high vacuum condition. The beam travels through multiple electromagnetic fields and lenses, which helps to focus the beam on the sample. Once the beam hits the sample, backscattered and secondary electrons and X-rays are ejected from the sample and captured by detectors to create an image.

The fine imaging capability of the SEM is due to the fact that the wavelength of elec-

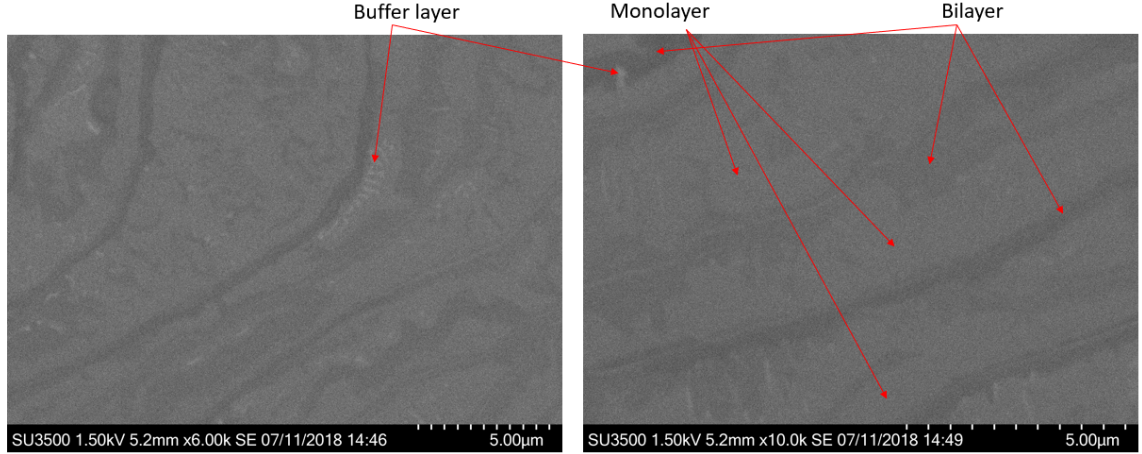


Figure 2.3: SEM Image of Si-face graphene consisting of buffer layer, monolayer and bilayer graphene patches in two different magnifications.

trons is orders of magnitude less than that of optical systems. At such small wavelengths, high spatial resolution can reveal excellent surface details. Features as small as $10nm$ can be ultimately resolved[86].

SEM is very helpful for characterizing graphene coverage and number of layers on the substrate. A SEM image taken on a Si-face graphene sample exhibits three different contrast levels, shown in Figure 2.3. These contrast levels in SEM are frequently used and reported for the estimation of number of graphene layers. The contrast between graphene and buffer layer or SiC substrate is due to the higher conductivity of graphene. From the more conductive graphene patch, less electrons are reflected and detected to the secondary electron detector, causing it darker in appearance[87]. Furthermore, the work function of epigraphene increases with an increasing number of layers, yielding lower secondary electron[88] Therefore, the darker strips shown on Figure 2.3 corresponds to bilayer graphene while brighter areas correspond to monolayer. Although a determination of the absolute number of layers is not straightforward, relative thickness are easily determined with SEM.

SEM is a powerful tool that gives fast and straightforward characterization of epigraphene growth. However, it will deposit hydrocarbon contamination on the sample, causing loss of resolution. Moreover, the hydrocarbon contamination may change the doping level and

increase scattering centers on pristine graphene and degrades the overall quality[89].

2.2.2 Atomic Force Microscopy

AFM is a method for measuring surface properties and profiles with atomic-scale topographical information. The AFM in our lab is working in either one of two modes: the Non-contact AFM (NC-AFM) and the Contact AFM (C-AFM). The main difference between these two modes is the interaction range, or the distance between the tip and the sample surface. In NC-AFM, as shown in Figure 2.4a, the tip is further away from the surface and has an attractive van der Waals electrostatic force. The sharp tip built at the end of a soft cantilever arm is oscillated perpendicular by the surface at a frequency close to the cantilever–tip resonant frequency. This attractive force has a strong dependence on the distance between the tip and the surface and correspondingly changes in the resonant frequency of the system. A feedback loop moves the sample up and down in order to maintain a constant oscillation amplitude. Hence a constant tip-sample separation distance is maintained as the tip scans the surface. NC-AFM can directly measure the atomic-scale surface topography while reducing tip wear and preventing any damage to the sample surface.

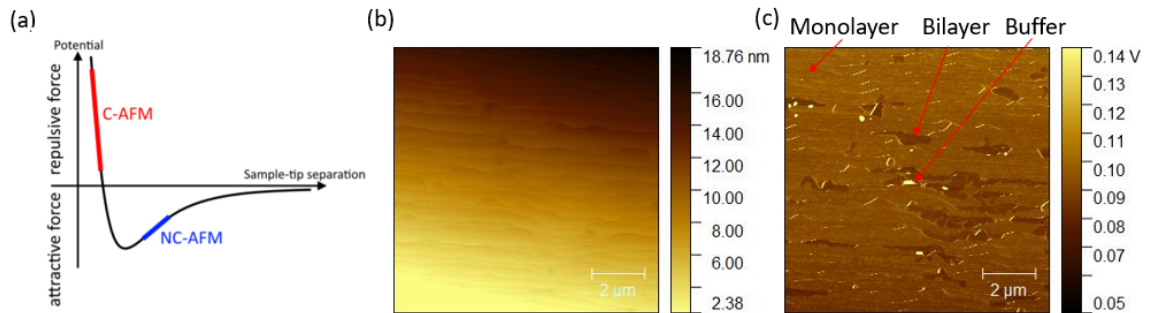


Figure 2.4: (a) Relationship between force and separation distance as it pertains to different AFM operating modes. Figure from [25]. (b) Topography of a Si-face sample after graphene growth. We can see the small steps whose height are around 0.5nm to 1nm. (c) C-AFM of the same area in b, exhibiting buffer layer, monolayer and bilayer graphene based on the frictional force contrast.

In C-AFM, a sharp tip scans the sample at a much smaller distance of the surface where the forces are repulsive. The tip is applied with a set point force ranging from $3nN$ to

$5nN$. The repulsive force from the sample surface pushes on the tip and bends the cantilever beam, which is then detected by the laser that focuses on the back of the cantilever. The advantage of C-AFM is that not only it is able to measure the topography of the surface, it also measures the surface frictional force at the same time. This is very critical to distinguish graphene and SiC or buffer layer because graphene has a much smaller frictional force than the SiC substrate or buffer layer. Moreover, we can distinguish single layer graphene from bilayer graphene patches, as shown in Figure 2.4c. Bilayer graphene has a slightly smaller lateral friction force because it is more flat, which corresponds to darker areas in Figure 2.4c. Also, we can see there are bright spots with very high friction that corresponds to the buffer layer. C-AFM is a powerful tool to characterize epigraphene samples, especially sidewall graphene nanoribbons, but its tip is wearing out fast and the imaging resolution decreases rapidly overtime.

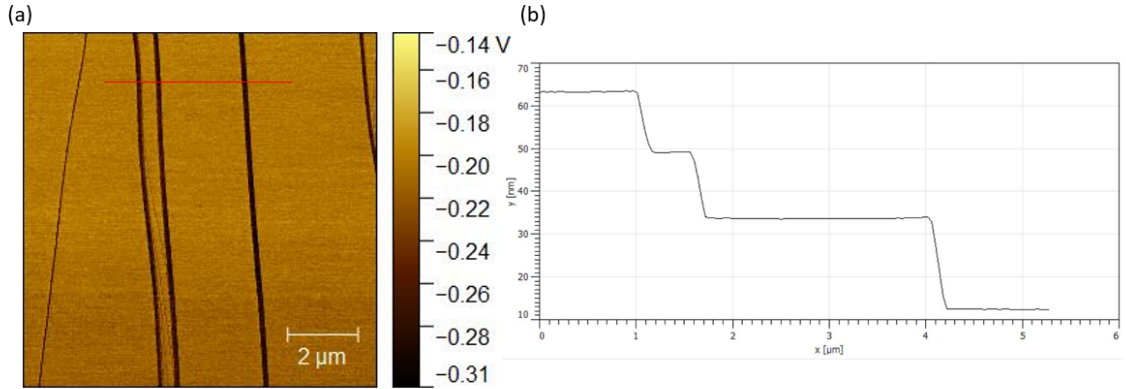


Figure 2.5: (a) Lateral force of several SWGNRs on the SiC natural steps.(b)Topography profile of the red line in (a).

Also C-AFM is a very useful tool to characterize the growth results of SWGNRs. The frictional force displays large contrast between the SiC substrate and graphene nanoribbons, as shown in Figure 2.5a. The darker strips have lower friction and therefore, correspond to graphene nanoribbons, while the rest of area is SiC substrate or buffer layer.

Raman spectroscopy (discussed in the next section) is a versatile tool to characterize graphene, however, in this situation, it is difficult to capture any signal from such a narrow

nanoribbon because the laser beam diameter is approximately $1\mu m^2$.

2.2.3 Raman Spectroscopy

Raman spectroscopy is a fast and non-destructive surface analysis tool that helps to determine the number and orientation of layers, strain, doping, disorder and functional groups of graphene[90]. Briefly speaking, when a sample is exposed to monochromatic light, it will undergo elastic Raleigh scattering or inelastic Raman scattering. The elastically scattered light at the incident wavelength is filtered out so that the remaining radiation that has undergone inelastic scattering can be analyzed. The change in energy of the inelastically scattered light measured with Raman spectroscopy corresponds to the energy of one of the system's phonon modes. The light can either excite the system into a higher energy state, resulting in a lower energy photon exiting the system through a process known as Stokes scattering; or the system can relax into a lower energy state than it was in prior to the absorption, releasing a higher energy photon through a process known as anti-Stokes scattering. Because the values of possible photon energy shift are specific to the phonon modes and electronic structure of a material, Raman spectroscopy provides a signature of the chemical bonds present in the sample. In this thesis, a Horiba Jobin Yvon Labram HR-800 Raman spectrometer with a $532nm$ excitation laser with $1\mu m$ radial beam size and approximately cm^{-1} spectral resolution was used to characterize graphene films grown on SiC.

The Raman spectra of our sample is a superposition of SiC substrate and graphene. Therefore, to get clean graphene Raman spectra, we need to subtract SiC background features from the raw data. After this subtraction, the Raman spectrum of graphene exhibits three significant peaks. The G peak, around $1582cm^{-1}$, and the 2D peak, around $2700cm^{-1}$, are always present, while the D peak, at around $1350cm^{-1}$, is only present when there is some structural disorder in the carbon lattice, for example, a disruption of the lattice periodicity such as defects, edges or grain boundaries. The G peak results from

a high frequency in plane vibrational mode corresponding to the E_{2g} phonon at the Brillouin zone center and can be observed in pristine graphene. The D peak results from the A_{1g} breathing mode of 6 atom rings and can only manifest near the edges or defects in the graphene lattice[91][90]. The 2D peak is an overtone of the D-peak resulting from two phonons with opposite wave vectors[90]. Because the opposite wave vectors of these two phonons satisfy conservation of momentum, the 2D-peak can be observed in pristine graphene even though the D-mode is not active.

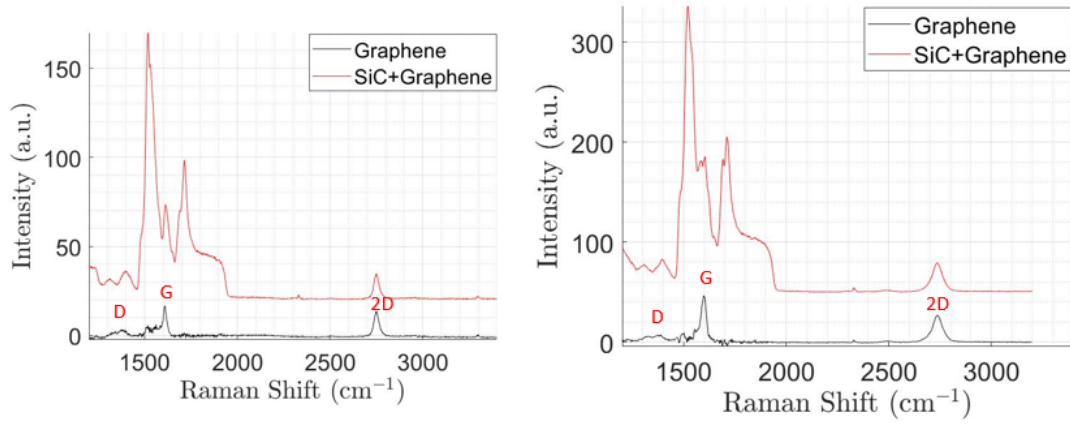


Figure 2.6: (a) Raman spectra of Si-face monolayer graphene before and after SiC background subtraction. D,G and 2D peaks are labelled and FWHM of 2D peak is 29cm^{-1} . (b) Raman spectra of Si-face bilayer graphene before and after SiC background subtraction. D,G and 2D peaks are labelled and FWHM of 2D peak is 55cm^{-1} .

We mainly use Raman spectroscopy to determine the number of graphene layers. For a Bernal stacked layer order, such as epigraphene on the Si-face, due to the electron bands degeneracy lifting by the symmetry breaking, the incoming photon generates electron-hole pairs in the two different bands with slightly different wave vectors. Since the momentum has to be conserved in the electron-phonon process, these electrons and holes activate phonons with slightly different energies. The result is that for bilayer graphene, the 2D band contains four components and has a larger Full-Width at Half-Maximum (FWHM) than monolayer graphene. Figure 2.6 shows the Raman spectrum of monolayer and bilayer graphene on the Si-face. After SiC background subtraction, the sharp 2D peak of mono-

layer graphene (in Figure 2.6a) has a FWHM 29cm^{-1} , while in bilayer graphene, FWHM of the same peak is much broader and is 55cm^{-1} . Based on my experience, monolayer graphene generally has a FWHM less than 35cm^{-1} and bilayer has a FWHM larger than 50cm^{-1} . Values in between might indicate a mixture of monolayer and bilayer patches.

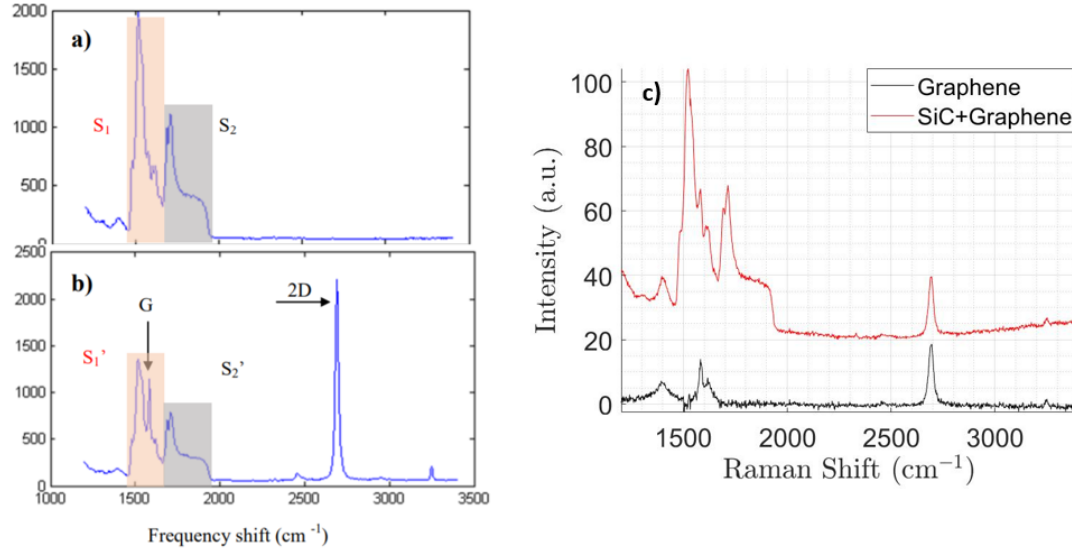


Figure 2.7: (a) A typical bare SiC Raman spectrum. S_1 is the total intensity from wavenumber 1460cm^{-1} to 1660cm^{-1} , and S_2 is the total intensity from 1660cm^{-1} to 1960cm^{-1} . (b) Raman spectrum for epigraphene on C-face. S_1' is defined as the combined signal of the SiC S_1 peak area and the graphene G peak, S_2' is the attenuated intensity from SiC S_2 peak area. (c) Monolayer graphene on SiC non-polar facet before and after SiC background subtraction. The relative intensity ratio G/S_2 is 0.074 in this spectrum.

However, for rotational stacked graphene such as on C-face or non-polar facet, the sublattice symmetry is preserved so that each layer behaves as if it were an isolated graphene layer. In this case, FWHM is not a good indicator of the number of layers. Instead, the peak intensity ratio is a more robust parameter and can be used to derive information about graphene. A Raman attenuation method proposed in Yike Hu's thesis is briefly summarized here[92]. Figure 2.7a is the Raman spectrum of a bare SiC. In that spectra, S_1 is the spectrum area intensity from wavenumber 1460cm^{-1} to 1660cm^{-1} and S_2 is the spectrum area intensity from wave number 1660cm^{-1} to 1960cm^{-1} . After the epigraphene growth, the graphene G peak that is around 1580cm^{-1} is overlaid with the SiC S_1 peak area. As

demonstrated in Figure 2.7b, the intensities of the SiC and graphene G peaks add up to $S1' = S1 + G$, while the SiC $S2$ peak area has no additional contribution from graphene. Therefore, we have

$$\frac{S1'}{S2'} = \frac{S1 + G}{S2} \rightarrow \frac{G}{S2} = \frac{S1'}{S2'} - \frac{S1}{S2} \quad (2.1)$$

By measuring $S1$, $S2$ for the bare SiC and $S1'$, $S2'$ for the epigraphene sample, the intensity ratio $\frac{G}{S2}$ can be calculated and gives a good indication of the number of graphene layers. For non-polar facet epigraphene sample, we find that monolayer graphene patches' intensity ratio usually falls between 0.07-0.08 and for bilayer number, this number increases to 0.13-0.15. More details about this method can be found in [92].

