Fabrication and Characterization of Nanopatterned Epitaxial Graphene Films for Carbon Based Electronics

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To my parents,

Weibei Song and Yuzhen Chen
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A.1 (a) Ballistic wire connecting to two wide electrodes, which emit electrons to the channel with the distribution functions corresponding to chemical potentials $\mu_1$ and $\mu_2$. The energy dispersion and occupation of the states are shown. In the electrodes the quasi-continuous transversal modes are filled up to their chemical potential. Due to the small transversal dimension in the ballistic conductor only a few modes are occupied; and the $+k/-k$ states have depending on which electrode they arrive from.
In this thesis, we show that planar graphene ribbons have properties similar to those of nanotubes. Both exhibit semiconducting or metallic properties depending on crystal orientation. The band gap varies approximately as the inverse of the ribbon width. Both can be doped and gated. Due to these similarities, the patterned graphene also has nanotube like transport properties, which include coherent transport, ballistic transport, and high current capabilities. In essential contrast to nanotubes, graphene ribbons can be rationally patterned using standard electron beam lithography methods, functional graphene devices could be fabricated eliminating the need for metal interconnects on the wafer. This would remove many obstacles faced by carbon nanotubes, while retaining the benefits of high carrier mobility and quasi-1D transport.

We have produced ultrathin epitaxial graphite films on single-crystal silicon carbide by vacuum graphitization, which show remarkable 2D electron gas (2DEG) behavior. The most highly ordered samples exhibit Shubnikov-de Haas oscillations that correspond to nonlinearities observed in the Hall resistance, indicating a potential new quantum Hall system. The transport properties, which are closely related to those of carbon nanotubes, are dominated by the single epitaxial graphene layer at the silicon carbide interface and reveal the Dirac nature of the charge carriers. Patterned structures show quantum confinement of electrons and phase coherence lengths beyond 1 micrometer at 4 kelvin, with mobilities exceeding 2.5 square meters per volt-second. We show that the high-mobility films can be patterned via conventional lithographic techniques, and we demonstrate modulation of the film conductance using a top-gate electrode. These key elements suggest electronic device applications based on nanopatterned epitaxial graphene (NPEG) with the potential for large-scale integration. The research created a foundation for graphene science and technology and established a path toward graphene-based nanoelectronics.
CHAPTER I

INTRODUCTION

1.1 Motivation

1.1.1 Silicon Based MOSFET

The gigantic semiconductor industry is built up primarily on the transistor. Since its invention, the dimensions of the transistors have shrunk dramatically, seven orders in size, or fourteen orders in area density. The change is remarkable, and prompted Gordon Moore, the co-funder of Intel, to propose his famous Moore’s law: The typical linear dimension of a feature on an integrated circuit decreases in size by a factor of two roughly every eighteen months [1, 2].

In the past 50 years, the development of semiconductor industry has obeyed this law quite well (Fig. 1.1). Intel has pushed the industry standard to 65 nm region for its dual-core processor in 2006, and continues component research on 45 nm and 22 nm Si technology. Although the development is satisfactory, key problems emerge with the traditional MOS-FET (Metal Oxide Semiconductor Field Effect Transistor) (Fig. 1.2) based silicon industry when the size of a transistor reaches the order of a few nanometers.[3]

Conventional transistors have three terminals: the source, the drain and the gate electrode. The source and drain are connected by a channel that is either N doped (PMOSFET) or P doped (NMOSFET) semiconductor material. The gate electrode is a layer of polysilicon, placed over the channel but separated from the channel by a thin insulating layer (traditionally $SiO_2$). When a voltage is applied between the gate and source terminals, the electric field generated penetrates through the oxide and creates an “inversion layer” below the oxide. The inversion layer is of the same type (P-type or N-type), as the source and drain, so that layer provides a channel through which current can pass. Varying the voltage between the gate and the source modulates the electron density of this layer and makes it possible to control the current flow between the drain and the source. This property allows
**Figure 1.1:** The development of Intel’s CPU obeys the Moore’s law very well.

**Figure 1.2:** (a) Schematic structure of a Si MOSFET used in various microchips for digital signal processing and (b) its current to voltage characteristics.
a transistor to operate as a switch. [4]

Depending on the voltages at the terminals, the operation of a MOSFET can be separated into three different modes: the cut off mode, the linear region, and the saturation mode. The cut off mode is at $V_{GS} < V_{th}$, where $V_{th}$ is the threshold voltage of the device. The transistor is turned off, and there is no conduction between the drain and source. The linear region is at $V_{GS} > V_{th}$ and $V_{DS} < V_{GS} - V_{th}$. The transistor is turned on, and a channel is created to allow current to flow between the source and drain, the MOSFET operates like a resistor. The saturation mode is at $V_{GS} > V_{th}$ and $V_{DS} > V_{GS} - V_{th}$. The drain voltage is higher than the gate voltage, and a portion of the channel is pinched off. The current is now relatively independent of the drain voltage, only controlled by gate voltage. [5, 6]

Today’s MOSFETs are similar in structure and function as those made twenty years ago, but much smaller. The advantage of the smaller size is three-fold. First, the MOSFET is like a resistor when it is on, so that a smaller MOSFET with a shorter channel has less resistance. Secondly, smaller MOSFET has smaller gate and thus lower gate capacitance. These two factors contribute to shorter switching time and higher processing speed. Thirdly, smaller MOSFET can be packed more densely resulting in chips with more computing power in the same area.

1.1.2 Limitations of Si Technology

Until the late 1990s, this size reduction resulted in great improvements to the MOSFETs operation with no deleterious consequences, the problems to decrease the size of the MOSFETs are all related to the semiconductor device fabrication process. Only recently, the size reduction of MOSFETs created operational problems, which are discussed below.

Because of the small MOSFET geometries, the gate voltage must be kept low to maintain reliability, the threshold voltage of the MOSFET has to be reduced as well to maintain performance. When threshold voltage is reduced, the transistor cannot be completely turned off, resulting in a weak-inversion layer that consumes power in the form of subthreshold leakage. Subthreshold leakage, which was ignored in the past, now can consume up to half
of the total chip power in the form of heat. [7, 8]

At high temperatures, circuits operate slower, and have shorter lifetimes and reduced reliability. Heatsink and other cooling methods are required for many integrated circuits including microprocessors. When the heatsink can not keep the temperature low enough, the on-state resistance rises with temperature, the dissipated power generates further heat, so the junction temperature may rise quickly and uncontrollably, and destroy the device.[9, 10]

Switching time is roughly proportional to the gate capacitance. However, with transistors becoming smaller and more transistors being placed on the chip, the interconnect capacitance (the capacitance of the wires connecting different parts of the chip) becomes a large percentage of the total capacitance. Signals have to travel through the interconnects, which leads to increased delay and lower performance. [11]

As the MOSFET channel region shrinks, its resistance will depend on the presence of only a few tens of dopant atoms in the channel. Statistical fluctuations in the number of dopant atoms become critical for a silicon semiconductor device. During chip manufacturing, random process variations change the transistor property dramatically. The transistor characteristics become less deterministic and more statistical. This statistical variation increases design difficulty and makes the transistor unstable in production and operation.

Furthermore, the conductor becomes so thin, the high current density causes electromigration. Under the influence of current, individual atom can be displaced from the metal lattice and migrate in the direction of the carriers flowing. This result in piling up of metal at the positively electrode end and a depletion at negative end. The electromigration process ultimately results in contact failure [12, 6, 13].

These problems inspire scientists and engineers to investigate alternative materials for nanoscale FETs. Among candidate materials, the nanotube has become the focus of many investigators due to its exceptional mechanical and electrical properties [14, 15, 16, 17, 18]. Carbon nanotubes (CNTs) seem providing an alternative solution to scale down the transistor and integrate into the well established silicon technology.
1.2 Carbon Nanotubes as an Alternative Material

1.2.1 Discovery and History

The carbon nanotube was discovered in 1991 by Sumio Iijima in the NEC Fundamental Research Laboratory in Tsukuba, Japan [19]. He found that carbon nanotubes consist of several concentric graphitic layers, called multi wall carbon nanotube. The adjacent shell separation is about 0.34 nm. Two years later, Iijima and collaborators produced single shell nanotubes, called single wall carbon nanotubes [20]. Since then extensive research has been carried out on carbon nanotube synthesis, characterization and application, and many exciting physical and electrical properties have been revealed [21]. Some significant applications include: using carbon nanotube as a field-emission electron sources (1995) [22, 23], hydrogen storage (1997) [24], carbon nanotube quantum resistors (1998) [25], nano size carbon nanotube balance (1999) [26], carbon nanotubes logic circuits (2001) [27, 28], and the first carbon nanotube IC (2006) [29].