2.3 Fabrication Methods

Producing electrical devices down to sub- μm scales to study electrical, magnetic or optical properties of graphene poses engineering challenges. Graphene's single atomic layer geometry makes it susceptible to crystal imperfections, fabrication residues and air contamination. Fortunately, most conventional nanofabrication techniques are generally available and successfully applied to fabricate small graphene devices on SiC substrate. Generally speaking, most nanofabrication techniques can be divided into three parts: lithography, etching and thin-film deposition.

2.3.1 Lithography

Lithography is the process of transferring patterns of geometric shapes to a thin layer of photosensitive or e-beam sensitive material (called photoresist or e-beam resist) covering the surface of a sample.

E-beam resist consists of inactive resin, e-beam sensitive compound and solvent. Depending on its chemistry, e-beam resist can be either positive or negative. For positive resist, the area undergoing high dosage of e-beam exposure will be dissolved in a specific

solvent (called developer). On the contrary, negative resist remains only where it has been exposed by e-beam. In this work, I use PMMA 950 A6 as a positive resist and Ma-N 2400 as a negative resist, both from MicroChem. Following MicroChem's recommendation to achieve better resolution, the developer for PMMA is a 3:1 mixture of Isopropyl alcohol (IPA) and Methyl isobutyl keton (MIBK). Also, we use the developer MF-319 to develop Ma-N 2400.

The resist is deposited on a chip by spin coating which yields a thin but homogeneous layer. Then the chip is baked on a hot plate to evaporate the solvents, leaving a solid polymer film. This coated chip is then placed into an e-beam lithography equipment where desired patterns have been drawn with CAD files. A certain electron dosage, which is equal to e-beam current multiply by time, is exposed on desired areas on the chip. After that the chip is dipped in the developer to remove exposed positive resist or non-exposed negative resist and inspected under an optical microscope to make sure the pattern transfer process is successful. With the SEM lithography in Howey Physics building, we can draw patterns down to $\approx 100nm$ size

2.3.2 Plasma Etch

Etching process is usually applied after lithography or thin-film deposition process. After either of these two processes, a pattern made of e-beam resist or a hard material is deposited on the chip and serves as a mask for etching. Plasma etch is used in this work to remove excessive materials outside the mask.

Common materials to be etched in this thesis include graphene, SiC and Al_2O_3 . Reactive ion etch (RIE) is a dry etch method involving chemical reactions of the surface of a material with the ions of a plasma. One or more gases are in a chamber where they are ionized by a high frequency electromagnetic field. The choice of gas is dependent on the material being etched. For graphene, 16W RF power and 4 sccm O_2 gas flow is sent for several seconds. While for SiC, 1:4 mixture of SF_6 and O_2 gas flow (0.8 sccm versus 3.2

sccm) at 100W RF power is used for 15 seconds to etch 20 nm deep SiC trench. For Al_2O_3 , large RF power is required to etch. Therefore, we need Inductive-coupling plasma (ICP) which can generate a much higher energy plasma to etch Al_2O_3 . The key differentiation between ICP and RIE is the separate ICP RF power source connected to the cathode that generates DC bias and attracts ions to the sample. Due to this high power, the etch rate is greatly increased and etch anisotropy is very small, which is used for etching deep trench on Si in industry. The gas to etch Al_2O_3 is BCl_3 and O_2 with RF power 300W. The etch rate is about 2nm per second with these parameters.

2.3.3 Thin Film Deposition

Semiconductor fabrication process requires that a variety of new materials deposited on the chip, including source and drain metals, gate dielectric materials and gate metals. In this thesis, most metals (Pd, Au, Al) are deposited using e-beam evaporation. Also we adapt amorphous carbon as a new metal contact material since it is high temperature compatible. For gate dielectric material, we use Al_2O_3 which is deposited by either e-beam evaporation or Atomic layer deposition (ALD).

Atomic Layer Deposition

ALD is a unique version of CVD. Unlike CVD, which introduces all vapor components at the same time into a chamber, ALD process only uses one precursor at a time and covers isotropically the whole chip surface. After the first precursor is sent and excess is pumped away, a second precursor is sent into the chamber and reacts with the first one deposited on the sample surface, and we can have a single layer uniform coverage of final product. This Al_2O_3 uses two precursors: Trimethylaluminum (TMA) and water vapor. Other materials like HfO_2 and TiO_2 have been used successfully for high- κ dielectric films in industry application.

However, ALD deposited Al_2O_3 on pristine graphene is challenging due to lack of

reactive surface sites on graphene. A variety of functionalization methods have been tested to achieve uniform growth but these significantly adversely affect the graphene properties. One way to overcome is to deposit a thin seed layer Al_2O_3 by e-beam evaporation followed by ALD deposition. Also, since ALD produces conformal coating, it is not suitable for lift-off process.

E-beam Evaporation

E-beam evaporation involves vaporizing a metal which is then deposited on the chip. The e-beam is focused onto the metal source using a magnetic field thereby locally melting it. This local heating, and the fact that the crucible is water cooled, ensures that the crucible containing the metal source does not overheat. Multiple targets are stored in the chamber and can be selected remotely, allowing sequential depositions without exposing the sample to air. The sample is placed on a stage situated around 50 cm away from the source. Unlike ALD, it produces a very directional deposition, so that coating on sidewalls of the material and resist is minimized, making it an ideal choice for lift-off process.

Titanium (Ti), palladium (Pd), gold (Au) and aluminum (Al) are commonly used for contacting graphene. We typically use a double layer consisting of 20nm of Pd deposited at a rate of $0.5\text{\AA}/s$ on the graphene and 30nm of Au deposited at $1\text{\AA}/s$ on top of it. Deposition chamber pressure is normally around 5×10^{-6} mbar.

We also use e-beam evaporation to deposit Al_2O_3 by depositing Al in an oxygen rich environment. Accordingly, pure O_2 is introduced in the ultrahigh vacuum chamber at a pressure of 5×10^{-5} mbar, which is small enough to avoid any filament oxidation. The deposition rate is well controlled at $0.1\text{\AA}/s$ so that each Al atom is fully oxidized in oxygen rich environment. This slow rate deposition method allows us to deposit and lift-off Al_2O_3 very easily.

This success of depositing Al_2O_3 with e-beam evaporation simplifies the fabrication process flow. We can apply lithography patterns for gate materials after fabricating the

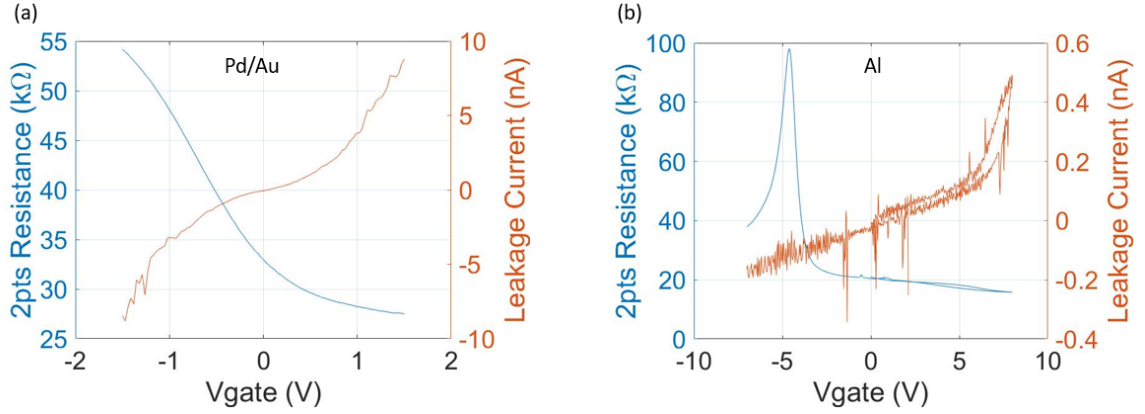


Figure 2.8: **(a)** Gate voltage sweep of e-beam evaporation Al_2O_3 with Pd/Au as gate metal on a Hallbar device, measured at room temperature. Leakage current is acceptable at $V_g = -2V$. **(b)** Gate voltage sweep of e-beam evaporation Al_2O_3 with Al as gate metal on another Hallbar device. Charge neutrality point can be seen at $V_g = -5V$ with less than $1nA$ of leakage current.

electrical devices and then deposit and lift-off Al_2O_3 and gate metal stack at the same time. The choice of gate metal is also important. Pd/Au and Al produce significant differences on gate response and leakage current, shown in Figure 2.8. Figure 2.8a shows a gate voltage sweep of 2-points resistance on a Si-face Hallbar device with Pd/Au gate metal. Figure 2.8b has a similar Hallbar structure as in a but with Al as gate metal. Thicknesses of the Al_2O_3 films are the same for two devices as $20nm$. As we can easily tell, the breakdown voltage for device with Pd/Au is less than $\pm 2V$ where leakage current has exponentially increased beyond $5nA$. This gate voltage, is not enough to reach CNP of graphene. In contrast, devices using Al as gate metal has a leakage current less than $1nA$ within $\pm 8V$. Also, we can see the maximum of 2-points resistance in this range which corresponds to the CNP of graphene. This significant difference between these two gate metal implies that leakage might come from the edge of $Al_2O_3/Pd/Au$ stack structure, while the edge of Al_2O_3/Al is also oxidized so that there is minimal leakage in this case.

Amorphous Carbon Deposition

aC is a high temperature compatible material that can be used as electrical contacts. Therefore, it is desirable to deposit aC with the ability to lift-off.

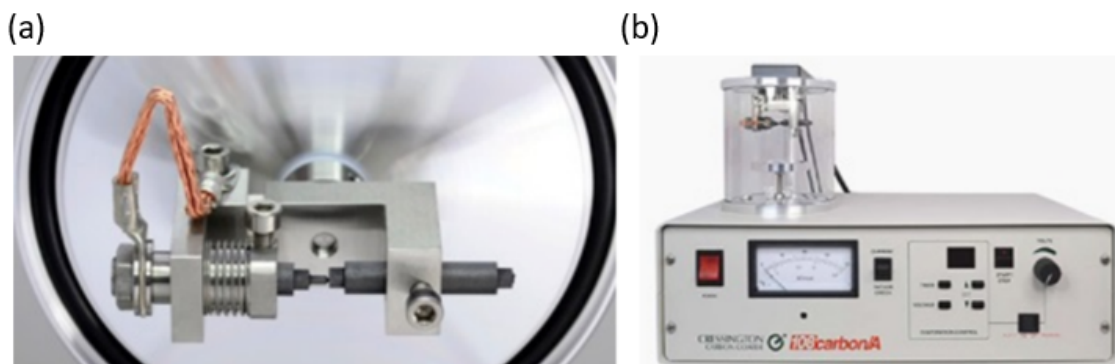


Figure 2.9: **(a)** The aC deposition system 108CarbonA from Cressington Scientific Instruments with its two graphite stick graphite stick setup. Rods are pushed towards each other with a spring mechanism. **(b)** The deposition chamber with the power supply that can run more than 150 Amps through the graphite rods. Images excerpt from [72].

We use the aC deposition system 108CarbonA from Cressington Scientific Instruments. There are two graphite rods contacting with each other, shown in Figure 2.9a. One with a sharpened pointing end and one with a flat end. The two rods are tightly pushed together using a spring mechanism. As the deposition proceeds, the spring keeps the rods in contact. A current of 120 Amps to 150 Amps passes through the rods causing carbon to sputter from the contact point which deposits on a sample placed beneath it. We found out that cycles using short and repetitive pulses of aC depositions over long periods creates aC layers that can survive the liftoff. We believe that the reason for it is to allow the rode to coll down between pulses. When the rod is not cooling down enough, deposited aC might burn the resist. This not only prevents unsuccessful liftoff later, but may also generate patches of irremovable aC in the burnt resist areas. More details about aC deposition can be found in [72].

2.3.4 Side Contact Between Metal and Graphene

As mentioned before, graphene is susceptible to contamination. In particular, e-beam resist deposited directly on top of graphene causes contamination as well. Polymer from e-beam resist, especially after RIE etch, is hard to wash off by conventional cleaning chemicals and resist residues are a serious issue in the literature. Therefore, an ideal graphene devices fabrication process would consists of covering graphene with an insulating layer right after the growth. This insulating layer should not interact with the graphene surface and also have a clean interface with graphene. Al_2O_3 turns out to be a suitable candidate due to its high- κ and inert properties. It has been commonly used as gate dielectric [93] and tunneling barrier[94] and proven to be protective from air contamination to graphene[95]. E-beam evaporation can immediately deposit Al_2O_3 on top of graphene right after growth, which can effectively prevents graphene from air and organic contamination.

However, fabrication process is very challenging, especially integrating Al_2O_3 etching to define contacts between metal and graphene without damaging graphene quality. Wet etch using Buffered oxide etch (BOE) is one possible method but the etch rate is fast and hard to control precisely. These problems are circumvented using so-called "side contacts",

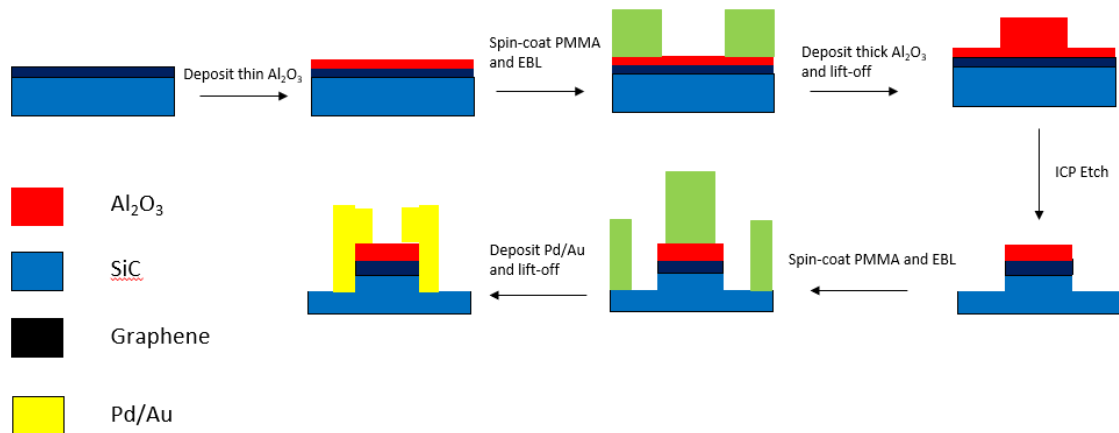


Figure 2.10: Fabrication process flow of electrical devices with side contacts. Al_2O_3 is deposited twice to form a mask for ICP etch. After etching, edges of graphene has been exposed and made contacts with Pd/Au deposited later.

as shown in Figure 2.10. Only the graphene edges are in contact with the metal. This method is first introduced in exfoliate graphene sandwiched between two exfoliate h-BN sheets by Wang et.al [96]. To expose the edges, an ICP etch with BCl_3 is used to produce a vertical sidewall. In contrast, conventional plasma or RIE does not expose the edges cleanly and cause unstable contact resistance. The drawback of using ICP etch is that the etch rate is relatively fast and we need to deposit a thicker Al_2O_3 as a hard mask. The contact resistance between metal and graphene is in the range of $k\Omega$, even at low temperature, which indicates a robust contact between the metal contact and the graphene.

2.3.5 Packaging-Coating of Graphene with h-BN

Other than Al_2O_3 , Hexagonal boron nitride (h-BN) is a good candidate for the protective layer. It is an insulating material that is lattice matched with graphene [97]. This property minimizes the interaction and helps graphene preserve its electrical properties. It has been widely used in exfoliate graphene research, where graphene is sandwiched between two h-BN sheets. This heterostructure has led to the observation of unique electronic features like Hofstadter's Butterfly [98] and unconventional superconductivity on "magic angle" twisted bilayer graphene[12]. Observations of these outstanding electrical properties of graphene restates the importance of preserving the pristine graphene crystal and preventing the graphene surface from residues and contamination before, during and after the fabrication process.

In essentially all studies, BN is mechanically deposited, which severely limits its utility. Recently we have achieved a MBE-based method to produce BN by the lateral growth method[99]. Moreover, recent research develops a promising way that we can grow epigraphene under sputtered BN so that graphene is under protection at the beginning. This method can improve the quality of graphene devices and serve as the next generation transport measurements.

2.4 Electrical Measurement

The last section of this chapter covers the electronic transport measurement techniques. For resistance measurement, including Van der Pauw method or 4-point probe method, 4 probes are required to avoid measurement error due to the contact resistance between the probe and sample. In the experimental set up, two probes inject current and another two probes measure the voltage difference on the chip[100]. Our 4-point probe station serves this experiment at room temperature with four sharp metal tips moving around in three-dimensional space. These tips can directly touch on top of the sample surface or in contact with metal electrodes on fabricated devices.

To measure resistance with high precision, a lock-in amplifier, which serves as a current source and a voltage measurement at the same time, is well suited for electrical characterization. Typically, the lock-in amplifier outputs a low frequency (10-50Hz) bias voltage V_{bias} and is in series with a large resistance R_{series} (10M Ω -500M Ω). Since R_{series} is much larger than sample resistance, we can safely assume $I_{inject} = V_{bias}/R_{series}$. Also, the lock-in amplifier measures voltage response of the device and extracts the component V_{meas} that is in phase as V_{bias} . This signal extraction relies on the orthogonality of sinusoidal functions and can effectively remove noise. For a 4-point probe setup, measured resistance would be $R_{meas} = V_{meas}/I_{inject}$.

We adapt a Hall bar geometry that can perform Hall effect measurement to measure electrical properties including carrier density, mobility and sheet resistance. When the sample is placed perpendicular with respect to a magnetic field, the mobile carriers experience a Lorentz force

$$\mathbf{F}_m = q\mathbf{v} \times \mathbf{B} \quad (2.2)$$

Therefore, a magnetic field is applied perpendicular to the plane of the electrical current I in a thin slab, causing the charge carriers to deviate towards one side of the slab. They accumulate on the side inducing a potential difference V_H in the slab perpendicularly to

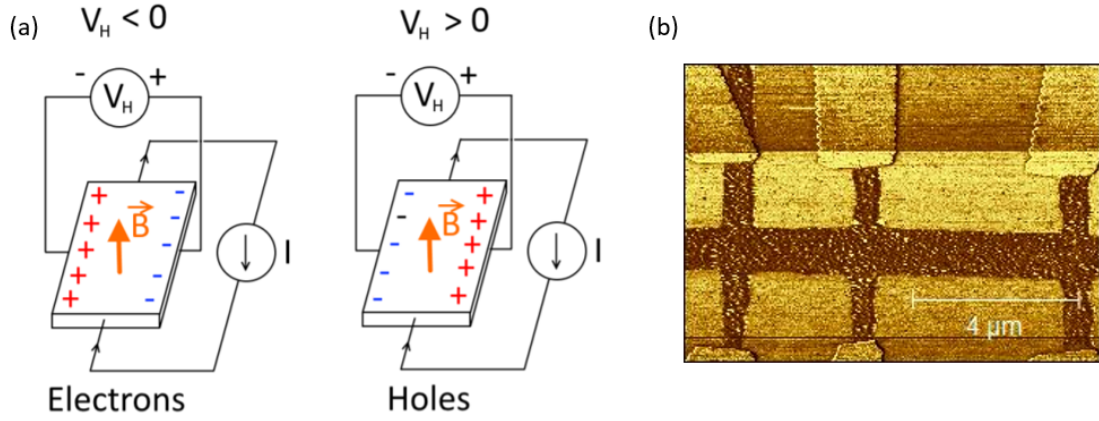


Figure 2.11: **(a)** The Hall effect for negative charge carrier (electrons) and positive ones (holes). The sign of the Hall voltage depends the sign of the charges. Excerpt from [Turmaud2018thesis] **(b)** Lateral force microscope shows the graphene Hallbar structure and metal leads. Darker areas are low frictional regions corresponding to graphene Hallbar. Brighter areas are metal leads.

the direction of current as depicted in Figure 2.11a. Figure 2.11b shows the lateral force microscope image of a standard Hall bar device that consists of a horizontal graphene channel and leads on the side. Metals contacts are overlapped on top of those graphene leads and also on SiC. In 2-dimensional material like graphene, the Hall coefficient is defined as $R_H = \frac{V_H}{BI}$ and is related to carrier density as

$$R_H = \frac{1}{ne} \quad (2.3)$$

Also, after obtaining the carrier density and 4-point resistance, we can easily calculate the mobility with conductivity equation $\sigma = ne\mu$.

CHAPTER 3

EPIGRAPHENE NANORIBBONS ON SiC(0001)

In this chapter we discuss epigraphene nanoribbons fabricated on Si-face. Unlike lithographically etched nanoribbons in the literature, we add a high temperature thermal annealing step after etching graphene, and use aC as contact material. Moreover, we develop a fabrication process flow that include thermal annealing and metal contacts, with a novel "side contact" structure.

3.1 Graphene Nanoribbons on SiC(0001) with Amorphous Carbon Contacts

Epigraphene on the Si-face has a strong substrate interaction causing the buffer layer to become insulating[101][26][102]. This interface buffer layer is a well-organized corrugated carbon layer that strongly couples to the SiC surface[27]. Monolayer graphene on top of this buffer layer is not intrinsically charge neutral but has a n-type doping on the order of 10^{13}cm^{-2} with mobility to around $1000\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ at this high charge density[37]. By lowering this high charge density, we want to explore if there are still ballistic channels. Therefore, we need to fabricate devices made of graphene nanoribbons on SiC Si-face and measure them. In order to minimize the edge roughness causing transport disorder, we want to have a high temperature thermal annealing step after the etch process. Therefore we use aC as the contact material that has been applied in SWGNR devices. The first step is to grow a monolayer graphene sheet without defect and minimize bilayer patches on the Si-face. We use the polymer-assisted method mentioned in Chapter 2. We place a 4H-SiC chip with spin-coated diluted photoresist in a graphite crucible and precisely control the temperature and time to achieve defect-free uniform coverage of monolayer graphene on the chip.

Lateral force microscope (LFM) and Raman spectroscopy are used to characterize the

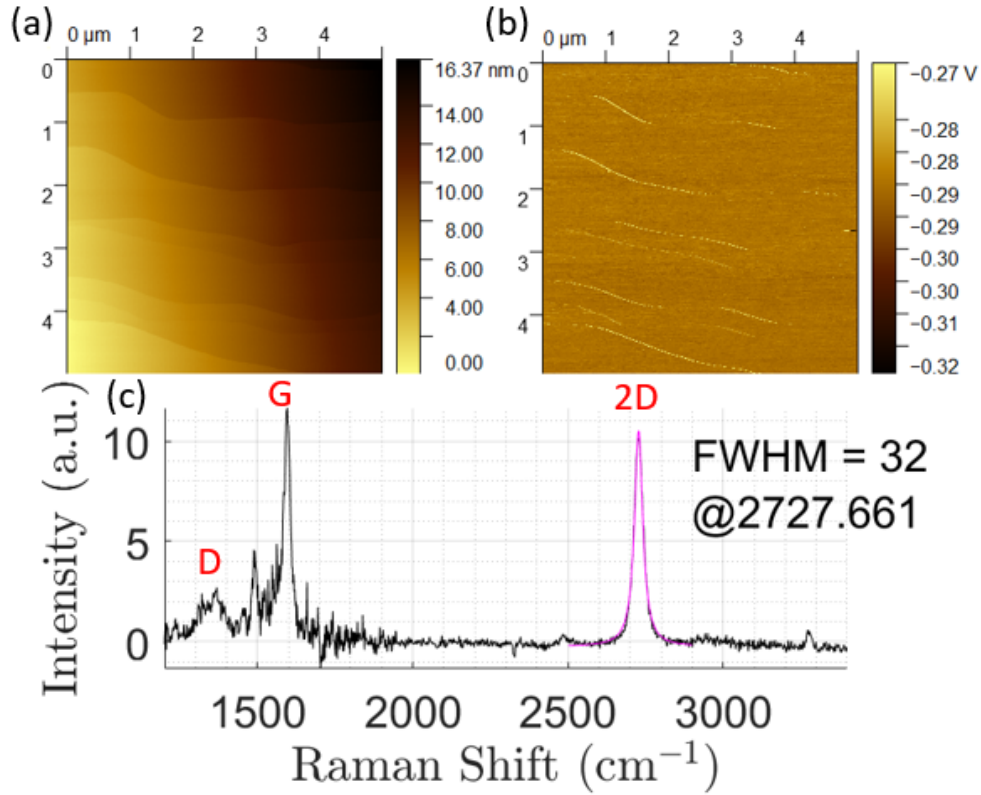


Figure 3.1: (a) Topography of full uniform coverage of graphene on Si-face. (b) Lateral Force of graphene on Si-face (c) Raman spectrum of monolayer graphene after SiC background subtraction

graphene samples. Figure 3.1a shows topography on Si-face after the growth process. The surface has several steps and each step height is about 0.5nm . Between those steps, terraces are atomically flat and free of contamination. Figure 3.1b shows the LFM image of the same area as in a and indicates that this sample has a full uniform coverage of graphene on the surface. We can use Raman spectroscopy to verify the number of layers of graphene. After SiC background subtraction, the FWHM of the 2D peak for monolayer graphene on Si-face is usually less than 35cm^{-1} . Figure 3.1c shows that graphene is indeed a single layer [85][90].

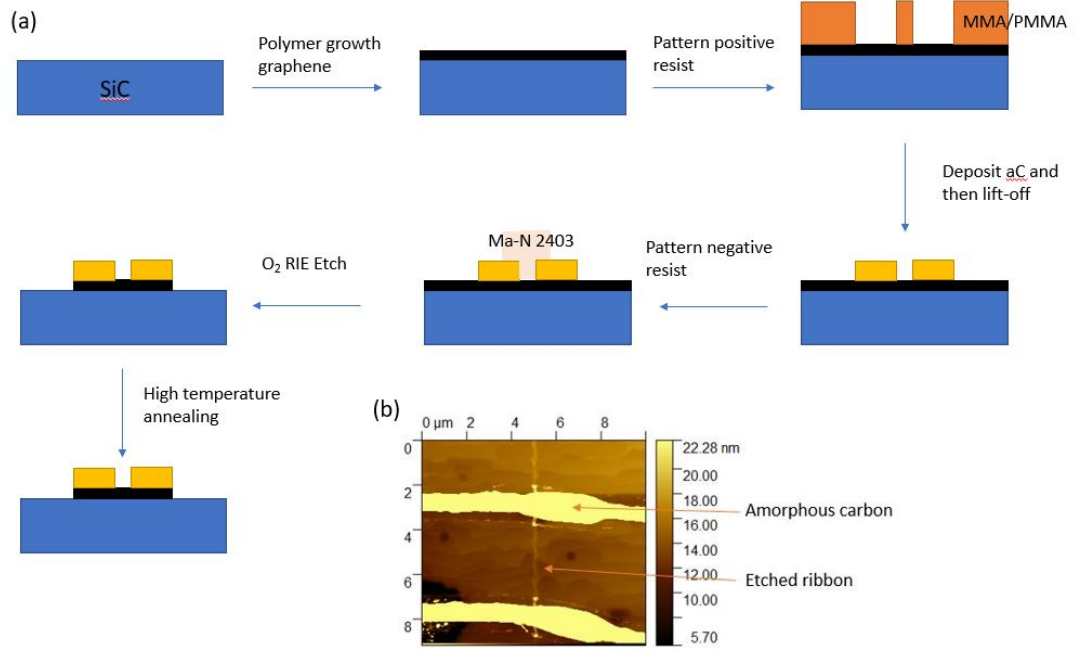


Figure 3.2: (a) Schematics diagram of the fabrication process flow of etched ribbon devices on the Si-face. (b) AFM image of two amorphous carbon contacts and nanoribbon in between.

Ribbon Fabrication and Carbon Contacts

The fabrication process flow for graphene nanoribbon devices with amorphous carbon contacts is shown in Figure 3.2a. Positive e-beam resist stack MMA/PMMA is first spin-coated, then patterned using high resolution e-beam lithography to define contacts. In this section, aC instead of metal is used as contact pads. After amorphous carbon deposition and lift-off, negative e-beam resist MaN-2403 is used to be spin-coated and patterned to define the ribbons. Then O_2 plasma is used to etch the excess graphene outside the aC and resist. we anneal the sample at $1300^\circ C$ for 15 minutes in Ar atmosphere. Figure 3.2b shows the AFM image of amorphous carbon contacts and etched ribbon between these contacts.

Thermal annealing process has been routinely used in CVD or exfoliated graphene to clean polymer resist residues[103]. Especially, annealing in Ar atmosphere at $400^\circ C$ leads to a significant reduction of PMMA residues minimizing carbon residues on the sur-

face[103]. Moreover, thermal annealing can tune the Fermi level of graphene[104] and help to attach exfoliated graphene edges to the SiO_2 substrate [105]. However, the annealing temperature in that case is not high enough to adequately remove all residues due to substrate and metal contacts temperature limitations. Therefore, epigraphene on SiC with amorphous carbon contacts could be a good method to achieve high temperature (larger than $1000^\circ C$) annealing conditions, which can decrease the contact resistance of amorphous carbon, and most importantly, smooth the edges of etched ribbons. Figure 3.3 shows SEM images of the same graphene nanoribbon before and after annealing. It is clearly seen that the nanoribbon without annealing has a rough and serrated edge, while the nanoribbon after annealing has a much smoother edge.

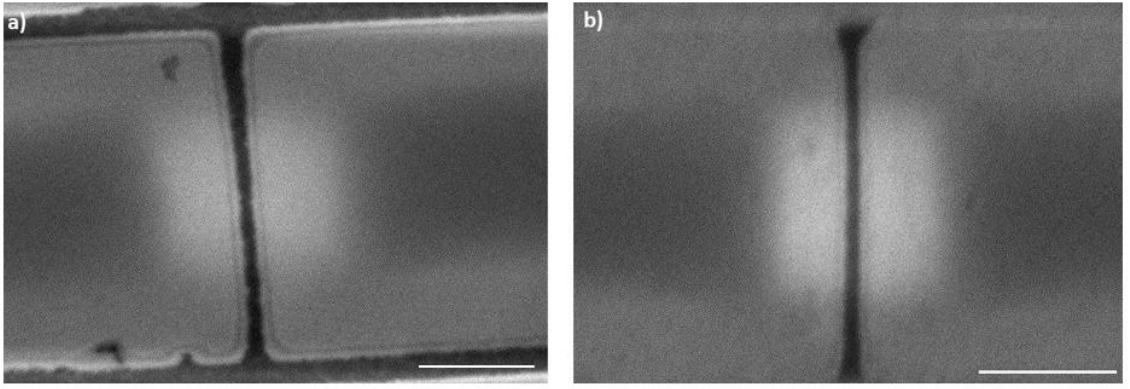


Figure 3.3: SEM of the same graphene nanoribbon (a) before $1200^\circ C$ thermal annealing and (b) after thermal annealing. Scale bar is 500 nm.

Sample Measurement

After fabricating the devices, we measure those devices at room temperature before and after annealing at the probe station. After that, we place the sample under vacuum condition ($10^{-4} mbar$) and measure again. The widths of these ribbons are between $80nm$ to $100nm$. All resistance measurements mentioned in this chapter are four-points resistance, using standard lock-in amplifier techniques with constant input current $100nA$. Results of resistance versus length are shown in Figure 3.4.

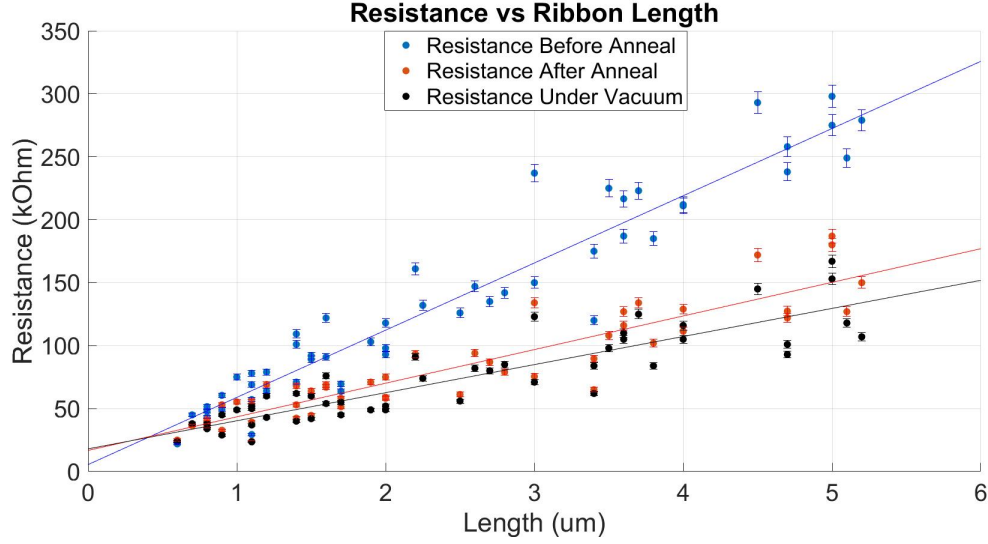


Figure 3.4: Four-points resistance of graphene nanoribbons versus length before annealing, after annealing and in vacuum at room temperature, dashed line is linear fit of measured data. Width of these ribbons are between $80nm$ to $100nm$.

The blue dots are the 4-points resistance obtained before the Ar annealing and the red dots are after Ar annealing, and black dots are measured in vacuum. All data points are measured at room temperature and error bars are from measurement fluctuations. Corresponding linear fit (dashed lines) are also shown in the figure. Specifically, linear fit of resistance before thermal annealing is $R_1(L) = 53.38(\pm 3.21) \times L + 5.51(\pm 4.23)$ and becomes $R_2(L) = 26.7(\pm 2.84) \times L + 16.76(\pm 2.39)$ after thermal annealing. This relation changes to $R_3(L) = 22.31(\pm 2.29) \times L + 18.01(\pm 2.56)$ for measurement done in vacuum. L has unit in μm and $R(L)$ has unit in $k\Omega$. It is seen that resistance has decreased a lot after annealing in Ar with the decreasing amount depending on the length of the ribbons, which shows cleaning effect of this annealing process. Also, linear fitting for values after annealing show a clear non-zero intercept, which indicates that at least one ballistic channels are involved in the electron transport. In contrast, resistance versus length fitting for values before annealing show an intercept very close to zero.

From Equation 1.12 and Figure 1.14, the mean free path of the ballistic channel is given by $\lambda_0 \approx \frac{R_0}{dR/dL} = \frac{25.8k\Omega}{dR/dL}$. Therefore, with the slopes of $R(L)$ fit, we can obtain the mean

free path of ballistic channel as $0.46\mu m$, $0.94\mu m$ and $1.2\mu m$ before, after annealing and measured in vacuum, respectively. These values are smaller than the SWGNRs in UHV, which might be due to the buffer layer that has strong interaction with the substrate, resist residue and various environmental contamination such as organic molecules that are not easily removed.

If we have a ballistic channel with long mean free path, we can separate the conductance of this channel from other diffusive channels from using Equation 1.16. If we assume all bulk states have the same mean free path, Equation 1.16 can be rewritten into an edge conduction and bulk conduction

$$G(L) = \frac{e^2}{h} \frac{1}{1 + L/\lambda_{edge}} + \sum \frac{e^2}{h} \frac{1}{1 + L/\lambda_{bulk}} \quad (3.1)$$

where the first term on the right-hand-side comes from the edge conduction and the second term comes from the bulk.

Monolayer graphene on the Si-face has an electron density around $5 \times 10^{12} \text{cm}^{-2}$ and the Fermi energy is given by Equation 1.14 and approximately equal to 0.253eV . Also, energy difference between each energy level is $\Delta E = 0.02 \text{eV}$, according to Equation 1.5 (assuming width 100nm). So there are totally $\frac{0.253}{0.02} \times 4 \approx 50$ channels involved in the electron transport (factor of 4 comes from the spin and valley degeneracy). We can use Equation 1.15 to fit λ_{edge} and λ_{bulk} with the data after annealing and measured in vacuum. Figure 3.5 shows the fitting curve with $\lambda_{edge} \approx 1.1\mu m$ and $\lambda_{bulk} \approx 4 \text{nm}$. The mean free path of the ballistic channel is very close to what we get from calculating the slope, which confirms that at long length scale, ballistic channel dominates the transport.