Among them, the Field emission carbon nanotube devices are the first and the only commercialized nanotechnology. Research on field emission electronic devices focuses on using both single wall nanotube and multi wall nanotube as field emission electron sources for flat panel displays, lamps, gas discharge tubes, and x-ray generators [30, 31, 32].

The power of carbon nanotubes as electron field emitters was apparent from the first article reporting extremely low turn-on fields and high current densities for electron emission in 1995 [33, 34]. When applying a potential between an anode and a carbon nanotube coated cathode, high local fields cause electrons to tunnel from the nanotube tip of the cathode into the vacuum and to be collected by anode. Since no heat is needed to emit electrons from a cathode surface, nanotube field emission electron sources require less energy and less stringent vacuum conditions than thermionic sources [18].

The exceptional field emitter property originates certainly from the small diameter and elongated shape of the tubes that lead to a high geometrical field enhancement [35]. Carbon nanotubes have diameters ranging from 1-100 nm, and lengths up to millimeter, and the ratio of diameters to lengths can reach one to one million. The carbon nanotube alignment is extremely important if high emission currents are needed at low voltages. Typically
carbon nanotubes are aligned perpendicular to the surface of substrate by chemical vapor deposition method as we discuss below. So at this time, the most practical application of carbon nanotube is working as field emission source. [33, 18]

1.2.2 Synthesis Methods

Mainly there are three methods to synthesize carbon nanotubes: arc discharge, laser ablation, and chemical vapor deposition (CVD). Arc discharge is used first by Iijima [19] to produce multi wall nanotube. De Heer et al. [36] further developed this method and produced defect free MWNTs as in Fig. 1.3. In the arc discharge method, a pure (catalyst-free) carbon arc (100A, 30V) is struck between two carbon electrodes in a helium atmosphere. When the helium pressure is low ($P_{He} \sim 10mb$), the arc emits a dense fullerene smoke; at higher pressures ($P_{He} \sim 100mb$), carbon nanotubes are formed [36].

The pure carbon anode is heated locally by electron bombardment from the cathode about 1mm away, causing the surface to locally liquefy and liquid carbon globules to be
ejected from the anode. Initially, due to the very high vapor pressure of liquid carbon, the surface of a globule will evaporative cool until the carbon vapor pressure at the its surface equals the helium pressure. The initial very efficient evaporative cooling of the surface causes the globule surface to glassily and possibly seal it. Once the carbon vapor pressure becomes smaller than the helium background pressure, then the evaporation rates diminish, and evaporative cooling essentially ceases. (For low $P_{He}$ evaporation continues, which explains why then no cathode deposit is formed then [37, 38].) The more gradual cooling of the interior of the globule causes the liquid carbon to supercool so that carbon crystals (nanotubes and small graphitic particles) homogeneously nucleate and grow. While the interior liquid transforms to higher density graphitic structures, the hot viscous glass skin adheres to the nanotubes, subsequently, capillary forces cause the glass coating to bead on the nanotubes. Finally, the hot, relatively plastic globules are deposited on the cathode to form the basaltic structure of aligned columns on the cathode.

After production, a 7\(\text{mm}\) diameter cylindrical carbonaceous deposit forms on the cathode from a 7\(\text{mm}\) diameter anode. The core of the deposit consists of a basaltic structure of carbon columns parallel to cylinder axis. The columns are about 1\(\text{mm}\) long and about 0.1\(\text{mm}\) wide. They are mechanically stable and easily separated from each other. The interior of a column is composed primarily (\(\sim 75\%\)) of densely packed randomly aligned MWNTs, nominally 3 to 20 nm in diameter and several microns in length, and facetted graphitic nanoparticles (\(\sim 20\%\)) and the balance is amorphous carbon.

With this method, pure carbon arc produced multi walled carbon nanotubes (pcaMWNTs) are essentially defect free, which is different from nanotubes produced by the other two methods involving catalysts. While the catalytic production process has been extensively studied, pcaMWNT formation is still under study. [36]

Laser ablation is a very similar method to arc discharge used to produce carbon nanotube [39]. A block of graphite and metal catalyst mixture is placed in an oven at approximately 1200\(\text{oC}\), and as a laser ablates the the target, nanotube is formed and carried by flowing Ar gas to a cooler copper collector. This method produces nanotube in a haphazard fashion and gives quite a low yield.
Endo and Kroto [40, 41] first created carbon nanotubes by chemical vapor deposition. The metal catalyst powder is patterned on substrate as seeds to nucleate the growth of nanotubes. The substrate is annealed in a chamber at approximately 600°C. Hydrocarbon gas, usually ethylene or acetylene, flows into the chamber and decomposes to release carbon atoms, which recombine in either the catalyst powder or at the end of carbon nanotube to increase the length of nanotube. The key parameters are the nature of hydrocarbon gas, catalysts, and growth temperature; best results are obtained with Fe, Ni, or Co nanoparticles as catalyst [41]. The method is relatively simple to apply, and it produces nanotubes in large quantities.

1.2.3 Structure of Carbon Nanotubes

A carbon nanotube can be thought of as graphene sheets rolling up into a seamless, hollow cylinder. Depending on how the graphene sheets are rolled up, three types of CNTs are possible: armchair, zigzag, and chirality. This image has been confirmed by structure studies with high resolution transmission electron microscopy (TEM).[42]

As shown in Fig 1.4, the chiral vector $c_h$ is defined as
Figure 1.5: (a-c) Shown are a (5, 5) armchair tube, a (9, 0) zigzag tube, and a (10, 5) chiral tube. (d) Atomically resolved STM image of an individual single-wall carbon nanotube. The diameter here was found to be $d = 1.3\, nm$ and the chiral angle $\theta = 7^\circ$. [42]
\[ \mathbf{c}_h = n \mathbf{a}_1 + m \mathbf{a}_2, \]  

(1.1)

\( \mathbf{a}_1, \mathbf{a}_2 \) are the unit vectors of the hexagonal honeycomb lattice of the graphene, coefficients \( m \) and \( n \) are integers. The chiral angle is the angle between \( \mathbf{c}_h \) and \( \mathbf{a}_1 \), and the chiral angle \( \theta \) is given by \( \theta = \tan^{-1}[\sqrt{3}n/(2m + n)] \). When rolling up the graphene sheet, the chiral vector’s ends meet each other to form cylindrical structure. The length of the chiral is the circumference of the CNTs’ cross section, and different values of \( m, n \) define different structure types of CNTs. When \( n = m \), the chiral angle is 30°, and metallic armchair CNTs are formed. When either \( n \) or \( m \) equal to 0, the chiral angle is 0°, resulting in semiconducting zigzag CNTs [43]. With all the other \( m, n \) combinations, the chiral angle is between 0° and 30°, resulting in chiral CNTs. The diameter of carbon nanotube \( D_t \) is determined by

\[ D_t = \sqrt{3}a_{c-c}(m^2 + mn + n^2)^{1/2}/\pi, \]  

(1.2)

where \( a_{c-c} \) is the distance between two adjacent carbon atoms \((1.42 \text{ Å}) [44]\).

The translation vector \( \mathbf{T} \) describes the distance along the nanotube before the pattern of the carbon atoms on the nanotube repeats itself, so that \( \mathbf{T} \) defines the nanotube unit cell.

\[ \mathbf{T} = t_1 \mathbf{a}_1 + t_2 \mathbf{a}_2, \]  

(1.3)

where

\[ t_1 = \frac{2m + n}{d_R}, t_2 = -\frac{2n + m}{d_R} \]  

(1.4)

\( t_1, t_2 \) are indices, \( d_R \) is the greatest common divisor of \( 2n+m \) and \( 2m+n \). Since the translation vector \( \mathbf{T} \) should be as small as possible and is parallel to the nanotube axis, normal to the chiral vector \( \mathbf{c}_h \), \( \mathbf{T} \cdot \mathbf{c}_h = 0 \) and \( \mathbf{T} \times \mathbf{c}_h \) is the size of a carbon nanotube unit cell [44].

\[ N = \frac{\mathbf{T} \times \mathbf{c}_h}{\mathbf{a}_1 \times \mathbf{a}_2} = \frac{2(m^2 + n^2 + mn)}{d_R} \]  

(1.5)

is the number of hexagons in the unit cell. We know it is two carbon atoms per hexagon, and 2N carbon atoms in the unit cell. The measurement of CNTs diameter and chiral angle
has been achieved by TEM and STM [42, 45]. Fig. 1.5 shows STM images of single-wall carbon nanotubes.

Theoretically, the band gap for semiconducting zigzag nanotube is on the order of

$$\Delta E = 2\gamma_0 a/D,$$

(1.6)

where $\gamma_0 \approx 3eV$, $a = 0.14nm$, and $D$ is the diameter of the nanotube in $nm$. For non-doped metallic armchair nanotube, two subbands with a linear dispersion cross exactly at the Fermi level, which gives the nanotube its metallic character. Valence subbands and conduction subbands are symmetrically positioned below and above the Fermi level, they do not cross Fermi level, and normally do not contribute to conductance [46]. We refer them as semiconducting subbands.

1.2.4 Transport Properties of Carbon Nanotubes

One of the most exciting electronic properties of CNTs is that they can conduct ballistically. This occurs when the length of the nanotube is smaller than the electronic mean free path, in this case each transverse wave guide mode or conducting channel contributes $G_0$ to the total conductance. $G_0 = 2e^2/h$, where $h$ is Planck’s constant, and $e$ is the charge of an electron [26, 47].

The fundamental reason for ballistic transport of carbon nanotubes is their perfectly symmetric and periodic structure, electrons can transport though nanotube with very little back scattering. That means there is no resistance and energy dissipation on carbon nanotube, resistance and joule heat are only present on the contact of metal and nanotube.

The first demonstration of ballistic conduction of carbon nanotubes at room temperature was given by de Heer et al. [25] as in Fig. 1.6. A high quality arc produced Multiwall carbon nanotube was attached to the tip of a scanning probe microscope. The z scanning mechanism of the microscope was used to submerge carbon nanotube into liquid mercury, the resistance of the carbon nanotube was measured. de Heer et al. reported that electrons flow ballistically through carbon nanotubes, and the conductance is quantized following the Landauer equation.
Figure 1.6: TEM image of a MWNT fiber tip opposing a mercury surface and the dipping process. (a) The nanotubes protrude from the fiber that is composed of densely packed carbon nanotubes and other graphitic nanostructures. The transport measurements are made by lowering the tip into the liquid metal and measuring the conductance as a function of the position. Inset: Example of cone shaped meniscus attached to the tip of the nanotube which occurs when the nanotube is pulled out of the (non-wetting) liquid just before contact is broken. (b) A full cycle conductance trace (conductance $G=I/V$ versus position) where the fiber is first lowered to the Hg and subsequently withdrawn (see upper axis). Note the asymmetry with respect to the turning point due to the non-wetting adhesive effects. [25]
According to the Landauer equation (Appendix A), the conductance of a system with multiple channels is

\[ G = \frac{2e^2}{h} \sum T_n \]  

(1.7)

where \( T_n \) is the transmission probability of the \( nth \) channel. For an ideal system (\( T = 1 \)) with \( N \) conducting channels \( G = N(2e^2/h) = NG_0 \). The conductance of an ideal metallic single wall nanotube should be \( 2G_0 \), independent of length and diameter. [48]

Most experiments do not follow this prediction very well. Studies have shown that defects may be introduced into the carbon nanotube during production and fabrication process, which causes back scattering and reduced \( T_n \) [48, 49]. While the effects of disorder are significantly reduced in metallic tubes for a number of reasons [50, 51, 49]. Experiments give evidence that a metallic tube can have a very long mean free path \( l_c \) on the order of microns [52, 53, 54]. Doped semiconducting tubes, however, have yielded \( l_c \) that are orders of magnitude shorter [55, 56]. These are surprising results, since the tubes are nearly structurally identical and the amount of disorder are similar.

It is well known now the electrical properties of individual carbon nanotube may vary from tube to tube [49]. Long length scale disorder due to localized charges near the tube breaks the semiconducting tube into a series of quantum dots with large barriers, which reduced conductance dramatically. This makes semiconducting carbon nanotube a diffusive conductor with mean free path of several nanometers. Metallic tubes, are insensitive to long length scale disorder and remain near-perfect 1D conductors. [57]

### 1.2.5 Carbon Nanotube FET

Before building sophisticated nanotube based circuits, one important thing is to grow nanotubes in specific locations, as well as construct nanotube devices at specific locations. The first large-scale synthesis of vertically aligned carbon nanotubes has been achieved by using CVD method. The first horizontally aligned growth of carbon nanotubes was achieved by Kroto’s group at University of Sussex, UK, and Cheetham’s group at the University of California at Santa Barbara, USA [58]. They deposited cobalt film on a silica substrate, then etched the cobalt film into tracks \( 1 - 20\mu m \) wide using laser beam. A laser beam
generated tracks free of cobalt, and left cobalt particles evenly positioned along the edges of the track. In a CVD oven, dense nanotubes grew from one edge to the other edge of the track, and the electrical field is introduced horizontally to enhance the directionality of nanotube growth. Even with the development of nanotube local growth method, device fabrication with nanotube is still a tedious and troublesome process [59].

The first field effect transistors were demonstrated using a semiconducting SWNT by Tans et al.[55], and using a MWNT by Avouris et al. [60]. Their fabrication method is still widely used in today’s research. But from the process discussion below, it is clear that this method is not proper for large scale production. Carbon nanotubes always stick together by Van der Waals force to form a carbon bundle, which can be ultrasonically vibrated in surfactant to get separated nanotubes solvent. Nanotube solvent is spin coated on a thick layer of silicon dioxide, which is grown on a silicon wafer. SEM and AFM are used to locate the useable nanotube and to mark the position. Titanium and gold are deposited on silicon dioxide surface as electrodes by electron beam lithography. By chance, there may be one nanotube acting as channel between two electrodes, which are the source and drain of the FET, the doped silicon wafer itself works as a back gate shown in Fig. 1.8.

There are two main types of carbon nanotube FETs differing by current injection methods: Schottky barrier CNTFETs [61, 62, 63], and MOS CNTFETs [64, 65]. In Schottky barrier FETs, Schottky barriers are created at the intersection between the metal carbide contacts and the semiconducting carbon nanotube. The current in CNTFETs is from the tunnelling of carriers through the Schottky barriers. The type of metal for the contacts is chosen so that its work function forces the metal Fermi Level to lie between the valance and conduction band of the CNT, approximately in the center of the energy bands. The work function for Al is 4.2 eV and Ti is 3.9 eV; these are similar to the work function of a CNT with a diameter of 1.4 nm (≈ 4.5 eV) [66]. Titanium is used most frequently because of its stable carbide [67]. With a negative gate voltage applied, the Schottky barrier width at the source is modulated, allowing for carriers to tunnel through the valence band and pass to the drain. The thickness of the source Schottky barrier at the metal Fermi level decreases exponentially with an increasing gate to source voltage. Thus, the tunnelling current through
**Figure 1.7:** Band diagrams along the length of a carbon nanotube attached to contacts at both ends. $E_c$: conduction band edge; $E_v$: valence band edge; $E_F$: Fermi level of metal contacts; S: source contact; D: drain contact. Typical metals make ohmic p-type contacts to carbon nanotubes. (a) represents zero gate voltage. There are no voltage drops either at the contact regions or in the gate dielectric. (b) A positive gate voltage pulls the bands below the Fermi level, and the nanotube is depleted of carriers in the bulk. Thermally activated carriers may aid transport. (c) A more positive gate voltage pulls the conduction band edge below the Fermi level. The main mechanisms for n-type conduction are now tunnelling from valence band states to conduction band states (horizontally) and thermal activation of electrons over the band gap barrier (vertically). Both become more relevant in large-diameter nanotubes, since the band gap is inversely proportional to diameter. [70]