The mean free path of the bulk $\lambda_{bulk} \approx 4 \text{nm}$ from measurements in vacuum corresponds to a mobility around $250 \text{cm}^2 \text{V}^{-1} \text{s}^{-1}$, assuming charge density $5 \times 10^{12} \text{cm}^{-2}$. This value is significantly lower than values in two-dimensional Hall bar geometry, which is about $700 \text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ at room temperature. This decrease of conductivity and mobility in

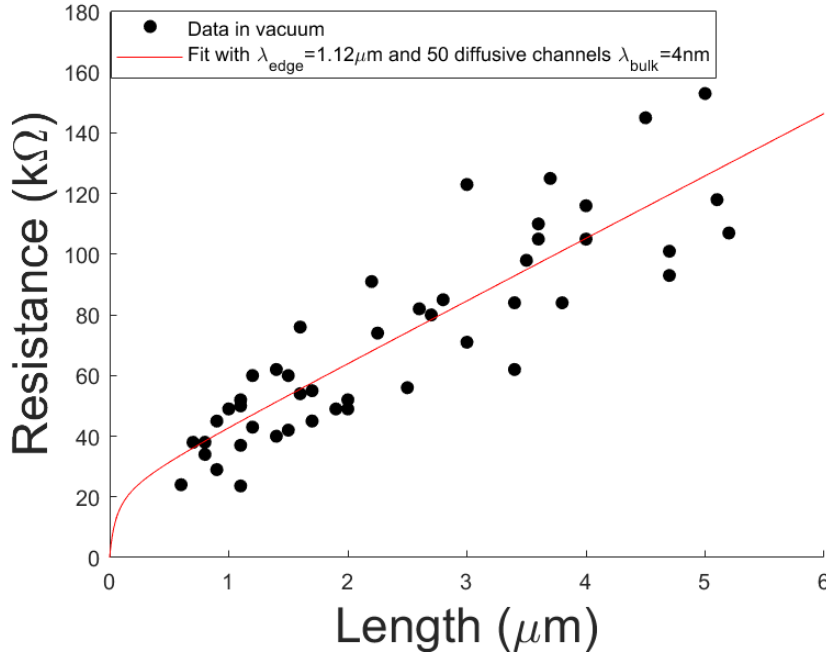


Figure 3.5: Resistance versus length after annealing, measured in vacuum, same as the black data points in Figure 3.4. Red line is the fitting using Equation 3.1.

etched graphene nanoribbons might be due to the lateral confinement of 1D nanoribbon and contamination from e-beam resist. But overall we can see that the resistivity of bulk states decreases a lot, possibly due to removing contamination and reducing scattering events by thermal annealing process.

3.2 Graphene Nanoribbons on SiC(0001) with Metal Contacts

Results from previous section are not inconsistent with the presence of a special channel with long mean free path up to around $1\mu m$ on etched graphene nanoribbons on SiC (0001). However, although amorphous carbon contacts can endure high temperature annealing, they are relatively high resistance and sometimes have unstable interface with graphene at low temperature[106]. Therefore, we want to fabricate graphene nanoribbons devices with metal contacts while keeping a thermal annealing process after etching ribbons.

Segmented Ribbon Devices

The fabrication process flow for the graphene nanoribbon devices with metal contacts is shown in Figure 3.6a. Similar to previous section, negative e-beam resist MaN-2403 is spin-coated, then patterned with e-beam lithography. O_2 plasma is used to etch the excessive graphene and define the ribbons and the chip is annealed at $1200^\circ C$ in vacuum to smooth the edges. Then the chip is immediately transferred within a minute to the e-beam evaporation chamber and covered with $5nm$ of Al_2O_3 . Positive e-beam resist MMA/PMMA is then used for contact patterning and serves as a mask to open windows in Al_2O_3 by ICP dry etching with BCl_3 gas. $30nm/20nm$ of Pd/Au are deposited and then lift-off through those openings. The width of ribbons is about 150 nm and the lengths are varied.

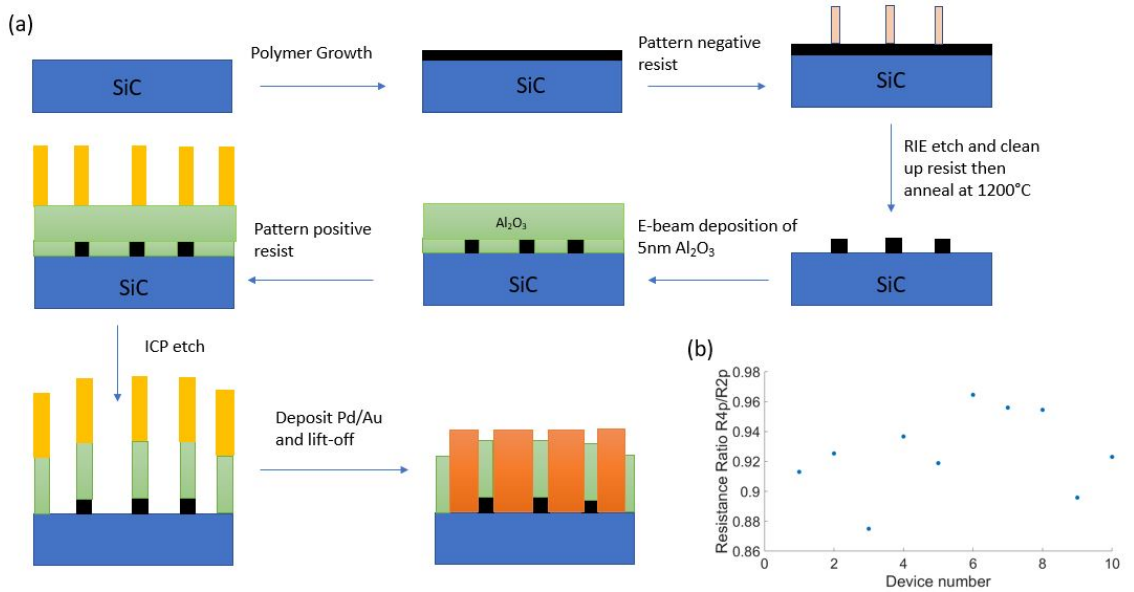


Figure 3.6: (a) Schematics diagram of fabrication process flow of etched ribbon devices with side contacts. (b) Measurements of resistance ratio R_{4p}/R_{2p} .

In this device configuration, probes are in contact with graphene through one-dimensional side contacts. As shown in Figure 3.7, a single ribbon is cut into pieces through ICP process and those gaps are filled with metals. Therefore, voltage probes in this case interrupt the ribbon and are completely invasive. Electrons which enter the probes are injected back

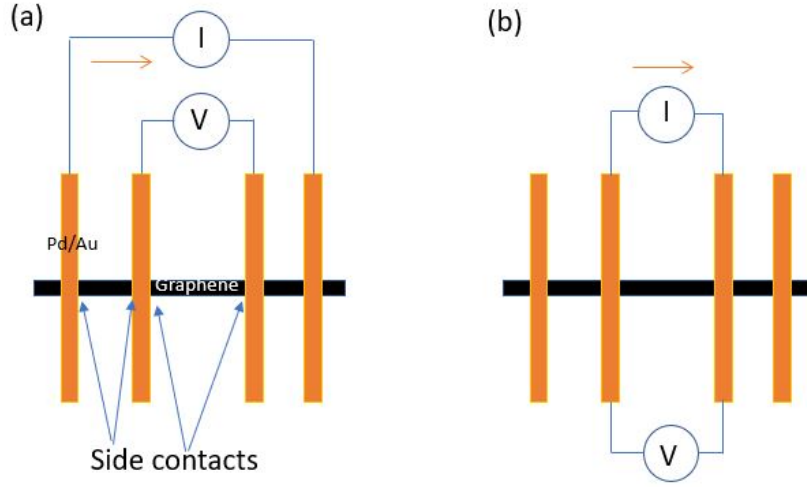


Figure 3.7: Schematic diagram of top view of the segmented ribbon devices. Measurements are done with (a) 4-points resistance R_{4p} and (b) 2-points resistance R_{2p} configurations.

to the system with losing information regarding the phase [107][108]. We conduct 4-points and 2-points resistance measurements using the configurations in Figure 3.7. In this case, the resistance ratio between 4-points and 2-points resistance on a ballistic conductor is $\frac{R_{4p}}{R_{2p}} = \frac{P}{2-P}$ [109] and P is the probe invasiveness. For a perfect invasive probe, it is equal to 1. Therefore, we should have $R_{4p} = R_{2p}$ for devices shown in Figure 3.6a. In contrast, non-invasive voltage probes on a ballistic conductor ($P = 0$) leads to $R_{4p} = 0$. In more common cases, probe invasiveness P is between 0 and 1, such as the device shown in Figure 3.2a, where amorphous carbon contact is on top of the ribbon. Figure 3.2b shows measurements of resistance ratio R_{4p}/R_{2p} , which is about 0.92. Note that R_{2p} includes both lead resistance R_{lead} and contact resistance $R_{contact}$. If we subtract $R_{lead} + R_{contact}$ contribution from R_{2p} , the resistance ratio R_{4p}/R_{2p} would be more closer to 1, confirming perfectly invasive probes in this configuration. $R_{2p} - R_{4p}$ are all between $5 - 10k\Omega$, indicating relatively low contact resistance between metal and graphene as well.

Figure 3.8a shows the 4-points resistance of several ribbons with width $150nm$ versus ribbon length, measured at room temperature. It clearly shows a non-zero intercept at

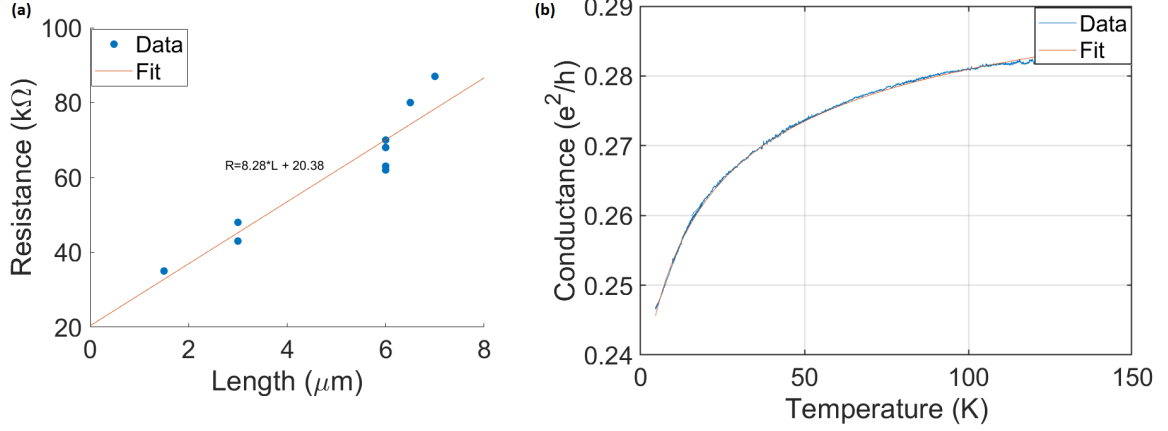


Figure 3.8: **(a)** Four-points resistance of graphene nanoribbons versus length and linear fit. Width is about $150nm$. Measured at room temperature **(b)** Temperature dependence plot of conductance. This ribbon length is $6\mu m$. The data is fitted by Equation 3.2.

around $20k\Omega \approx 0.8R_0 = 0.8\frac{h}{e^2}$ at $L=0$. Remarkably, this value is very similar to that found for a single channel ballistic conduction on the SiC sidewalls [69][1]. If we assume there is a single ballistic channel, the electron mean free path is $3.1\mu m$ from Equation 1.12. This value is significantly larger than the value using amorphous carbon contacts in the previous section. Possible explanations are due to the Al_2O_3 protection layer right after thermal annealing process, which effectively reduces contamination and scattering centers from air and later process.

The conductance $G(T) = 1/R(T)$ increases monotonically with increasing temperature, as shown in Figure 3.8b. This behavior is reminiscent of the result from sidewall graphene nanoribbons[1]. To illustrate the similarity, we use the equation from [1]

$$G(T) = \alpha \frac{e^2}{h} \left[1 + 0.5 \exp \left\{ - \left(\frac{T^*}{T - T_0} \right)^{1/2} \right\} \right] \quad (3.2)$$

to fit the temperature dependent data. As shown in Figure 3.8b, the fit is remarkably well, with $\alpha = 0.233$, $T^* = 7.36K$ and $T_0 = 5.21K$. The expected activation temperature T^* is given by [1]

$$T^* = 1.4 \frac{\pi \hbar v_f}{k_B L}, \quad (3.3)$$

which relates T^* to ribbon length L . For a $6\mu m$ length ribbon, expected value $T^* = 5.6K$, which is close to what we get. Equation 3.2 and Equation 3.3 resembles Mott's expression for one-dimensional variable range hopping[110]. It consists of a temperature independent constant conductance term that includes one ballistic channel along with other diffusive channels, and a thermally activated transport channel. In [1], this temperature dependent channel is attributed to 0_- mode that is related with $E_{1,0}$ mode in Equation 1.5. Following the argument in that reference, charge carrier lifetime $\tau = 4\pi\hbar/k_B T^* = 1.3 * 10^{-11}s = 2.16L/c^*$, which is on the order of (but larger than) the ballistic transit time through the ribbon, similar to the case in sidewall graphene nanoribbons[1].

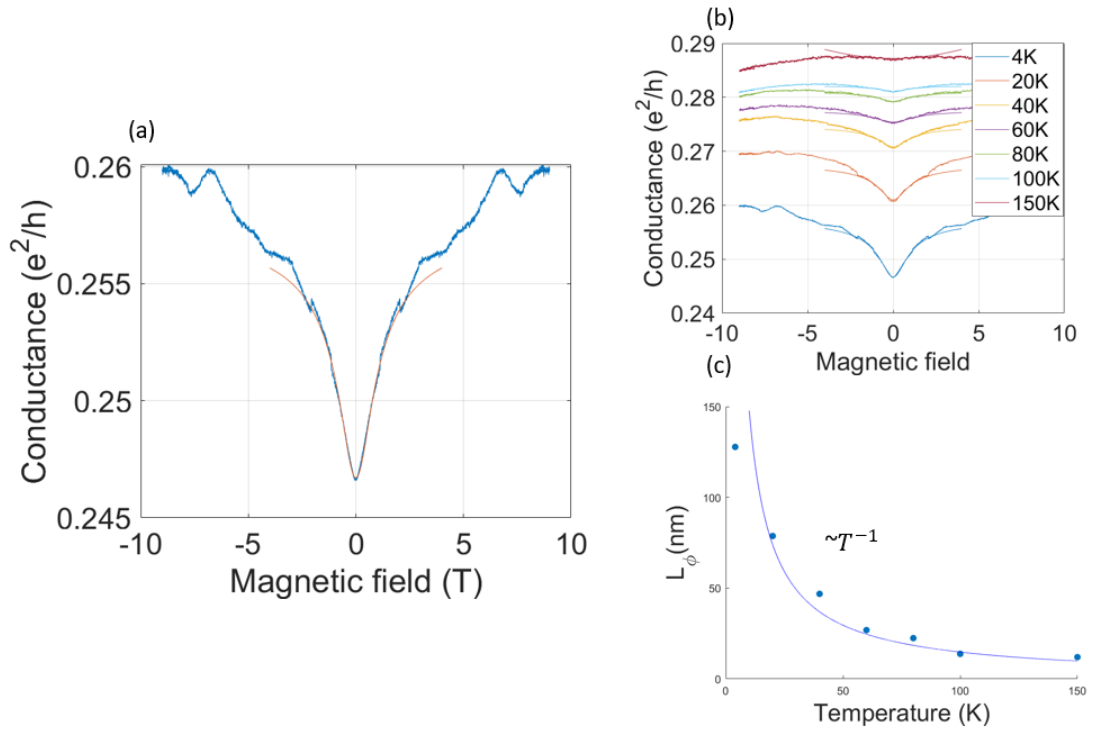


Figure 3.9: **(a)** Magnetoconductance (in units of quantum conductance) versus applied magnetic field. Measured at 4K. Fit with weak localization equation Equation 3.5 **(b)** Magnetoconductance versus applied magnetic field at different temperature from 4K to 150K. Fit with Equation 3.5. **c** Phase coherence length L_ϕ versus temperature from fitting.

Figure 3.9a shows the 4-points conductance $G(B)$ with respect to magnetic field. The magnetic field was applied perpendicular to the device and the substrate. The prominent feature is this V-shape positive magnetoconductance. At $T=4K$, $G(B)$ increases almost

linearly with magnetic field up to about 2-3T. At larger magnetic field, it changes its slope and increases more slowly and starts to have oscillations, possibly due to SdH oscillations. Similar features have been observed in multi-wall carbon nanotubes and SWGNRs, shown in Appendix D. [111][1].

The most intuitive way to explain this positive magnetoconductance is Weak localization (WL) effect. It originates from the constructive interference of backscattered electronic wavefunctions, which increases the probability of localizing an electron. This phenomenon manifests itself by an increased resistance at zero magnetic field, which is easily broken by applying a magnetic field to destroy coherent superposition. Temperature increases electron dephasing rate, which also suppresses WL effect, and this is shown in Figure 3.9b. As the temperature raises, the magnetoconductance dip gradually reduces. The change in resistances upon applied magnetic field are 6% at 4K and drops to 3.4%, 1.5%, 0.78% at 20K, 40K and 60K, respectively. At 150K, this V-shaped positive conductance has almost vanished.