While early transistors used Au as contact metals, significant performance improvements were obtained by using palladium contacts instead, which seem to eliminate the Schottky barrier for carriers and produce near-ballistic conductance.[69]

MOS CNTFETs, analog to Si MOSFETs, are based on an energy band gap in semiconducting CNTs’ band structure. CNTs conduct poorly when the Fermi level lies within the gap. The position of the Fermi level in a semiconducting nanotube can be tuned by a nearby charged gate electrode as in a Si MOSFET. Negative (positive) charge builds up in the nanotube as a result of a positive (negative) charged gate electrode. The additional charge changes the position of the valence and conduction bands relative to the Fermi level in the nanotube as shown in Fig. 1.7. Under typical experimental conditions, nanotubes
are p-type. They are doped with an excess of positive charge. This is attributed to nearby charges on the substrate which are left over from sample preparation \[60\]. Additionally, metals such as Au make p-type contacts. For this reason, transport in semiconducting nanotubes happens primarily due to holes. Sweeping the gate voltage is similar to the creation of an inversion layer in a MOSFET. Given enough positive gate voltage, the bottom of the conduction band can be pulled below the Fermi level in the nanotube. This corresponds to n-type behavior,\[69, 64\]

### 1.2.6 Limitations of Nanotube Transistor

Carbon nanotube is proposed to be the base for next generation processor in the near future. While still several problems hinder its application,\[71, 61\]

The nanotube field effect transistor is fabricated by depositing electrodes to nanotubes, which are either randomly distributed on a silicon dioxide substrate or positioned on the substrate with an atomic force microscope. A transistor assembled in this way may or may not work, depending on whether the chosen nanotube is semiconducting or metallic, over which we can not control at this time. It is possible to selectively peel outer layers from a MWNT until a nanotube cylinder with the desired electronic properties is obtained, however this process is not yet very reliable and is probably unsuitable for mass production,\[72, 71\]

Although a metallic nanotube can carry current density up to $10^9 A/cm^2$, whereas the
maximum for normal metals is $10^5 A/cm^2$ [73, 74]. The ballistic current carrying capability is less useful for presently envisioned applications because of necessarily large contact resistances. An electronic circuit involving electrical leads to and from a nanotube will have a resistance about $1 M\Omega$. Contacting all layers in a MWNT may reduce this contact resistance, but it cannot be totally eliminated.

And the device sizes for current nanotube FET, including contacts, are several hundred nanometers, not smaller than silicon-based field-effect transistors, a further reduction in size is required. It is clear that a revolutionary processing method must be developed before carbon nanotubes be used in large scale nanoelectronics.

### 1.3 Summary

In this chapter, we have discussed the limitation of Si technology, and properties, applications of one new material – carbon nanotube. Carbon nanotubes based FETs provide solutions to some problems of Si based FETs. For instance, nanotubes are metals or semiconductors depending only on their geometry and need not be doped. Nanotubes can sustain extremely high current densities without degradation. Nanotube is one dimensional ballistic conductor at room temperature, which produces much less heat as electronic device.

On the other hand, there are serious problems with nanotubes as electronic elements. Basic nanotube properties (metal versus semiconductor) depend sensitively on their geometry which current production methods cannot control. Nanotube products always include both metallic and semiconducting mixture with large variation of length and diameter. Currently we are not able to mass manufacture a single or even just a couple of specific carbon nanotubes yet. This remains a major hurdle for carbon nanotube applications. The current fabrication of carbon nanotube transistors relies on arduous contacting of randomly dispersed carbon nanotubes from solvent, or time consuming manipulation by AFM. It is unclear how reliable large-scale integration of nanotube devices is to be achieved.

At the same time, even though it is well known that carbon nanotubes are rolled up graphene sheets, the importance of graphene itself as a new material is under valued. As we will see in the next chapter, graphene has very a similar band structure and similar
electronic transport properties as carbon nanotubes [75, 76]. Hence, the proposed graphene based devices will achieve most of the advantages of carbon nanotubes, and as such is a promising new microelectronic material.
CHAPTER II

GRAPHENE

In this chapter we show that planar graphene nanostructures not only retain the advantageous properties of nanotubes as an electronic material, but they also provide solutions to the problems related to integrated electronics mentioned in chapter I. Moreover, nanopatterned graphene opens the door to a host of novel electronic phenomena.

2.1 Single Crystal Graphite

Graphite is one of the allotropes of carbon, and every carbon atom is covalently bonded to the three nearest carbon atoms, which forms a hexagonal structure in layers [77]. There is no covalent bonding between layers, only van der Waals force, which is much smaller than the intra-layer interaction force [78]. Therefore, the layers easily slide over each other, which make graphite a soft material used in pencils and lubricants.

Crystal graphite is composed of graphene sheets, mostly stacked in ABAB sequence [79, 80], or called Bernal structure. In ABAB sequence each unit cell of graphite includes four atoms, labelled $A, A', B, B'$ as in Fig. 2.1. $A, B$ are in one layer, $A', B'$ are in adjacent layer. The difference between $A, A'$ and $B, B'$ is $A, A'$ have carbon atoms directly above and below them in adjacent layer, $B, B'$ do not. The middle point of $A, A'$ is the symmetric center of the structure [79].

The room temperature electrical resistivity of single crystal graphite is about $5 \times 10^{-5}\text{ohm} \cdot \text{cm}$, which corresponds to that of a poor metal, the resistivity of a good metal (silver) is about $10^{-10}\text{ohm} \cdot \text{cm}$. Similar to metal, the single crystal graphite has positive temperature coefficient (PTC); its resistivity decreases with temperature decreasing [81, 79]. Polycrystalline graphite has much higher resistivity than single crystal graphite because of the impurity atoms on crystal boundary [82, 83].
Figure 2.1: The crystal structure of graphite with in-plane bond length 1.42\(\text{Å}\) and interlayer distance 3.35\(\text{Å}\). The primitive unit cell is hexagonal with four atoms \(A, A', B, B'\). The atoms \(A\) and \(A'\) are shown with full circles, the atoms \(B\) and \(B'\) are shown with open circles.
Figure 2.2: (a) Fragment of the graphene lattice. The primitive lattice vectors \(a_1\) and \(a_2\) define the unit cell (shaded). There are two carbon atoms per unit cell, denoted by 1 and 2. (b) Reciprocal lattice of graphene with the 1st Brillouin zone (shaded). The primitive lattice vectors are \(b_1\) and \(b_2\).

### 2.2 Band Structure of 2D Graphene

The electronic band structure of graphene is calculated using simple tight binding methods [79]. Carbon is the sixth element in the periodic table, has six electrons around the nucleus. These six electrons occupy the \(1s^2, 2s^2, 2p^2\) orbitals respectively. The two \(1s^2\) electrons are tightly bound to the nucleus. The four \(2s^2, 2p^2\) valence electrons are more weakly bound. Because there is only a little difference between the \(2s, 2p\) orbitals, a mixing of these orbitals takes place [84, 78]. For the graphene structure, one \(2s\) and two \(2p(p_x, p_y)\) electrons participate in the mixing (\(sp^2\) hybridization), which forms strong \(\gamma\) bonding with three nearest carbon atoms [85, 86].

In graphene \(sp^2\) hybridization forms \(\sigma\) and \(\sigma^*\) states, which are strongly separated in energy (the energy gap is larger than 10eV), these states do not contribute to electrical transport. The remaining single \(2p\) electron remains in the \(p_z\) state. The \(p_z\) states mix together forming \(\pi\) bond with a range of energies including the Fermi energy. Hence in an finite graphene sheet the \(p_z\) electrons develop into the \(\pi\) bands, which are responsible for the electrical conductivity of graphene and the weak van der Waals force between the graphene layers [87].

In the Fig. 2.2 of graphene hexagonal lattice, there are two carbon atoms in each
unit cell, \( \mathbf{a}_1, \mathbf{a}_2 \) are the unit vector of the unit cell, \( \mathbf{a}_1 = (\frac{a}{2}, \frac{\sqrt{3}}{2}a) \), \( \mathbf{a}_2 = (-\frac{a}{2}, \frac{\sqrt{3}}{2}a) \). 
\( a = 1.42\text{Å} \times \sqrt{3} = 2.46\text{Å} \) is the lattice constant.

Since three of the four 2s, 2p electrons form \( \sigma \) bonds, the band structure of graphene around the Fermi level is determined by the \( p_z \) orbitals. A common approximation of the low energy electronic property is a tight binding Hamiltonian including only \( p_z \) states [88]. Linear combination of \( p_z \) orbitals \( \psi_k(\mathbf{r}) = \exp(i\mathbf{k} \cdot \mathbf{r})u(\mathbf{r}) \) satisfies the periodicity of the graphene lattice. Considering the interaction between nearest neighbor \( p_z \) wave functions, a simple approximation for the electronic structure of a graphene layer is obtained:

\[
E(k_x, k_y) = \pm \gamma_1\sqrt{1 + 4\cos(\frac{\sqrt{3}k_xa}{2})\cos(\frac{k_ya}{2}) + 4\cos^2(\frac{k_ya}{2})},
\tag{2.1}
\]

where \( \gamma_1 \approx -3.033\text{eV} \) is the nearest neighbor overlap energy integral, and \( a = 2.46\text{Å} \) is the lattice constant. Fig. 2.3 is drawn from equation 2.1. The Fermi level pass through the conical intersections, where the Fermi surface consists of six points.

2.3 Graphene Ribbon

2.3.1 Band Structure of Graphene Ribbon

As we discussed in chapter I, a carbon nanotube can be thought of as a rolled up graphene sheet to form a one dimensional structure. In another approach, graphene sheets can be cut into finite size graphene ribbons, which show similar properties to nanotubes [89]. For a graphene ribbon with width \( L \), wave vector in x-direction \( K_x \) is continuous, but in y-direction due to confinement \( K_y \) can only take discrete values, \( n\pi L \), where \( n \) is integer. Another difference from graphene, which has no edge, is that ribbon’s boundary condition plays an important role in the band structure.

There are two basic prototype shapes of graphene edges: zigzag and armchair as shown in Fig. 2.4. If the edges of the ribbon have a zigzag structure, it is known as a zigzag ribbon (ZZGR), which has localized energy state near Fermi level. If the edges have an armchair structure, it is known as an armchair ribbon (ACGR), which can be either semiconducting or metallic depending on the ribbon width. Armchair edge and zigzag edge have an angle difference of 30° between the two edge orientations which is the same in carbon nanotube
Figure 2.3: Band structure of two dimensional graphene

Figure 2.4: (a) The network skeleton of an armchair ribbon (N=10) and (b) a zigzag ribbon (N=5). The edge sites are indicated by solid circles on each side. Periodic boundary conditions are assumed for the edges. The arrows indicate the translational directions of the graphene ribbons. [92]
Since dangling carbon bonds on edges are highly reactive, in practice they are chemically passivated (for example by hydrogen and oxygen). The dangling bonds make no contribution to the electronic state near the Fermi level. The band structure depends on the ribbon width. For an armchair ribbon, the direct gap tends to decrease with the increase of the ribbon width, the gap reaches zero in the limit of very large width, which is similar to graphene. It is shown in Fig. 2.5, calculated band structure of an armchair ribbon (N=30) and the band structure of 2D graphene projected onto an armchair axis. It is seen that the projected band structure of 2D graphene is almost reproduced by that of a wide armchair ribbon.

2.3.2 Similarities with Nanotubes

As originally pointed out by Dresselhaus, the band structures of nanotubes and graphene ribbons have much in common. Both their electronic properties come from the confinement of the π electrons imposed by the boundaries of the system. The confinement opens a gap in the density of states at the Fermi level, this gap is inversely proportional to the width. For a nanotube, the gap varies approximately as $E_{\text{tube}} = 1.2/D[\text{eV}]$, where $D$ is the diameter in nm. For a ribbon $E_{\text{rib}} = 1.0/W[\text{eV}]$ where $W$ is the width in nm. As for graphene ribbon, electronic properties near the Fermi level are well described in the tight-binding approximation which considers only the π orbitals. Hence even relatively low-level theory reproduces the density of states (DOS) and wave function character for states near $E_F$, as compared with high-level calculations.

Another important property shared by both nanotubes and graphene ribbons is that for certain geometries, two 1D subbands span the energy gap giving the structures metallic properties. For nanotube this occurs when the chiral index $(n-m)$ is a multiple of three, for armchair ribbon this occurs when the number of hexagons (aromatic rings) across the width is a multiple of three minus one. Zigzag ribbons, on the other hand, always have two conducting 1D subbands asymptotically approaching the Fermi level, which are associated with the edge states of the ribbon.
Figure 2.5: (a-c) Calculated band structure $E(k)$ of armchair ribbons of various widths. (d) calculated band structure of an armchair ribbon of $N=30$, and (e) the projected band structure of 2D graphite onto an armchair axis.[92]
2.3.3 Differences with Nanotubes

An important difference between nanotubes and graphene ribbons is that graphene ribbons have edges [97]. As we discussed above, ribbon edges are chemically passivated [93, 94]. Calculations indicate that chemical properties of the passivated groups do not distract the general electronic structure of the graphene ribbon: Passivated atoms or groups may localize carriers, introduce impurity bands, and affect the density of states at \( E_F \), but will not significantly change the size of the gap [98].

A real graphene ribbon has more irregular and complicated edges (i.e. rough edges). A rough edge can be characterized as a less developed zigzag or armchair edge with additional or fewer hexagons [99, 96]. A rough edged armchair ribbon is found to be theoretically semiconducting [91, 100].

There is an advantage of the edges. The carrier density of graphene ribbon may be adjusted by introducing different chemical “dopants” bound to the edges. Nitro groups \((-\text{NO}_2)\), for instance, might be used to deplete electrons in the ribbon.

2.3.4 Conclusion

In summary, as for carbon nanotubes, the electronic properties of graphene ribbons are determined by their structure. Band gaps can be tuned from about 0\(eV\) to 1\(eV\) by changing the width. The conducting and semiconducting properties can be tailored as well. These are highly desirable properties for nanoelectronics.

2.4 Graphene Devices

From the properties discussed above, graphene is a novel material that has properties similar to carbon nanotubes. Geim et al. [101] has fabricated transistors using few layer graphite sheets. The typical dependence of its sheet resistivity \(\rho\) on gate voltage \(V_g\) exhibits a sharp peak to a value of several kilohms and decays to \(\sim 100\text{ohms}\) at high \(V_g\). Its conductivity \(\sigma = 1/\rho\) increases linearly with \(V_g\) on both sides of the resistivity peak. At the same \(V_g\) where \(\rho\) has its peak, the Hall coefficient \(R_H\) exhibits a sharp reversal of its sign as shown in Fig. 2.6. The observed behavior resembles the ambipolar field effect in semiconductors,
conducting channel can be switched between 2D electron and hole gases by changing the gate voltage. This shows few layer graphite can be gated, where the source to drain current is modulated by adjusting the Fermi level of the channel.

This graphene FET closely resembles its silicon microelectronic counterpart. Furthermore, with the novel properties of graphene, the new device structures and architectures may be achieved. A gated ballistic device is sketched in Fig. 2.7 a, where an electrostatic gate potential causes reflections of the incoming electrons and thereby gates the device.

For a quantum ballistic system (the electronic coherence length is longer than the device size), quantum interference effects will be important for the transmission. In the quantum interference device (QUID) [102] (see Fig. 2.7 b), the electrons can take two paths from the left terminal to the right terminal, either over the hole or under the hole. Electrons will interfere with each other depending on the relative phases of the wave functions of the two paths. This in turn depends on the magnetic flux through the hole. Hence this device functions as a sensitive magnetic field sensor.

A side gate (Fig. 2.7 c) will modify the electronic wavelength and thereby alter the phase relation of the two electronic paths. Consequently, the transmission through the device will modulated by the gate potential.