In a weak magnetic field, there is a phase difference ϕ developing between clockwise and counterclockwise electron propagation around a closed loop, which is equal to [112]

$$\phi = \frac{2eBS}{\hbar} = \frac{2eBS}{\hbar} = \frac{2S}{l_m^2}, \quad (3.4)$$

where S is the area of the enclosed loop and l_m is defined as $\sqrt{\frac{\hbar}{eB}}$. Different loop areas both contribute to the WL effect. In a magnetic field when the loops area is on the order of l_m^2 , the contribution to the WL effect is almost vanished because on average the two trajectories no longer interfere constructively[112]. Therefore, the critical magnetic field to destroy the coherent backscattering is approximately $B_c \approx \frac{\hbar}{eL_\phi^2}$ where L_ϕ is the phase coherent length[74]. In a narrow channel, the critical field is greatly enhanced due to flux cancellation effect. Briefly speaking, an electron travels ballistic between two channel boundaries and its trajectories enclose two loops with the same area but opposite direc-

tion, so it encloses zero flux[112]. Therefore, in a narrow wire, the critical magnetic field increases to $B_c \sim \frac{h}{eWL_\phi}$ where W is the width of the channel[74].

One dimensional weak localization correction of magnetoconductance is given by [113]

$$G(B) - G(0) = -\frac{2e^2L_\phi}{h} \left[\frac{1}{\sqrt{1 + \frac{1}{3}B^2/B_\phi B_\perp}} - 1 \right] \quad (3.5)$$

where $B_\perp \equiv \hbar c/eL_\perp^2$, $L_\phi \equiv \sqrt{D\tau_\phi}$ and $B_\phi \equiv \frac{\hbar c}{4De\tau_\phi}$ with τ_ϕ is the phase relaxation time [113]. We use this equation to fit the magnetoconductance data at low magnetic field ($B < 0.5T$) plotted in Figure 3.9a at 4K with two parameters L_ϕ and $B_\perp$. The fitted line is shown in the figure with fitting parameter $L_\phi \approx 120nm$ and $B_\perp \approx 0.1T$. We can see that the fitting is reasonably well at low field region. We also fit the magnetoconductance data at several different temperatures up to 150K with Equation 3.5, and values of L_{phi} versus temperature are shown in Figure 3.9c. Also, phase-coherence length seems to follow a power law dependence $L_\phi \propto T^{-1}$, consistent with the trend seen in epigraphene on the C-face [114], indicating dephasing mechanism being the electron-electron interaction with small energy transfer. Moreover, phase-coherence length tends to saturate at low temperature, which might be attributed to the finite dephasing rate at low temperature when phase-breaking length becomes comparable to the length of the wire [115][116].

However, the fitting equation has magnetic field range up to $2\pi B_\perp \approx 0.3T$ and therefore does not apply to the strong magnetic field up to 3T and fails to explain the saturation of magnetoconductance. Moreover, the T^{-1} temperature dependence of phase coherent length is only valid in two-dimensional channel, which contradicts the 1D weak localization assumption. In contrast, 1D channel should have a temperature dependence of $T^{-\frac{1}{3}}$ [112][117].

Later, evidence from non-polar SiC substrate epigraphene measurements points out that this V-shape positive magnetoconductance results from edge conduction. This peak is missing from edgeless Corbino ring geometry measurement but emerges from standard

Hall bar devices[42]. Moreover, this anomalous increase of magnetoconductance are also shown in charge-neutral SWGNRs and carbon nanotubes, which proves that this behavior is due to the edge state instead of bulk subbands. However, since the edge state is an one-dimensional channel, there is no backscattering along the ribbon. Therefore, one feasible explanation is that the WL effect happens at the metal contact interface with the graphene. This theory needs to be further studied.

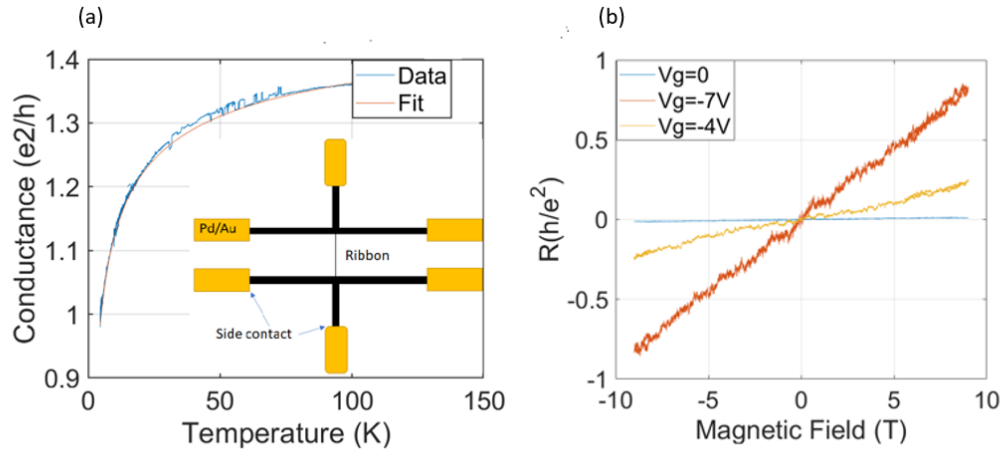


Figure 3.10: **(a)** Temperature dependence plot for 4-points conductance. Fit with Equation 3.2. Inset: schematic diagram of graphene nanoribbon hallbar device. Gate pad and dielectric are not shown. **(b)** Hall Resistance at $V_g=0, -4, -7V$.

Also, we fabricate Hallbar nanoribbon device that consists of a single nanoribbon connecting with graphene leads, shown in Figure 3.10a inset. Metal pads are contacting with graphene leads through one-dimensional side contacts and the fabrication process is similar to previous devices. Finally, Al_2O_3 and Al are deposited to serve as dielectric and gate material. This ribbon is $1.5\mu m$ long and $110nm$ wide. Figure 3.10a plots the temperature dependence of 4-points conductance measured from 100K to 4K. Conductance decreases as the temperature drops, with a similar shape shown in Figure 3.8. We adapt the same equation Equation 3.2 to fit the data and fitting is reasonably well. The fitting parameters are $\alpha = 0.965$, $T^* = 11.43K$ and $T_0 = 4.55K$ (compared with $T_m^* = 7.5K$

with $T_p^* = 1.4\pi\hbar c^*/k_B L$). These numbers are of the same order of magnitude as a single ribbon device shown previously, indicating a similar thermally activated transport channel between these two devices.

We can apply a gate voltage to tune the charge density within the channel. To decrease electron doping level, we need to apply a negative gate voltage. Shown in Figure 3.10b are Hall resistance under three different gate voltages $V_g = 0V, -4V$ and $-7V$. From the slope of the Hall resistance, we can calculate the electron density as $1.85 \times 10^{13} cm^{-2}$, $9.26 \times 10^{11} cm^{-2}$, $1.78 \times 10^{11} cm^{-2}$ at gate voltage $0V, -4V$ and $-7V$, respectively. Those numbers are consistent with conventional Hall bar measurement on Si-face graphene[118]. 4-points magnetoconductance with respect to magnetic field exhibits a sharp V-shaped positive peak between $\pm 2T$ for different charge density level, shown in Figure 3.11a. This confirms this V-shaped peak is universal in different doping level, and therefore not likely from a bulk subband, more likely from edge states that are at $E = 0$ level.

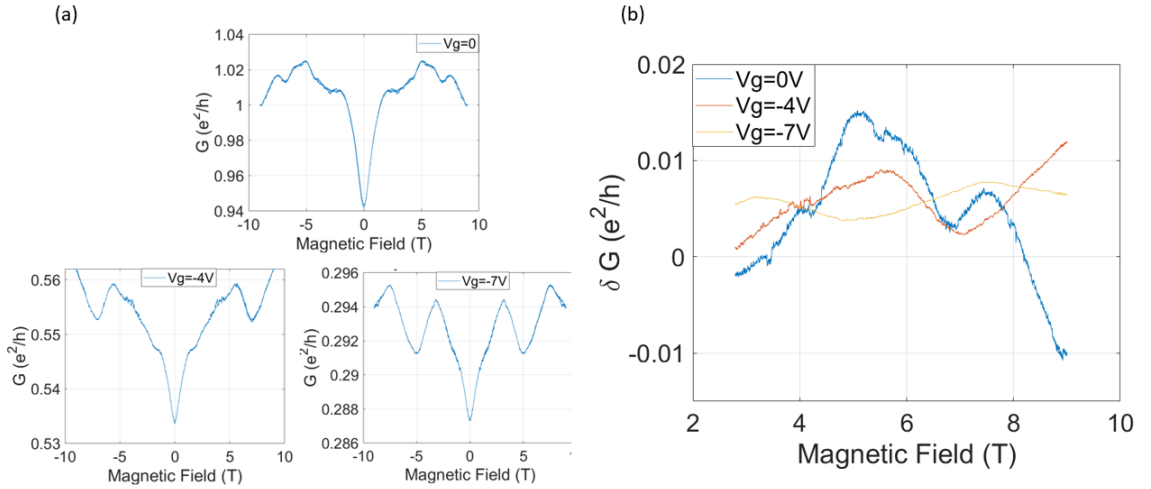


Figure 3.11: **(a)** Magnetoconductance of ribbon hallbar devices at 4K at $V_g = 0, -4, -7V$. **(b)** The residual magnetoconductance used to estimate electron density from Equation 3.6.

Also, we can subtract a smooth background from magnetoconductance from plots in Figure 3.11a and residual resistance left is plotted in Figure 3.11b. SdH oscillations can be

observed and we can estimate the charge density by the oscillation of the peaks

$$n_s = \frac{4e}{h(1/B_1 - 1/B_2)} \quad (3.6)$$

where B_1 and B_2 are the local maximum of the magnetoconductance [56]. Using Equation 3.6, we estimate the charge density to be $1.59 \times 10^{13} \text{cm}^{-2}$, $9.65 \times 10^{11} \text{cm}^{-2}$, $2.03 \times 10^{11} \text{cm}^{-2}$ at gate voltage 0V, -4V and -7V, respectively, which corroborate the numbers obtained from Hall resistance. With the 4-points resistance and charge density numbers, we estimate the mobility to be around $1156 \text{cm}^2 \text{V}^{-1} \text{s}^{-1}$, independent of gate voltage, which is lower than 2-dimensional Hallbar devices, for example, in Appendix A. This might be due to the lateral confinement of the graphene nanoribbon and therefore, increase the overall resistance.

3.3 Summary

In this chapter, we have demonstrated that etched graphene nanoribbons on the Si-face have a ballistic transport channel and show similar results to SWGNRs. These electrical transport results show distinguished transport behaviors than other etched nanoribbons in the literature. With high temperature thermal annealing and improved fabrication process flow to smooth edges and minimize contamination, edge state channels reveal mean free path on the order of μm and positive V-shape magnetoconductance. Next chapter we switch the focus on graphene devices on non-polar facet of SiC.

CHAPTER 4

EDGE STATES OF EPIGRAPHENE ON NON-POLAR FACETS

In this chapter, I discuss the fabrication and measurements of epigraphene Hallbar devices on non-polar SiC facets. Two samples with different fabrication processes are presented here to explore how the fabrication process affects the properties of ballistic edge state channels with long mean paths.

4.1 Sample TKYU1 Hallbar

Sample TKYU1 is on 4H-SiC AC orientation 37° facet. Conducting SiC wafer is cut and polished in TICNN. The bare SiC chip was annealed at 1500°C for 30 minutes in Ar atmosphere to flatten the surface and followed by graphene growth at 1600°C for one hour. I used Raman spectroscopy to identify low-strain monolayer graphene patches on the surface. Before depositing the protective Al_2O_3 layer, the chip was annealed at 1000°C for 30 minutes in vacuum to remove contamination or molecules on surface and then immediately transferred to e-beam evaporation chamber for deposition. Therefore, the interface between graphene and Al_2O_3 is always clean and graphene is protected in the following fabrication process later, shown in Figure 4.1a. After depositing 5nm of Al_2O_3 as the protection layer, the sample went through the EBL process to define channel region (in this case, a Hallbar shape) and another thick layer 20nm Al_2O_3 was deposited followed by lift-off in acetone. This thick Al_2O_3 serves as a mask for inductive-coupled plasma (ICP) etch. This powerful plasma etch can remove the excess Al_2O_3 and the unmasked graphene. The chip is then annealed at 1200°C for 15 minutes. The Al_2O_3 will shrink slightly near the edges due to compressive strain release. Therefore, a second ICP etch and vacuum annealing is needed to ensure smooth edges and a uniform dielectric thickness. Then a second EBL step is used to pattern contacts and subsequently Pd/Au with a thickness of $20\text{nm}/30\text{nm}$ is deposited

to make one-dimensional side contacts. Figure 4.1**b** displays the AFM image of a device with contacts that overlaps with the Hallbar graphene/ Al_2O_3 leads. Finally, an additional $15nm$ Al_2O_3 and $30nm$ of Al is deposited as a gate dielectric and gate metal. Additional characterization results of annealed Al_2O_3 on graphene can be found in Appendix B.

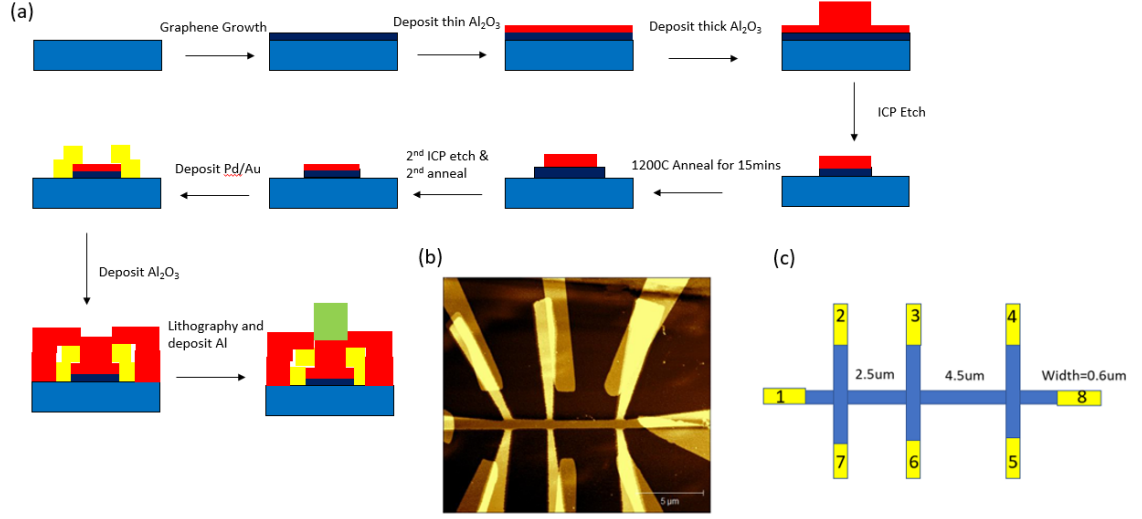


Figure 4.1: (a) Fabrication process flow of sample TKYU1. (b) AFM image of device before dielectric and gate deposition. Hallbar channel is graphene/ Al_2O_3 stack and leads are Pd/Au. (c) Schematic notation of Hallbar device and channel dimension.

The Hallbar consists of 3 transverse arms and totally 8 leads which are labeled in Figure 4.1c. Lengths of these two segments are $2.5\mu m$ and $4.5\mu m$ and width is $0.6\mu m$. The Hallbar channel is along the AC direction. We use the following notation for the resistance and conductance measurement:

$$R_{ij,kl} = V_{kl}/I_{ij}, G_{ij,kl} = 1/R_{ij,kl} \quad (4.1)$$

Recall from the first chapter, for electrical transport in 1D system, ignoring the interference effect and interband scattering, we can separate the Landauer's equation into edge

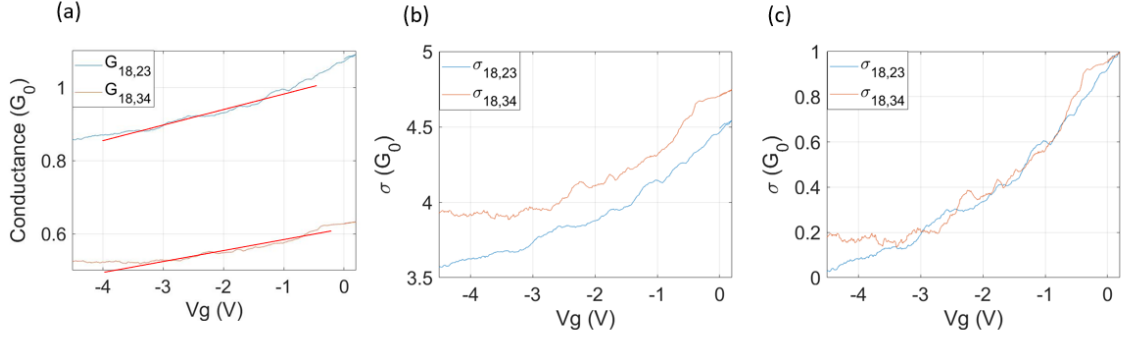


Figure 4.2: **(a)** Conductance change of segments $G_{18,23}$ and $G_{18,34}$ with respect to gate voltage from $0.2V$ to $-4.5V$ at $4K$ **(b)** Conductivity versus gate voltage V_g from $0.2V$ to $-4.5V$ by Equation 4.4. **(c)** Bulk conductivity after subtracting edge state conductance contribution by Equation 4.5

conduction and bulk conduction

$$G = G_{edge} + G_{bulk} = \frac{e^2}{h} \frac{1}{1 + L/\lambda_{edge}} + \sum_{n=1}^M \frac{e^2}{h} \frac{1}{1 + L/\lambda_{bulk}}, \quad (4.2)$$

which assumes there is an edge channel 0_+ that has long mean free path and other states (including 0_-) are in diffusive regime at low temperature. When we apply the gate voltage V_g on the devices, the Fermi level moves away or toward CNP and therefore, number of bulk states are either filled or depleted. But since the edge state pins the Fermi level at $E = 0$ due to very large density of states at the edge[119], the edge conduction stays constant despite carrier density change induced by V_g . Therefore

$$G(V_g) = G_{edge} + G_{bulk}(V_g) = \frac{e^2}{h} \frac{1}{1 + L/\lambda_{edge}} + (ne\mu) \frac{W}{L}, \quad (4.3)$$

where the carrier density n is related with gate voltage V_g . Figure 4.2a plots the conductance of two segments $G_{18,23}$ and $G_{18,34}$ versus gate voltage sweep at $4K$ temperature. Both segments' conductance decrease as the gate voltage turns negative, indicating a n-type doping on the channel. $G_{18,34}$ clearly reaches a minimum plateau while $G_{18,23}$ has a rounding minimum. These conductance differences near CNP may be due to the charge inhom-

geneities caused by the gate dielectric. In either cases, we can extrapolate the measured conductance away from the rounding at CNP to give $G_{18,34}^{Res} = 0.5G_0$ and $G_{18,23}^{Res} = 0.85G_0$. The conductance values of the two segments at CNP can be used to determine the mean free path of the edge channel, assuming that the conductance of the edge state is $1G_0$ [119]. From Equation 4.3, the mean free path of this edge channel λ_{edge}^{AC} is found to be $\approx 5\mu m$, consistent with [119].