Other ballistic devices rely on the well known non-linear properties of asymmetric contacts to ballistic conductors. Such asymmetric structures function analogously to directional couplers for microwave structures (Fig. 2.7 d), the back scattering of electrons that pass through the channel depends on the potential profile in the junction. There are several possible schemes to influence this potential. One is to construct a control lead that is coupled to the junction via a Schottky barrier. A voltage applied to the control lead will enhance or reduce the transmission through the device, which hence functions as a ballistic transistor.

### 2.5 Graphene ribbons over Nanotubes

The above analysis indicates that conducting and semiconducting graphene ribbons can be made by appropriately patterning a graphene sheet and hence graphene ribbon transistors analogous to nanotube transistors can be produced. Besides the similarities, graphene
Figure 2.6: Field effect in FLG. (A) Typical dependencies of FLG’s resistivity $\rho$ on gate voltage for different temperatures ($T = 5, 70,$ and $300$ K for top to bottom curves, respectively). (B) Example of changes in the film’s conductivity $\sigma = 1/\rho(V_g)$ obtained by inverting the $70$ K curve (dots). (C) Hall coefficient $R_H$ versus $V_g$ for the same film; $T = 5$ K. (D) Temperature dependence of carrier concentration $n_0$ in the mixed state for the film in (A) (open circles), a thicker FLG film (squares), and multilayer graphene ($d=5$ nm; solid circles. [101]
Figure 2.7: Examples of prototype device structures. (a) Side gated field effect transistor. (b) Aharonov Bohm effect loop. (c) Electrostatic quantum interference device; relies on phase difference between the two paths induced by the electrostatic field. (d) Ballistic directional coupler.
devices show great advantages over their nanotube counterparts in fabrication and contacts.

Nanotube production still faces great challenges in controlling the nanotube size, length, and position, while graphene can easily overcome those challenges by rational patterning. The metallic or semiconducting properties of ribbons are controlled by lithography orientation; the band gap can be tailored by changing the ribbon width; integrated circuits can be produced with wafer-scale lithography; and gate structures themselves may be graphitic. Overall, the planar lithography process, the cornerstone of current Si technology, is compatible with the graphene processing.

Another major consideration and potential advantage of patterned graphene over carbon nanotubes is related to contacts. The nanotube approach to nanoelectronics is severely restricted, not only because it is still impossible to chemically synthesize and to reliably position carbon nanotubes, but also because of nanotube’s geometry. Their cylindrical shape makes it impossible to seamlessly interconnect them, which indicates that they must be interconnected using lithographically patterned metal wires. These metal to nanotube contacts pose impedance problems due to their nanoscopic size. Currently, it is still very difficult to make reliable, low resistance, and durable metal contacts to nanotubes.

Patterned graphene will not require metal contacts since the contacts themselves can also be graphene. An armchair ribbon of 10nm width will generally have semiconducting properties, while a zigzag ribbon of 100nm width will be metallic at room temperature. These two structures can be connected seamlessly, so that there is no interface between different materials[100, 91]. This connection not only makes integration of structures far simpler, it also insures the long-term integrity of the structures. The semiconducting to metallic interface itself represents an interesting electronic system too.

2.6 Summary

In this chapter, we see that planar graphene ribbons have properties similar to those of nanotubes. They both exhibit semiconducting or metallic properties depending on crystal orientation. The band gap (or pseudo band gap) varies approximately as the inverse of the width $L$. Both can be doped and gated. Due to these similarities, the patterned
graphene also has nanotube like transport properties, which include coherent transport, ballistic transport, and high current capabilities.

In essential contrast to nanotubes, graphene ribbon can be rationally patterned using standard electron beam lithography methods, functional graphene devices could be fabricated eliminating the need for metal interconnects on the wafer. This would remove many obstacles faced by carbon nanotubes, while retaining the benefits of high carrier mobility and quasi-1D transport. These characteristics show that graphene is a promising material for future semiconducting industry.
CHAPTER III

EXPERIMENTAL METHODS AND PROCEDURES

After reviewing the properties of graphene in last chapter, we will discuss experiment procedures from graphene production to device measurement in this chapter. The simplified process procedure is illustrated in Fig. 3.1: we obtain commercially available single crystal SiC wafers from the Cree Company, hydrogen etch the wafers to reach atomically flat surfaces, epitaxially grow graphene films on SiC substrate by thermal decomposition, deposit electrodes using metal evaporators, spin coat the resist, pattern structure using standard lithography methods, after development, we use oxygen plasmas to transfer pattern from the resist mask to the graphene films. Finally, we package the chips using wire bonding and measure them in a cryostat. In the following sections, we will discuss each step in detail.

3.1 Silicon Carbide

We grow graphene films by a thermal decomposition of silicon carbide (SiC)[103, 104, 105, 106]. SiC is a IV-IV compound semiconductor with outstanding properties: it has a wide band gap, a high breakdown field, high electron saturation, and high thermal stability. These properties make SiC an ideal material for today’s high temperature, high power, and high frequency device applications.

These electrical and mechanical properties come from the atomic structure of SiC. In the prime structure, SiC has a hexagonal frame with a carbon atom situated above the center of a triangle of Si atoms and underneath a Si atom belonging to the next layer as in Fig. 3.2. The distance (a) between neighboring silicon or carbon atoms is approximately 3.08Å. The carbon atom is positioned at the center of mass of the tetragonal structure outlined by the four neighboring Si atoms so that the distance between the C atom to each of the Si atoms is the same, approximately equal to 1.89Å. The distance between two silicon planes is approximately 2.52Å, which is the height of a unit cell. [107, 108]
Figure 3.1: Simplified fabrication procedure.

Figure 3.2: Tetrahedron crystal structure of SiC.
It is clear from Fig. 3.2 that the carbon atom is closer to the plane of the three bottom silicon atoms (0.63 Å) than to the top silicon atom (1.89 Å), so that cutting SiC perpendicular to the (0001) direction will most likely break the bonds between carbon atoms and the top Si atoms, and the crystal will be split into two different faces, one denoted as C-face and the other as Si-face.

SiC has more than 200 polytypes, all of which have the same chemical composition but different stacking orders of the double layers of carbon and silicon atoms (Fig. 3.3 a). If the first double layer is called the A position, the next layer will be placed on the B position or the C position according to a closed packed structure (Fig. 3.3 b). The different polytypes are constructed by permutations of these three positions. The three most common polytypes are 3C-SiC (cubic) (Fig. 3.3 c), 4H-SiC (hexagonal) (Fig. 3.3 d), and 6H-SiC (hexagonal) (Fig. 3.3 e). 3C-SiC is the SiC polytypes with 3 layers per period along the stacking direction with cubic crystal system. Similarly, 4H-SiC and 6H-SiC are the SiC polytypes with 4 and 6 layers, respectively, per period along the stacking direction with hexagonal crystal system.

We have grown graphene films on both 6H-SiC and 4H-SiC substrates. The 6H-SiC wafers are Si face (0001) polished, N doped polytype with resistivity 0.053 Ω cm. The miscut angle is about 0.01°. The 4H-SiC wafers are both faces polished and are undoped. They are transparent with resistivity > 10^5 Ω cm, miscut angle < 0.14°. The SiC wafers are diced to 3.5mm × 4.5mm pieces with dicing machine at the MIRC. SiC wafers are masked with blue tape during dicing to minimize the damage from the dicing blade.

### 3.2 Hydrogen Etching

The epitaxial growth of graphene films on SiC substrate is sensitive to the surface quality of SiC [105, 106]. The commercial SiC crystal wafers that we obtained have a large number of deep scratches (about 10 nm deep) covering the surface due to polishing damage. Before using SiC substrate for epitaxial growth, we tried several methods (oxygen etching, hydrogen etching [109, 110, 111]) to remove these defects. Hydrogen etching is the most effective method for removing polishing scratches and obtaining large atomically flat terraces (Fig.
Figure 3.3: Three most common polytypes of SiC. (a) A double layer of carbon and silicon atoms is denoted as a ball. (b) The first layer marked as “A” two arrangements of “B” and “C” are possible for the second layer. (c) 3C-SiC has 3 layers per period along the stacking direction. (d) 4H-SiC has 4 layers per period along the stacking direction. (e) 6H-SiC has 6 layers per period along the stacking direction.
SiC etching is performed in a home made induction oven (Fig. 3.4), which operates with forming gas of 5% hydrogen and 95% argon at 1 bar pressure. The forming gas flows over SiC sample during the entire process, from the start of annealing to SiC cool down to room temperature. At about 1450°C, the hydrogen gas produces regular arrays of wide atomic flat terraces separated by steps of 10Å, which are about 1 unit cell in height. Measurement with a Vecco CPII AFM (Fig. 3.5) shows that hydrogen etching improves surface flatness by removing several hundred nanometers of bulk material. The steps on the surface reflect the miscut of the wafer. When there are patterned structures on SiC surface, the step orientation will be affected by the patterned structure as show in SEM images Fig. 3.6 (b).

In certain locations, shown in Fig. 3.6 (a), the shallow part of the depressions contains 6 facets, which are rotated by 60° with respect to their neighbors around the center. The vertical offset between steps in 2 adjacent facets is 5Å, which is half of a unit cell. This may originate from the etching of screw dislocations. Similar structures have been reported by Ramachandran et al. [112].
Figure 3.5: AFM images of SiC surface at different stages of hydrogen etching.

Figure 3.6: SEM image of SiC surface after hydrogen etching. (a) Screw dislocation on SiC surface (b) SiC surface with patterned structure.
3.3 Graphene Films Growth

Geim’s group obtained few layer graphene films by mechanical exfoliation (repeated peeling) of small mesas of highly oriented pyrolytic graphite (HOPG) in 2004 [101]. One piece of 1 mm thick HOPG was dry etched in oxygen plasma to form 5µm deep mesas on the top of surface. The structured surface was then pressed against a layer of fresh wet photoresist film spun over a glass substrate. After baking, the mesas became attached to the photoresist layer, and can be cleaved off the rest of the HOPG sample. Then, after repeatedly peeling flakes of graphite off the mesas with scotch tape, only thin flakes are left in the photoresist, which is dissolved in acetone. A Si wafer with 300nm SiO₂ was dipped in the solution and then washed in water and propanol, so that some flakes became captured on the wafer surface. After ultrasonic cleaning in propanol, which removed most thick flakes, thin flakes (d < 10nm) were found to attach strongly to SiO₂ due to van der Waals and capillary forces. SEM and AFM were used to locate the graphite films position and corresponding thickness.

These are very exciting result, while 10µm size graphene films produced by mechanical exfoliation method can not provide base for integrated device fabrication. We use the more advanced thermal decomposition method to grow graphene films. [103, 104, 105, 106]

After we achieve atomically flat surface SiC samples, we grow high quality graphene films in both an ultra high vacuum (UHV) (10⁻¹⁰torr) and a moderate vacuum (10⁻⁵torr) oven [113, 114, 115, 116]. In the UHV oven when annealing a SiC sample at elevated temperatures (normally 1000°C – 1400°C), the Si atoms evaporate due to the relatively high vapor pressure, and the C atoms in the C rich surface collapse and reconstruct to graphene films as in Fig. 3.7. [103, 104, 105, 106]

Traditionally, epitaxial graphene films are grown in a UHV environment to protect the SiC substrate from oxidation as well as to protect the grown graphene from reacting with residual oxygen. This is a costly process for commercial application. More than that, since SiC substrates are typically heated by a high energy electron beam bombardment from the back of the substrate, the thermal uniformity on the front surfaces of the samples and the samples’ size limitation are big challenges towards mass production. Also, the heat
transport process from the back side to the front side expedites the accumulation of defects on the front surface of diffusion driven by thermal gradients.

We have developed a very promising moderate vacuum furnace-based method to produce high quality epitaxial graphene films as an alternative to the UHV high temperature treatment. In this method, the sample is heated in an inductively-heated carbon oven to temperatures in the range of 1100°C - 1500°C. The graphene films growth mechanism is different from that in UHV oven. In the moderate vacuum chamber, the residue of O₂, CO₂, and H₂O react at temperature above 1000°C to form a small amount of CO, which helps the growth of graphene films as Equ. 3.1. [116, 117, 118]

\[
SiC(\text{solid}) + (CO) \rightarrow SiO(\text{gas}) \uparrow + C(\text{solid}) \tag{3.1}
\]

This CVD related growth method produces graphene films on both the carbon and the silicon faces of 4H-SiC and 6H-SiC. Fig. 3.8 shows the cross section of graphene films on C-face of 4H-SiC: The left part is SiC, the right layer structure is graphene films, and the gap between them is due to the mechanical process of slicing samples.

This route towards epitaxial graphene production is important, since it is more adaptable to large scale production. Fine-tuning the background gas composition promises to further improve the graphene quality.

### 3.4 Metal Deposition

After growing a high quality graphene films on the SiC substrate, we use metal depositors to pattern electrodes on the samples. The electrode pattern is defined by a kapton shadow.
Figure 3.8: TEM image of graphene films cross section on SiC substrate. The left part of this image is SiC, the layer structure is graphite films, the gap between them is due to the polishing process during the TEM sample preparation. (by Daniel Ugarte)
mask, which is made by an excimer laser. Three kinds of depositors have been used: electron beam (e-Beam) evaporator, DC sputter, and filament evaporator.

3.4.1 Ebeam Evaporator Deposition

The e-Beam evaporator works by focusing a high density electron beam on the center of a crucible containing the metal target, the energy of the electron beam melts a region of the source metal material, which evaporates from the crucible and coats the sample. The diagram of the evaporator is shown in Fig. 3.9.

The e-Beam evaporator is the most used metallization machine in our group; it has the capability to process a variety of sample sizes ranging from millimeter chips to 4 inch wafers. The system can deposit any metal including palladium, titanium, chrome, gold, nickel, platinum, aluminum, and copper. Dielectrics such as silicon dioxide, aluminum oxide can be deposited, but the quality of the dielectric layer is not good since introducing oxygen into the chamber is not permitted.
The main components of the e-Beam evaporator are the ion gauge, valve controller, deposition controller, power supply, crucible selector, XY sweep, shutter, and hoist controller. The ion gauge is used to display the chamber pressure when under high vacuum. The valve controller controls the valves that adjust the chamber pressure. The lights on the left side of the gauge indicates the status of the valves, and a light is on when the corresponding valve is open. The deposition controller allows the operator to setup, program, start, and stop the e-Beam system. The crucible selector moves the selected crucible into position for evaporation. There are six independent crucibles in the chamber, so that a maximum of six different metal layers can be coated on samples in a single run. The power supply adjusts the energy of e-Beam, which is most critical for uniform evaporation. The XY sweep controller controls the position of the electron beam. For proper operation, the beam must move in a circle inside the crucible, otherwise the e-Beam focus on one point and drill a hole in the crucible. To avoid the contamination to samples, the beam should not touch the edges of the crucible. The shutter control opens and closes the shutter. Normally the shutter is closed. Once the metal is evaporating at the correct rate, the shutter is opened and exposes the sample to the evaporation. When the desired amount of metal is deposited, the shutter is closed to prevent further deposition.

Before the deposition, the shutter controller and evaporation sensor should be checked to ensure the proper function, and the whole chamber should be cleaned with a rubber head vacuum. In our process, the sample is put face down into the chamber, which is pumped to $10^{-6}$ torr in about 40 minutes. Low vacuum is preferred because it increases the mean free path of metal atoms by reducing the collision from air molecules.

When the power supply is turned on, the metal is heated to the point of vaporization by a high-intensity beam of electrons. This process causes the metal molecules to travel in a straight line to be deposited on the samples. The e-Beam position is adjusted in the soak process to ensure that e-Beam hits the center of crucible. Then the shutter control is set to the manual position with shutter closed, and metal source is evaporated for 5 minutes to remove the oxide layer on metal target. Then shutter is opened by switching control to automatic, and deposition on the sample is started.
The deposition rate for this system ranges from 1 Å to 5 Å, the slower the deposition, the more uniform the metal layer. Typically, we deposit Pd on our samples at 1 Å/s for 30 nm followed by Au at 2 Å/s for 100 nm.

Unlike the DC sputter that we will discuss below, the e-Beam evaporator has good directionality, and only coats the surface facing metal target as in Fig. 3.10 a. e-Beam evaporators provide very little coating to the sidewalls perpendicular to the surface, which is suitable for a lifting off process. One problem with the e-Beam evaporator is that it produces X rays during operation which may damage the samples and expose photoresist coated on the sample surface.