Also, we can confirm this edge channel by calculating the conductivity

$$\sigma_{18,23/34} = \frac{L}{W} G_{18,23/34}. \quad (4.4)$$

For diffusive ribbons, conductance depends on width over length ratio but conductivity should be the same for two segments. However, from Figure 4.2b, we can clearly see that the conductance difference between the two ribbons is approximately constant. Instead, if we subtract the minimum conductance at CNP from the total conductance and calculate the bulk conductivity,

$$\sigma_{18,23/34bulk} = \frac{L}{W} (G_{18,23/34} - G_{18,23/34@CNP}). \quad (4.5)$$

we find that the resulting conductivity of the two segments are essentially the same, as shown in Figure 4.2c. We deduce that the conductance at CNP is due to the ballistic edge edge state which does not scale as L/W . These results are quantitatively similar to what we found in [119].

Figure 4.3 plots the Hall measurements $R_{18,36}$ at two gate voltages $V_g = 0V$ and $-3.5V$. At $V_g = 0V$, we can see a plateau near $R_{Hall} \approx 0.25R_0$. This quantized plateau is unusual, since for monolayer graphene the Hall plateau should be at $\frac{1}{4n+2} \frac{h}{e^2}$. For bilayer graphene, the Hall plateau appears at the $\frac{1}{4n} \frac{h}{e^2}$, which suggests that the channel is a bilayer graphene. However, the conductance of CNP from the edge conductance channel effectively shorts the bulk Hall voltage, by the current through the bulk by roughly half. For

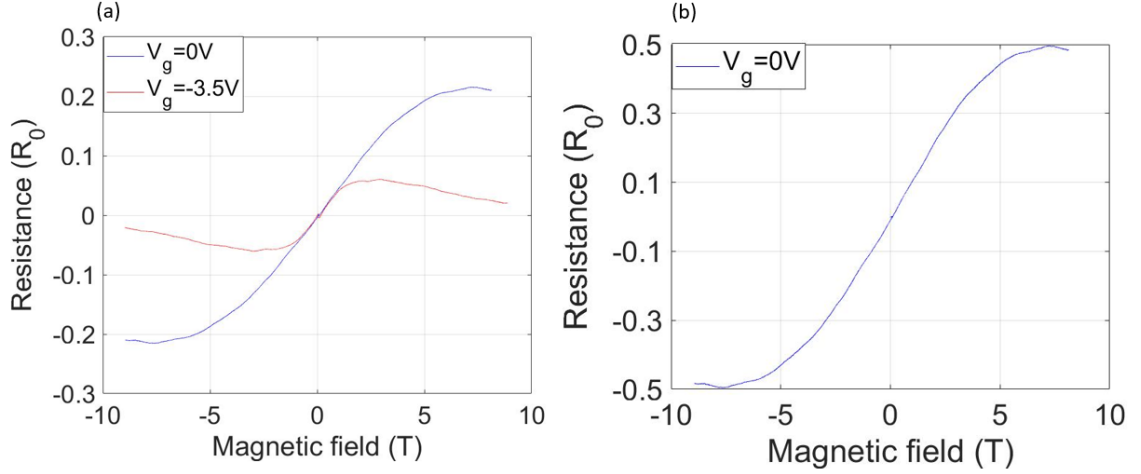


Figure 4.3: **(a)** Hall resistance of $R_{18,36}$ with respect to magnetic field at 4K with gate voltage $V_g = 0V$ or $-3.5V$. **(b)** Hall resistance after subtracting the edge conduction current.

$V_g = -3.5V$ at the CNP, the Hall resistance essentially vanishes at high magnetic fields, shown in Figure 4.3a. Since the polarity of the Hall voltage corresponds to the polarity of the charge carriers, the vanishing of the Hall voltage at CNP indicates that the transport involves equal electron and hole contributions, as in a perfectly compensated semimetal. However in a semimetal, two subbands must be involved, but the conductance of the edge state is $1G_0$ which implies that only one subband involves. There is no simple explanation for this discrepancy. As mentioned above, the edge state produces a current but no Hall voltage. Therefore it effectively reduces the measured Hall resistance of the bulk. We subtract the edge state current contribution from Hall resistance,

$$R_{\text{bulk}}^H(V_G, B) = \frac{V^H(V_G, B)}{I_{\text{bulk}}} = R_{\text{meas}}^H(V_G, B) \left(1 - \frac{G^L(V_{G=\text{CNP}}, B)}{G^L(V_G, B)} \right)^{-1} \quad (4.6)$$

and plot the results in Figure 4.3b. We can now clearly recover a conventional $0.5R_0$ monolayer graphene quantum Hall plateau, consistent with a single layer graphene. From the bulk Hall voltage we can determine the bulk charge density as $2 \times 10^{11} \text{cm}^{-2}$ at $V_g = 0V$ by calculating the slope of Hall resistance at low magnetic field. From the bulk conductivity

in Figure 4.2c, we can find the mobility of the bulk to be around $928 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and mean free path of bulk $\lambda_{bulk} = 8 \text{ nm}$ at charge density $2 \times 10^{11} \text{ cm}^{-2}$. The mean free path of the bulk is order of magnitude less than the mean free path of edge state channel 0_+ , which is about $5 \mu\text{m}$ almost 3 orders of magnitude larger than the values in bulk states.

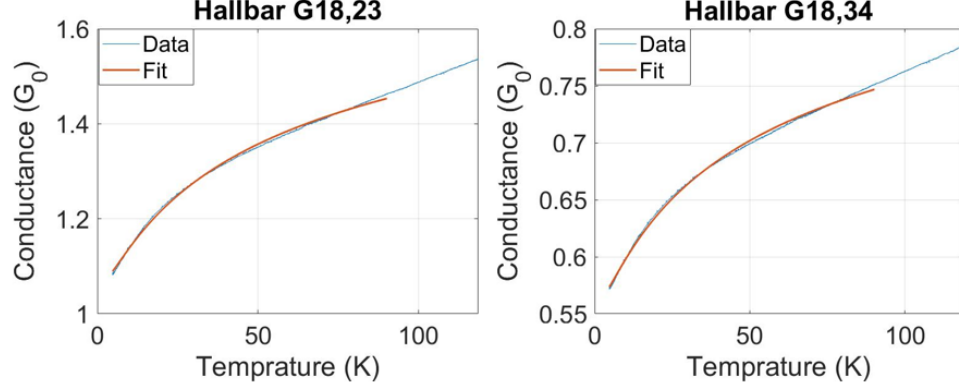


Figure 4.4: Temperature dependent plot of 4-points conductance of $G_{18,23}$ and $G_{18,34}$. Data is fitted with equation Equation 4.7

The temperature dependence of the 4-points conductance measurements is plotted in Figure 4.4. It has a similar trend as observed sidewall graphene nanoribbon and etched graphene nanoribbon on Si-face in last chapter. Therefore, we adapt the similar equation to fit the data

$$G(T) = \alpha \frac{e^2}{h} \left[1 + \beta \exp \left\{ - \left(\frac{T^*}{T - T_0} \right)^{1/2} \right\} \right] \quad (4.7)$$

with fitting parameters $\alpha = 1.0659$, $T^* = 62.64 \text{ K}$, $T_0 = 0$, $\beta = 0.8364$ for segment $G_{18,23}$ and $\alpha = 0.5614$, $T^* = 59.11 \text{ K}$, $T_0 = 0$, $\beta = 0.7422$ for segment $G_{18,34}$. As we can see, the equation fits data very well. The activation temperature is approximately inversely related with sample length.

Figure 4.5 shows 4-point magnetoconductances which exhibit similar V-shape positive magnetoconductance between $-2T$ and $2T$ as in SWGNRs and etched graphene nanoribbons on the Si-face in Chapter 3. This unusual increase of magnetoconductance is attributed to weak localization effect at the contact interface, as discussed in Chapter 3.

Unfortunately, the gate of this sample was failed during a measurement at higher gate

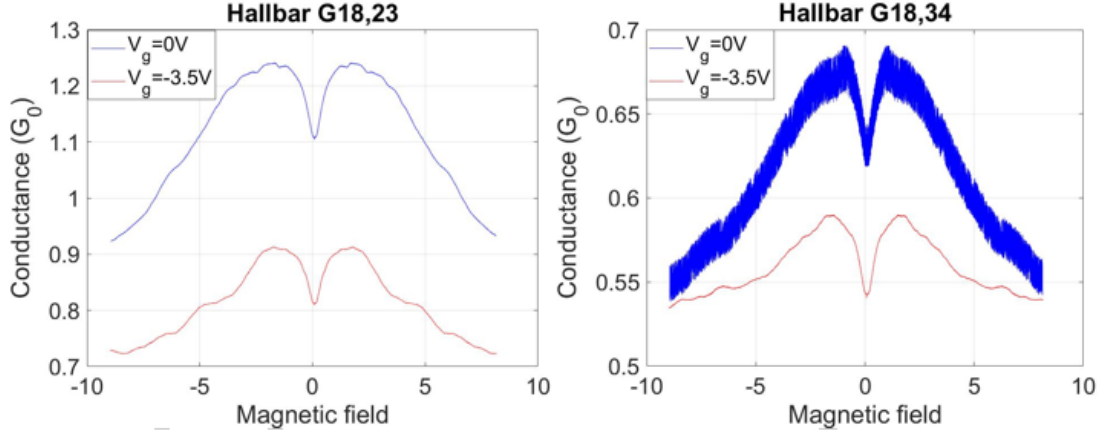


Figure 4.5: Magnetic field dependent plot of 4points magnetoconductance of $G_{18,23}$ and $G_{18,23}$.

voltages. To save this device, we remove the Al_2O_3 and Al using Al etchant type A. Then the sample was rinsed with DI water and then deposited with a new gate stack consisting of $15nm$ of Al_2O_3 and $30nm$ of Al .

Note that Al etchant type A is a standard aluminum etchant for use on silicon devices and other microelectronic applications. It mainly consists of phosphoric acid, acetic acid and very small amount of nitric acid [120]. Metal contacts palladium and gold are not affected by this chemical etchant.

The electric transport measurement shows a significant differences compared with previous run. Figure 4.6a plots the conductivity versus gate voltage sweep. Note that now the conductivity decreases as the gate voltage increases, which indicates a p-type doping. In the previous run, the graphene channel was n-type doped with charge density $2 \times 10^{11} cm^{-2}$. This shows that the p-type doping is due to the wet etching process. Also, the same two segments now have the same conductivity with respect to gate voltage, which implies that the transport system becomes diffusive. For a diffusive conductor, the resistance is proportional to the width over length ratio, which suggests that the ballistic edge states was destroyed in the wet etch process.

The Hall resistance and magnetoconductance are measured with respect to magnetic

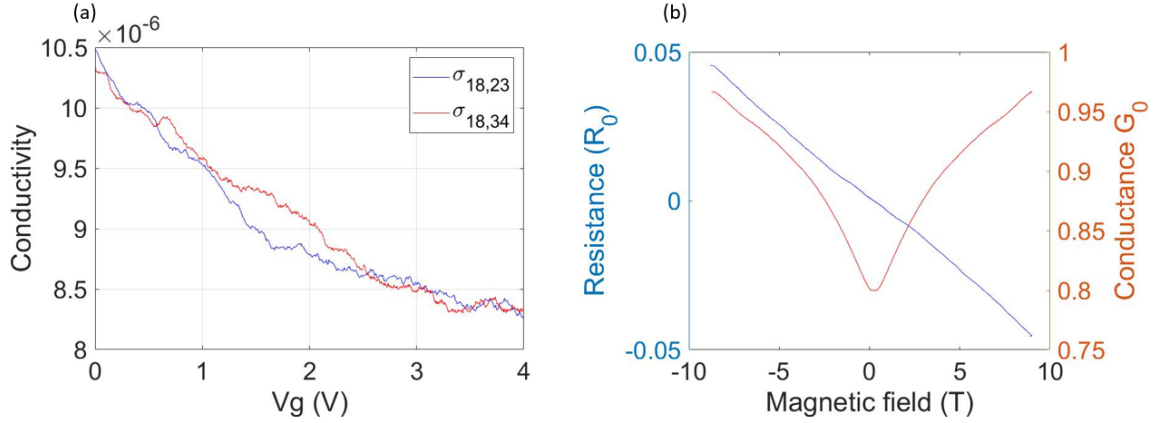


Figure 4.6: Electrical measurement after Al etchant removing gate oxide and gate metal. Sample is then re-deposited with new layer of Al_2O_3 and Al as gate oxide and metal. (a) Conductivity of segments $G_{18,23}$ and $G_{18,34}$ under gate voltage sweep. (b) Hall resistance and magnetoconductance with respect to magnetic field at $V_g = 0$

field, as shown in Figure 4.6b. The polarity of Hall resistance is the opposite as Figure 4.3, confirming the flipping of mobile carriers from electrons to holes. From the slope of the Hall resistance, the charge density is $5 \times 10^{12} \text{ cm}^{-2}$ at $V_g = 0$, which corresponds to a mobility of about $700 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, which is significantly smaller than before. This low mobility indicates that the acids in the wet etching process cause defects. Magnetoconductance also shows an increasing trend with respect to magnetic field without any saturation at high magnetic field. This is also notably different from previous measurements that exhibits saturation at about $\pm 2T$. Diffuse scattering at defects can cause this negative magnetoresistance as is seen in highly disordered materials [121]. When the linear dimension between defects is on the order of 10 nm , this diffuse scattering becomes one of the predominant processes that affects the mean free path of the conduction carriers. An applied magnetic field on the sample will tend to increase the mean free path and hence result in a positive magnetoconductance. This increasing conductance is roughly given by

$$\text{Magnetoconductance} = \frac{l_0}{\delta l} = -K_1 B^{-2}, \quad (4.8)$$

where δl is increment of the mean free path caused by the magnetic field, l_0 is the mean

free path of the carrier without magnetic field, and $K1$ is a constant[122]. This is consistent with our results that the magnetoconductance increases quadratic instead of linear. Note that non-saturating increasing magnetoconductance has been observed in carbon-based materials such as graphite and graphene with ion-irradiation damage [123].

4.2 Sample TKYU3 Hallbar

Sample Fabrication

The previous TKYU1 sample shows strong evidence of a ballistic channel that has long mean path in μm range and vanishing Hall resistance. High temperature annealing seems to be an important factor that most likely bonds the edges to the SiC, as is seen in cross sectional TEM of sidewall ribbons thereby restoring edge state after etching. However, graphene edges are also exposed under high temperature plasma BCl_3 where ion temperatures can locally exceed 5000K. Therefore, we want to see if the edge state can be produced by thermal annealing, without ICP etching and edge passivation using BCl_3 gas species. We also want to see if edge states that are destroyed by acid etching can be restored by high temperature annealing.

The non-polar SiC substrate of sample TKYU3 is the same as TKYU1, which was cut and polished at TICNN. The chip was first annealed at $1550^\circ C$ for 30 minutes to flatten the surface and followed by graphene growth at $1650^\circ C$ for 1 hour. The sample has low-strain graphene as indicated by Raman spectra after SiC background subtraction, shown in Figure 4.7c. The G/S_2 intensity ratio is 0.07, which implies the patch is a single layer graphene. Hallbar structures were fabricated with the process that is described in Figure 4.7a. After the graphene growth, the chip is patterned with positive resist and deposit and lift off using Al_2O_3 . Al_2O_3 serves as a mask for O_2 plasma etch and in this case, it has a Hallbar pattern. After the RIE etch, the chip is dipped in Al etchant to remove Al_2O_3 and was thermal annealed at $1200^\circ C$ for 15 minutes. Then the sample is patterned and deposited with Pd/Au metal contacts and subsequently deposited $15nm$ of Al_2O_3 as gate

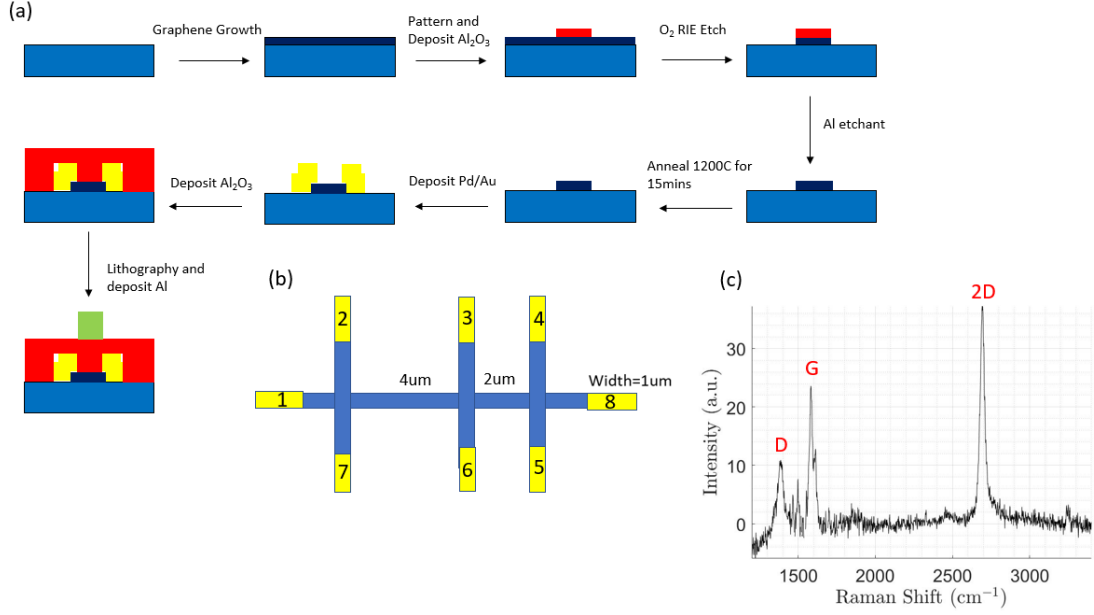


Figure 4.7: (a) Fabrication process flow of TKYU3. (b) Schematic notation of Hallbar device and channel dimension. (c) Raman spectra of sample TKYU3 after background subtraction, showing signature D,G and 2D peaks.

oxide and 30nm of Al as gate metal. This process flow eliminates the ICP etch process and uses Al_2O_3 as mask for the RIE etch to produce the Hallbar structure. The Hall bar consists of 3 transverse arms and in total has 8 leads which are labeled as shown in Figure 4.7b, with channels length 4 μm and 2 μm with width 1 μm . The hall bar channel is along the ZZ direction.

Transport Measurements

As discussed above, for electrical transport in 1D system, ballistic edge state and the diffusive bulk both contribute to the total conductance when charge density is large ($10^{12} cm^{-2}$). Therefore, we can use Equation 4.3 to add up the conductance from edge and bulk conduction.

Figure 4.8a plots the 4-points conductance of two segments $G_{18,23}$ and $G_{18,34}$ with respect to gate voltage. A negative gate voltage depletes charge level and causes the conductance to decrease, indicating the channel is n-type doped. Both these two segments exhibit

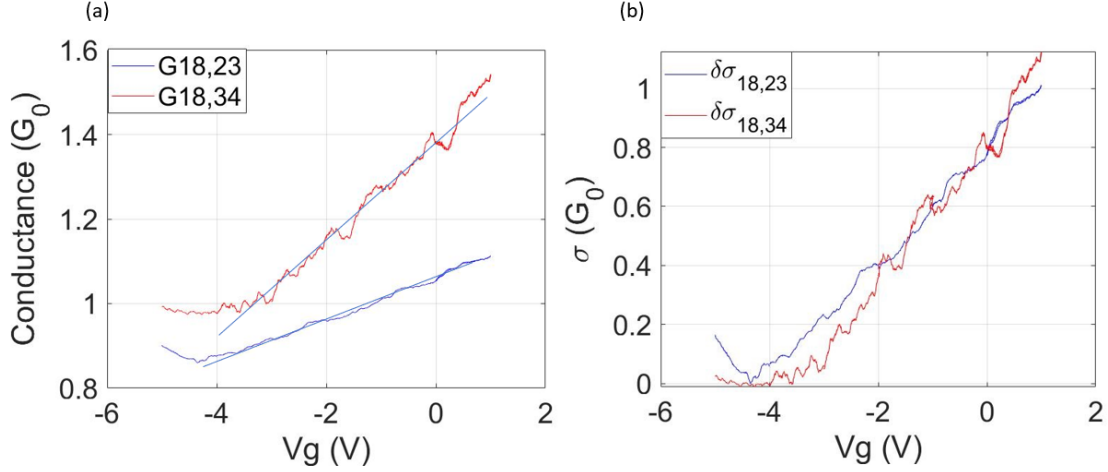


Figure 4.8: **(a)** 4-points conductance versus gate voltage V_g at 4K. Linear extrapolation of conductance reveal large residual conductance at CNP. **(b)** Conductivity calculated with the edge state conductance subtracted.

a minimum conductance slightly less than $1G_0$. Linear extrapolation reveal that residual conductance at CNP is $0.85G_0$ for $G_{18,23}$ and $0.93G_0$ for $G_{18,34}$, which is consistent with a $1G_0$ edge state of the ballistic edge channel in these two segments. Consequently, we find that the mean free path $\lambda_{edge}^{ZZ} \approx 35\mu m$ from the CNP conductance $G_{Res} = \frac{e^2}{h} \frac{1}{1+L/\lambda_{edge}}$.

After we subtract the CNP conductance G_{CNP} from the total conductance, and calculate the conductivity of two segments is

$$\delta\sigma = (G(V_g) - G_{CNP}) \frac{L}{W}, \quad (4.9)$$

as shown in Figure 4.8**b**. We can see that the two curves overlap through out the V_g range. The conductivity increases linearly with V_g indicating almost constant mobility. This shows that the bulk conduction is in the diffusive conduction regime while the edge conduction of 0_+ is ballistic. Using Equation 1.16, we can estimate the mean free path of the bulk transport on the other hand, is approximately $12nm$. We also measure the gate voltage dependence of the conductance of the same segment along the top and bottom edges $G_{18,23}$ and $G_{18,76}$, as shown in Appendix C. Two values are identical which implies that edge state transport involves both sides of the ribbons equally, i.e, the edge state transport is one

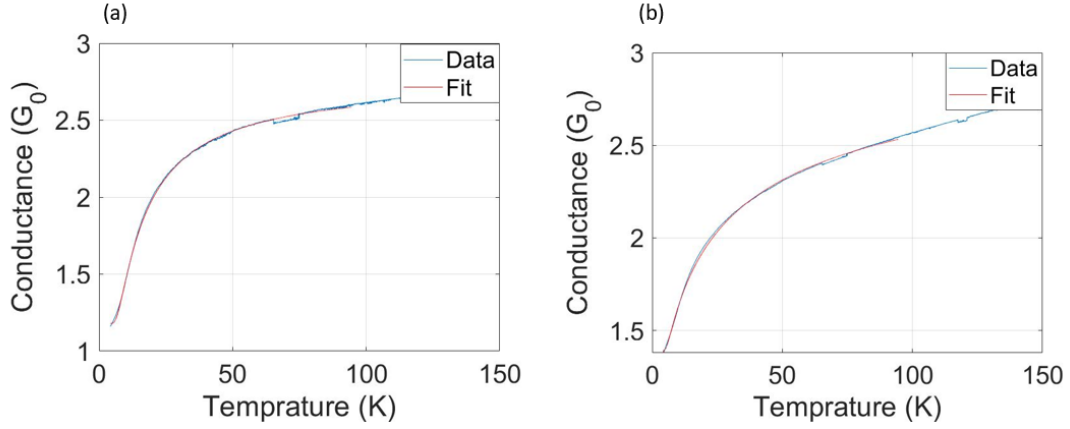


Figure 4.9: 4-points conductance versus temperature from 150K to 4K. Fit with Equation 4.10.

dimensional.

Figure 4.9 plots the conductance versus temperature for the two segments. The temperature dependent conductance measurement is similar to that of TKYU1 and of sidewall graphene nanoribbons [1]. Conductance decreases and saturates as the temperature decreases. We again fit the data to the stretched exponential:

$$G(T) = \alpha \frac{e^2}{h} \left[1 + \beta \exp \left\{ - \left(\frac{T^*}{T - T_0} \right)^{1/2} \right\} \right] \quad (4.10)$$

The fitting parameters are $\alpha = 1.1501$, $T^* = 11.14K$, $T_0 = 3.53K$ and $\beta = 1.34$ for segment $G_{18,23}$ and $\alpha = 1.37$, $T^* = 17.13K$, $T_0 = 0.2K$ and $\beta = 1.15$ for segment $G_{18,34}$. Since the channel width is $1\mu m$, which is comparable with channel length, implies that Hall bar structure has a two-dimensional geometry. However, we observe a one-dimensional thermally activated transport channel that exists in a two-dimensional geometry, which confirms that this temperature dependence channel is caused by the one-dimensional edge state. Hence we conclude that the edge states has two components, 0_+ that is temperature independent, and 0_- that is thermally activated, consistent with observations in SWGNRs.

Figure 4.10a shows the magnetoconductance $G_{18,23}$ with respect to magnetic field at

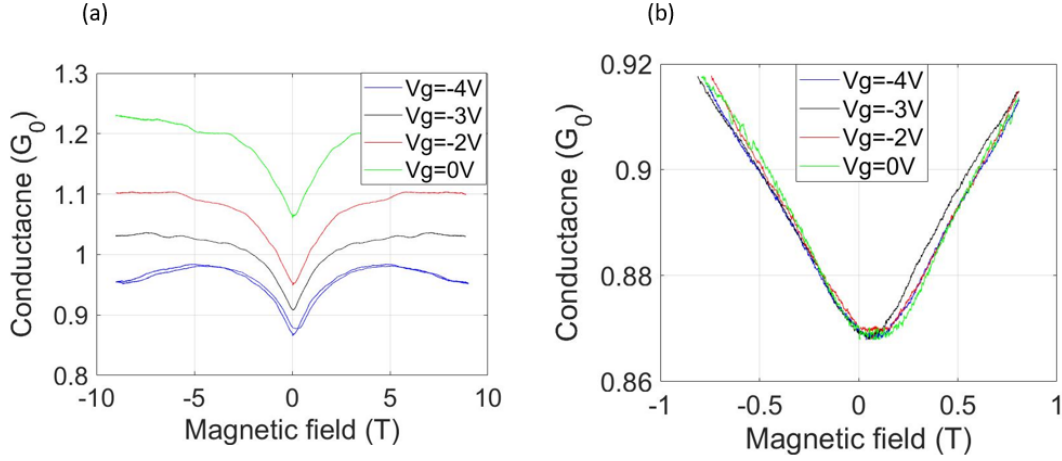


Figure 4.10: **(a)** 4-points conductance $G_{18,23}$ versus magnetic field from at different gate voltage $V_g = 0, -2, -3, -4V$. **(b)** After subtracting a constant for magnetoconductance plot in **a**

several gate voltage $V_g = 0, -2, -3, -4V$. $G_{18,34}$ is similar. Again, similar with previous measurements, the magnetoconductance exhibits a V-shape positive conductance up to $\pm 2T$ and this trend saturates and becomes almost flat at larger magnetic fields. If we zoom in between $\pm 1T$ and subtract a constant in Figure 4.10a for $V_g = 0, -2, -3V$ then all curves overlap. This shows that the V-shape positive magnetoconductance is independent of charge density, and therefore, likely come from the edge state channel 0_- .

Figure 4.11a plots the Hall resistance of junction $R_{18,45}$ at different gate voltages. Other junctions are similar. We can see that the slope in the Hall resistance decreases as we approach CNP. However, from previous gate sweep measurement, we know that negative V_g is closer to CNP. At CNP $V_g = -4V$, the Hall resistance essentially vanishes. For gate voltages $V_g = -2V, -3V$, an unusual ambipolar Hall resistance that switches at large magnetic fields. In some cases the two-carrier Drude model can explain a change of sign of ρ_{xy} . At low magnetic field, $\rho_{xy} \simeq (n_e \mu_e^2 - n_h \mu_h^2) / (n_h \mu_h + n_e \mu_e)^2$ and in large magnetic field, $\rho_{xy} \simeq 1 / (n_e - n_h)$ [124]. However, ρ_{xy} is negative at low B, indicating holes are more mobile than electrons in graphene, which contradicts with previous analyses on graphene[125]. Moreover, the two-carrier Drude model is inconsistent with the quantum

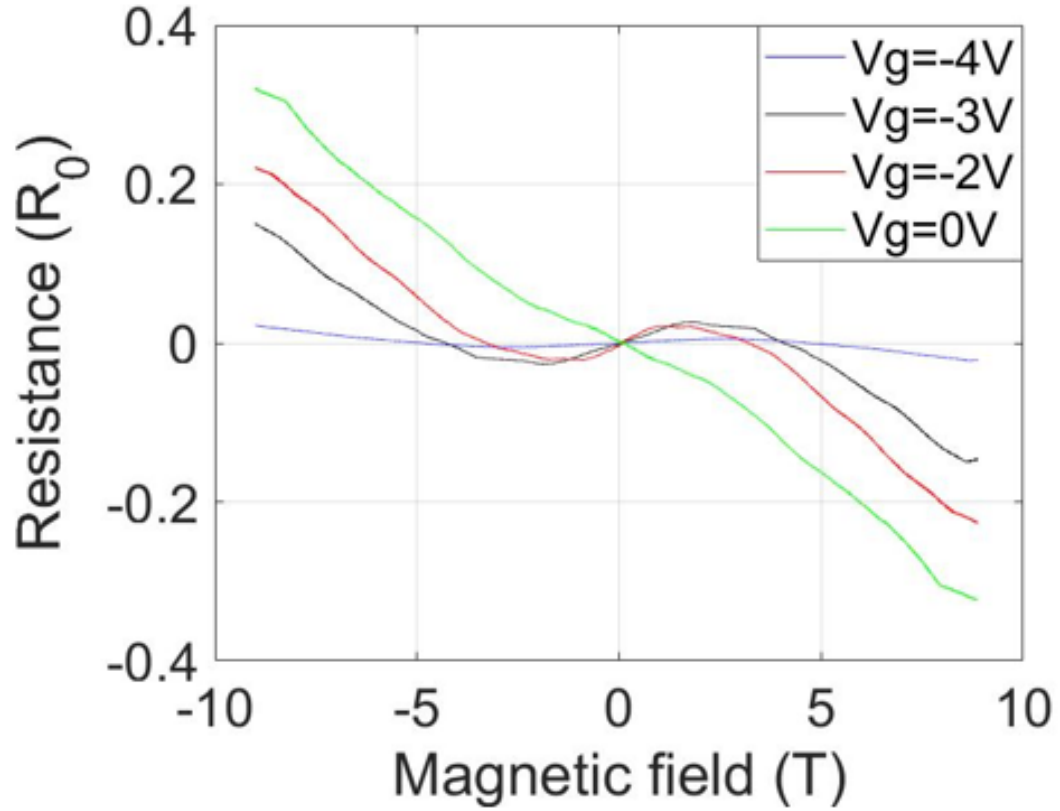


Figure 4.11: (a) 4-points Hall resistance $R_{18,45}$ versus magnetic field from at different gate voltage $V_g = 0, -2, -3, -4V$.

Hall regime studied here and predicts a monotonous positive longitudinal magnetoresistance[126], in contradiction with the observation of a decrease of magnetoresistance shown in Figure 4.10. Therefore, we need an another theory to explain the anomalous Hall resistance.

A rather similar ambipolar behavior was reported in graphene on SiO_2 substrate and interpreted as being due to important disorder[127]. Here, ρ_{xy} changes sign at much smaller B, suggesting that the disorder amplitude is also much smaller. Also, charge puddles, induced by disorder, have also been identified in epitaxial graphene when the overall top gate is degraded[128]. In this case, addition charge traps between graphene and Al_2O_3

might induce uneven charge distributions in the sample.

4.3 Summary

The two samples presented in this chapter are both on 4H-SiC AC orientation 37° facet which is a non-polar facet. Epitaxial graphene on top are grown by conventional CCS method and single layer low-strain graphene areas are confirmed by Raman spectrum. We fabricated Hallbar devices on these two samples with two different process flows. We find out that transport behaviors with respect to temperature and magnetic field and gate voltage are very similar as those observed in SWGNRs and CNT in previous reports[1][129][69]. We demonstrate $1G_0$ edge state conductance with mean free path of $5\mu m$ along the AC direction and $35\mu m$ along the ZZ direction, consistent with the SWGNRs[1][130]. These results show that in a Hall bar channel that has a two-dimensional device structure, we can still get very similar results as in SWGNRs and CNT, which are charge-neutral and purely one-dimensional electrical transport systems. Therefore, the edge states likely dominate the transport among all these carbon based materials.

CHAPTER 5

CONCLUSION

In this thesis, epigraphene nanoribbons and Hallbar devices are fabricated on both SiC Si-face and non-polar facet to study the edge states that arise from the pinned flatband at the edge. These edges states were first observed in SWGNRs and exhibit exceptional transport under UHV conditions[1].

With the polymer-assisted growth method, we can produce large area defect-free monolayer graphene on the Si-face and then fabricate graphene nanoribbon devices by plasma etching. The high temperature thermal annealing is the key to produce edges that are bonded to the substrate, which is essential for the edge state. Therefore, it is desirable to use amorphous carbon because of their high temperature compatibility. Moreover, we developed a new process that involves both high temperature annealing and metal contacts. With a new side contact structure, we have obtained long mean free paths of ballistic edge state around $3\mu m$.

Graphene on the non-polar SiC facets are found to have much lower charge densities than graphene grown on the conventional SiC polar faces. We have also succeed in isolating single layer low-strain graphene patches on SiC on which to produce Hall bar devices. We developed a new fabrication method using Al_2O_3 as a protective layer to minimize contamination and to improve edge smoothness. We that the electrical transport of Hall bar devices are similar to those of SWGNRs and carbon nanotubes, which confirms the existence of edge state transport in these carbon based materials.

The discovery and study of edge states are promising for the future of epitaxial graphene nanoelectronics development due to scalable production of epigraphene on SiC. We can easily investigate the fundamental physical properties using conventional but improved fabrication process methods. It also allows us to build interconnected edge state nanostructures

and therefore opening the door to a new graphene nanoelectronics platform.

Appendices

APPENDIX A

ELECTRICAL MEASUREMENT OF POLYMER-ASSISTED GRAPHENE ON SI-FACE

A.0.1 Temperature Dependence

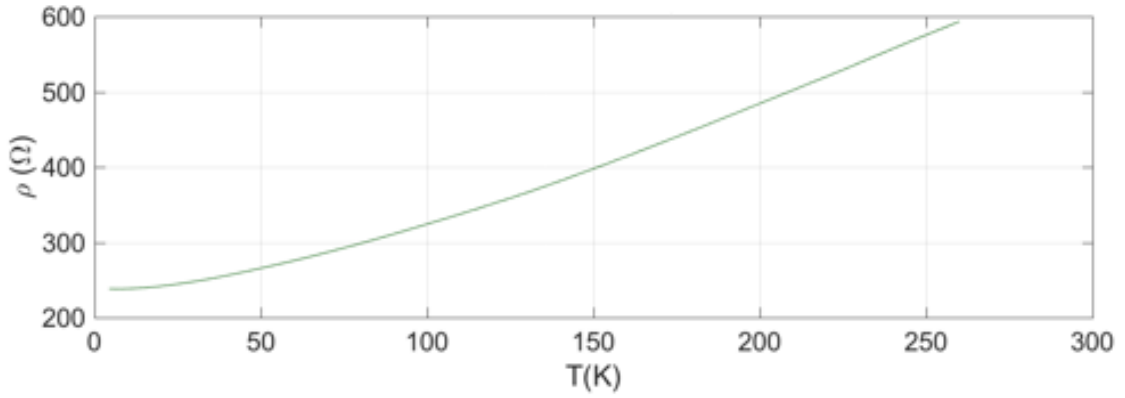


Figure A.1: Sheet resistance versus temperature on graphene Hall bar

A Hallbar sample made of polymer-assisted growth monolayer epitaxial graphene on the Si-face was fabricated using conventional E-beam lithography and O_2 plasma etch techniques. The width of this Hall bar is $1\mu m$ and length is $2.5\mu m$. Figure A.1 is the sheet resistance versus temperature curve. The decreasing resistance with the decreasing temperature is expected from the metallic property of graphene due to decreasing scattering from acoustic phonons[131][132].

A.0.2 SdH Oscillation

The electronic properties of this polymer-assisted graphene have been examined by transport measurements at low temperature 4K. Figure A.2a shows magnetotransport measurement at $T=4K$. The black curve is the magnetoresistance that exhibits Shubnikov–de Haas (SdH) oscillation, and the red line is the Hall resistance. All these values are 4-points re-

sistance with a constant input current $I=100\text{nA}$. From the slope of Hall resistance, we calculate the carrier density as $1.33 \times 10^{13}\text{cm}^{-2}$ (electron doping) and the mobility as around $2000\text{cm}^2\text{V}^{-1}\text{s}^{-1}$. The mobility is very high for a graphene on Si-face of that high charge density[133].

From the SdH oscillation, we can extract the field of each minimum resistance and plot them as a function of the Landau index n , shown in Figure A.2**b**. The intercept of this linear fit is 0.47, which is very close to 0.5, corresponding to the Berry phase of graphene. This number is a signature and specifies transport with Dirac particles[134]. All the evidence proves polymer-assist growth graphene is indeed monolayer and has excellent electronic properties and therefore becomes a good implementation of conventional CCS method.

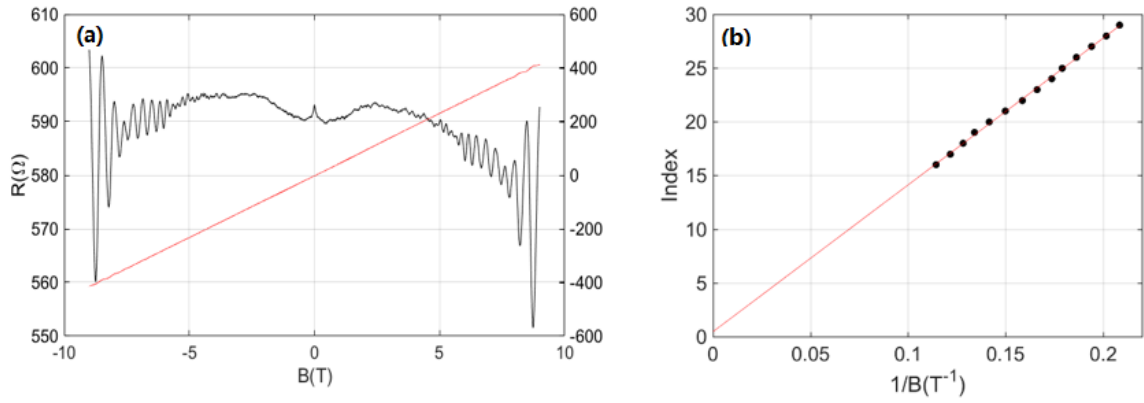


Figure A.2: **a**, Magneto and Hall resistance measured at $T=4\text{K}$. Black line is the 4-points magnetoresistance and red line is Hall resistance **b**, : Landau index versus the measured inverse MR minimum positions $1/B_n$ on the peak index n oscillations

APPENDIX B

ALUMINA AFTER THERMAL ANNEALING

As in previous sections, thermal annealing after etching is one of the key process to recover edge states and improve the overall device quality. Also, we use Al_2O_3 as protective layer right after growth to keep graphene clean and avoid contamination from air and organic e-beam resist. Therefore, a fabrication process flow that involves using annealed Al_2O_3 as gate oxide is needed. Especially, the properties of annealed Al_2O_3 is briefly presented here.

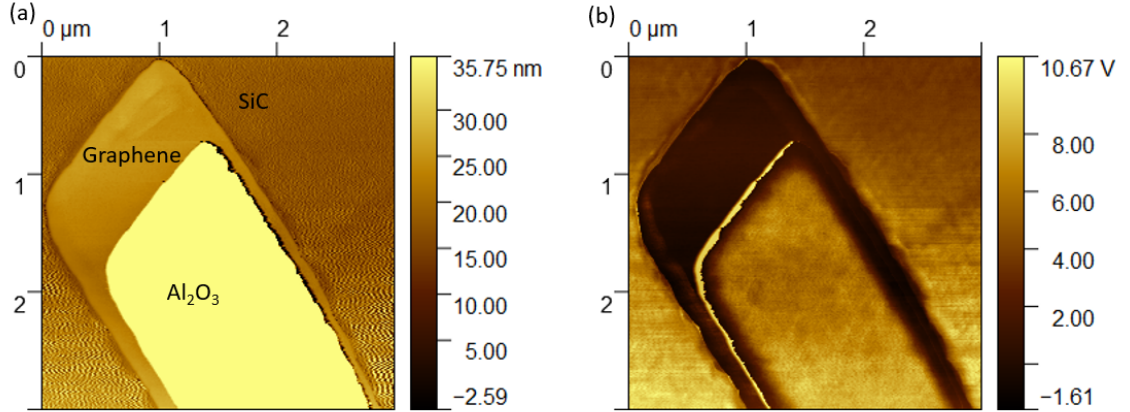


Figure B.1: **a** Topography after 1200°C annealing of graphene/ Al_2O_3 stack. **b** LFM of same region as in **a**, dark region corresponds to lower friction.

Figure B.1 shows the topography and LFM images of a graphene/ Al_2O_3 stack structure. Before thermal annealing, 30nm of Al_2O_3 is deposited onto graphene with e-beam evaporation and then lift-off to have a certain shape. Then RIE etch is used to remove excessive graphene outside Al_2O_3 mask. Then the chip is annealed at 1200°C for 15 minutes. In Figure B.1a, we can clearly see that Al_2O_3 layer is shrinking and exposing the graphene along the edges. The LFM image shown in Figure B.1b confirms the exposing part is graphene, with low frictional force. Also, the shrinking amount is larger with longer arm connecting to it, which implies that the high-temperature annealing process may re-

lease the tensile stress in deposited Al_2O_3 film. This tensile stress from e-beam evaporation deposited Al_2O_3 is consistent with Al_2O_3 deposited by ALD method[135].

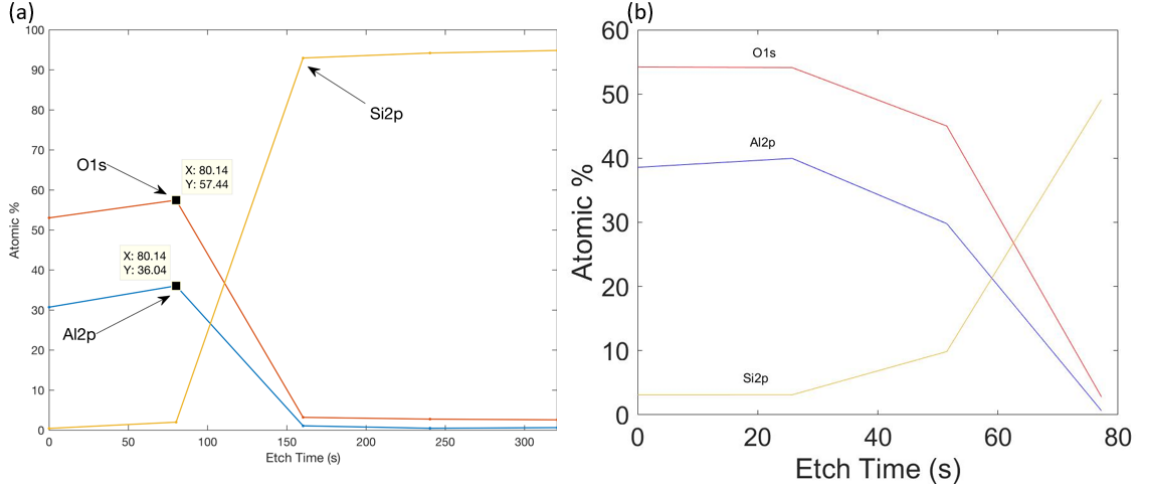


Figure B.2: **a** XPS results of e-beam evaporated Al_2O_3 on bare Si chip **b** XPS results of e-beam evaporated Al_2O_3 on epitaxial graphene after 1200°C annealing for 15 minutes.

We also characterize this e-beam evaporation deposited Al_2O_3 using X-ray photoelectron spectroscopy (XPS), which is a surface analysis tool to identify the elements that exist within a material. Figure B.2a shows the atom concentration percentage along the sample depth direction, which has 20nm of Al_2O_3 on top of a Si chip. As we can see, the oxygen atom has concentration about 1.5 times higher than Al atoms, which confirms the deposited material as Al_2O_3 . As the depth is moving further into the substrate, the Si atoms are dominating as expected. A second sample is an epitaxial graphene on SiC substrate and 20nm of Al_2O_3 covers the whole surface. The chip went through a 1200°C annealing for 15 minutes and then checked with XPS, shown in Figure B.2b. Again, ratio between O and Al atoms is still about 1.5, indicating no evaporation or sublimation during this high temperature annealing process and assuring the existence of Al_2O_3 on epitaxial graphene.

However, using annealed Al_2O_3 as gate dielectric also has temperature upper limit. Figure B.3 shows the AFM topography and lateral force after annealing Al_2O_3 under 1400°C for 15 minutes in vacuum. Before the annealing, a fully covered graphene sample is patterned and deposited with Al_2O_3 and then lift-off. So we have Al_2O_3 pads on top of

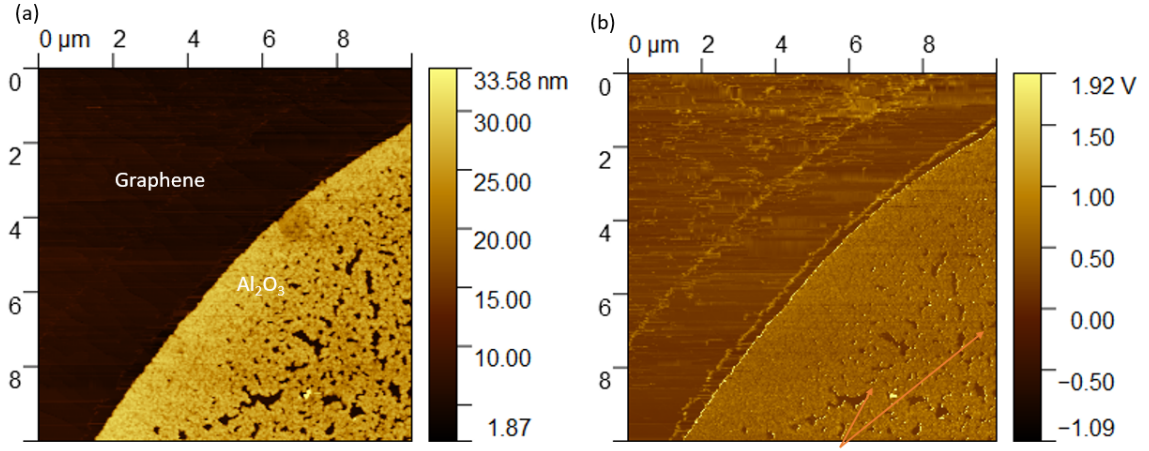


Figure B.3: **a** AFM topography of e-beam evaporated Al_2O_3 on epitaxial graphene after $1400^\circ C$ annealing for 15 minutes. **b** LFM results of the same area in **a**

graphene. We can clearly see the pinholes starting to emerge within the Al_2O_3 covered surface from topography in Figure B.3a. LFM image in Figure B.3b confirms the lower topography regions within the Al_2O_3 pads are graphene due to very low friction. These pinholes is going to cause leakage current when we used this Al_2O_3 layer as the dielectric material later.

APPENDIX C
ADDITIONAL TKYU3 V_G SWEEP

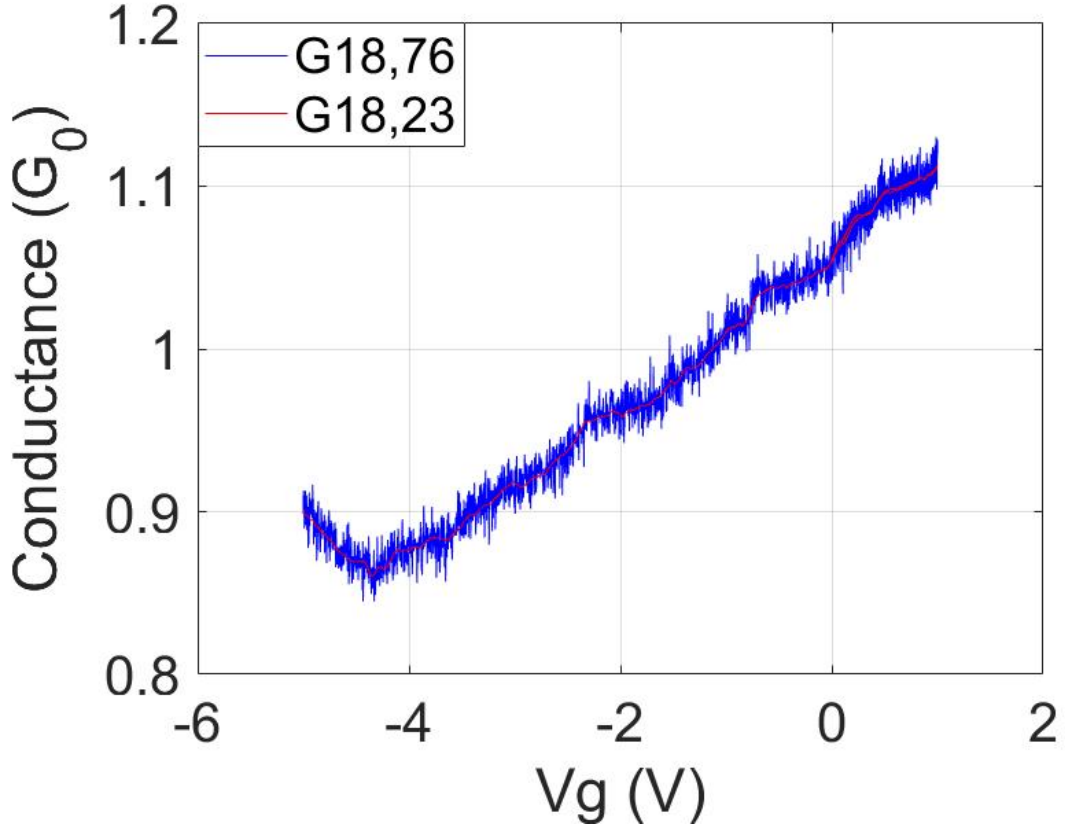


Figure C.1: TKYU3 V_g sweep of segments $G_{18,23}$ and $G_{18,76}$. They are corresponding the same segment within the Hall bar device.

Figure C.1 shows the conductance of the same segment measured along the top and bottom edges. Contact 6 is unstable which causes large fluctuations of $G_{18,76}$. But two results are essentially identical which proves that edge state transport involves both sides of the ribbons.

APPENDIX D

MAGNETOCONDUCTANCE OF SWGNR AND CNT

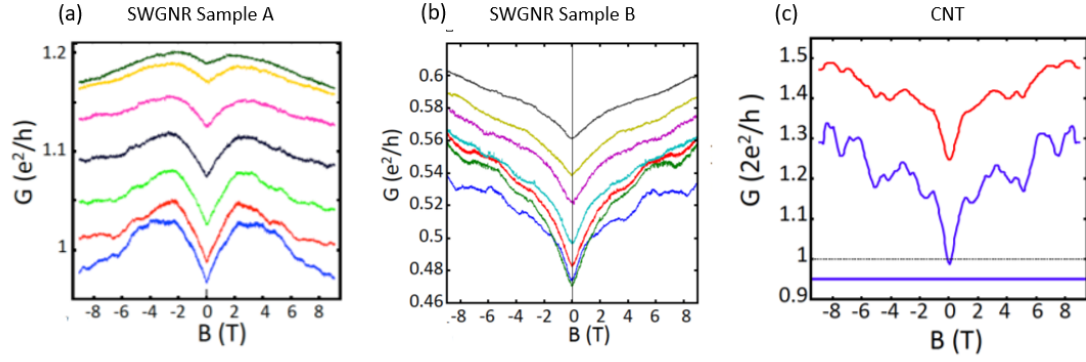


Figure D.1: SWGNR and CNT magnetoconductance measured at low temperature. **a** Sample A is gated SWGNR with length $1.6\mu m$. Conductance versus magnetic field for $T = 4.2, 7, 12, 20, 35, 55$ and 80 K from bottom to top. **b** Sample B is gated SWGNR with length $1\mu m$. Conductance versus magnetic field for $T = 4.2, 7, 12, 20, 35, 55$ and 80 K from bottom to top. **c** CNT conductance of magnetic field dependence for $T = 2.5$ K (blue) and 12 K (red). Figures from [1].

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