3.4.2 DC Sputter Deposition

The DC sputter is used to coat samples with metals on all exposed surfaces as shown in Fig. 3.10 b. Sputtering is a physical process where accelerated Ar ions bombard the surface of a sputter target, which causes metal atoms to be knocked off of the target and deposited on the sample as in Fig. 3.11. The DC sputter is mostly used to deposit aluminum, copper, titanium, chrome, gold, platinum, and nickel-chrome.

The DC sputter process is as following. DC sputter automatically opens the roughing valve, and the mechanical pump vacuums the chamber to 300 millitorr (mT). After that, the roughing valve is closed and the high vacuum valve is opened. A cryo-pump brings the chamber to the pressure of $5 \times 10^{-6}$ torr to remove impurities before starting. The ion gauge is turned on, which works when below $1 \times 10^{-4}$ torr. The throttle valve is then closed,
partially obstructing the path from the chamber to the cryo-pump. Argon is injected into the chamber, and the chamber pressure is raised to 6 mT, which is the gas pressure for the deposition process. Different from other deposition facilities, which should keep as low pressure as possible ($10^{-6}$ torr for e-Beam evaporator), the DC sputter operates at millitorr pressure.

During process, two parameters are most critical to the system: the 3” gun power that should be below 7% of max power supply, and the 8” gun power that should be below 40% of max power supply. Exceeding the ranges will damage the power supply, cathode assembly, and sputter target of the system.

The main advantages of the DC sputter are that there is no heating and the substrate temperatures remains low during deposition. This makes DC sputtering an ideal method to deposit contact metals onto low melting temperature materials. On the down side, during sputter deposition, samples are bombarded by energetic ions and neutral atoms, which may damage the surface of samples.

### 3.4.3 Filament Evaporator Deposition

The filament evaporator is ordinarily used to coat gold, nickel, chromium, aluminum, and copper. It can not coat palladium, whose melting temperature ($1552.95^\circ C$) is too high for
the system. The alternative, Au and Pd alloy, can be coated. For PVD 75 filament evaporator, the metal evaporation source is heated to a high temperature by a tungsten filament (melting temperature 3410°C). This causes the metal to evaporate and be deposited on the samples.

The PVD 75 filament evaporator has three tungsten boat holders in the chamber, so that up to three different metals can be deposited in one run. Before deposition, the source selector is set to the proper electrode pair, and pellets are placed in each boat depending the deposition metal thickness. Two pellets correspond to about 120 nm deposition layer thickness. The deposition process is monitored to ensure proper execution. When the deposition power increases more than 30% and deposition rate decreases, the process should be stopped immediately because that signals the running out of deposition metal. The sample holder is rotated during deposition to ensure the uniformity of the metal film.

### 3.5 Lithography

#### 3.5.1 Photolithography

After electrodes are deposited on samples, we use photolithography and e-Beam lithography to pattern the graphene films.

Photolithography has been used for over 30 years as the preferred method in the manufacturing process of silicon devices and other semiconductor components. It produces good results with features on the micron size, which is ultimately determined by the wavelength of the light used. Diffraction of the light will blur the structure of smaller features.

There are two photolithography mask aligners, the MA6 and the MJB3, which are used to transfer a pattern from a mask to photoresist film. Ultra-violet (UV) light goes through the photo mask, which casts a shadow on the surface to define the photoresist pattern. Different photoresist films are sensitive to light at different wavelengths. It is important to select an output wavelength optimized for the resist.

We use the MA6 mask aligner in our process, which is compatible with 4”, 5”, and 7” masks. The MA6 uses a 350W mercury lamp that exposes across the spectrum 230 nm to 400 nm. It has two intensity settings, CI-1 and CI-2. CI-1 is calibrated for 5mW/cm² at
365 nm, and CI-2 is calibrated for $20\text{mW/cm}^2$ at 405 nm. Both can maintain a constant intensity during exposure.

There are six exposure modes available for this system: flood exposure, soft contact, hard contact, low vacuum contact, vacuum contact, and proximity mode. Flood exposure is used when no mask is installed. In the soft contact mode, the sample is held against the mask, but remains secured to the chuck by vacuum. In hard contact mode, the wafer is held against the mask, the vacuum that holds the wafer to the chuck is released, and nitrogen is used to apply pressure to the bottom of the wafer. In low vacuum contact mode, the space between the wafer and mask is partially evacuated, nitrogen is bled in to prevent complete evacuation, which causes less wear to the wafer and mask than vacuum contact. In vacuum contact mode, the space between the wafer and mask is evacuated, bringing the wafer in very tight contact with the mask. And finally, in proximity mode, the wafer is not placed into contact with the mask. The space between the wafer and mask can be set using the exposure gap parameter. Usually we use soft contact mode or proximity mode, which does less damage to the sample surface.
3.5.2 E-Beam Lithography

e-Beam lithography is a process similar to photolithography, but uses an electron beam rather than UV light to expose resist. In photolithography the resolution is limited by the UV light wavelength, which must be much smaller than the feature size. This is not a problem for e-Beam lithography, since electron wavelength is only \(0.2\AA - 0.5\AA\) at 100 keV. Another advantage of e-Beam lithography is no physical mask needed, which eliminates costs and time delays associated with mask production. Furthermore patterns can be optimized and changed simply by using flexible CAD software.[119, 120]

Although the diffraction effect is not critical in e-Beam lithography, electron scattering in the resist and substrate strongly limits its resolution. When the e-Beam strikes the material, electrons collide with resist atoms and substrate atoms, and get scattered. This causes the written pattern to significantly deviate from the intended size.

There are two kinds of scattering: back scattering and forward scattering. Back scattering is an elastic scattering, which happens when electrons collide with the heavy nucleus. The electron retains most of its energy but changes its direction [121]. After several large angle scattering events in the substrate, electrons may return back through the resist at a significant distance from the incident beam (Fig. 3.13), and thereby cause additional resist exposure and introduce an undesired influence called the proximity effect [122]. The proximity effect is a complicated phenomena related to resist type, resist thickness, electron voltage, exposure time (dose), development time. The fraction of electrons that got back-scattered is mainly affected by resist and substrate atomic mass. The lower the atomic mass, the less the back scattering. In our experiment, the HSQ (hydrogen silsesquioxaneis) resist sample has much stronger back scattering than the PMMA (polymer) resist sample. Another method is to use the multiple layer structure to reduce proximity effect and increase pattern resolution. The top layer is used to define the pattern, and the bottom layer’s function is to absorb back scattered electrons. But this method increases the complexity of the process.

More often, electrons collide with electrons from resist or substrate atoms and are pushed away an angle from origin direction (Fig. 3.14). This action is called forward scattering.
Electron beam forward scattering from resist atoms broadens the beam size, and hence widens the pattern. The effective beam diameter can be calculated from [123]

\[ d_f = (0.9R_t/V_b)^{1.5} \]  

(3.2)

where \( d_f \) is the effective beam diameter in nanometers, \( R_t \) is the resist thickness in nanometers, and \( V_b \) is the beam voltage in kilovolts. So, higher e-Beam voltages and thinner resist thicknesses will reduce the effective beam diameter.

Our electron beam lithography systems use electron beams with 10-100 keV energy per electron (primary electron). When the primary electrons slows down, much of their energy is transformed to secondary electrons with energy 2 − 50eV, which is the main resist exposure source. Since the secondary electrons have relatively small energy, the distance
Table 3.1: Proximity parameters as a function of the beam energy, α is the forward scattering range parameter, and β is the backscattering range parameter [124].

<table>
<thead>
<tr>
<th>Beam energy (keV)</th>
<th>α (µm)</th>
<th>β (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>1.33</td>
<td>0.18</td>
</tr>
<tr>
<td>10</td>
<td>0.39</td>
<td>0.60</td>
</tr>
<tr>
<td>20</td>
<td>0.12</td>
<td>2.0</td>
</tr>
<tr>
<td>50</td>
<td>0.024</td>
<td>9.5</td>
</tr>
<tr>
<td>100</td>
<td>0.007</td>
<td>31.2</td>
</tr>
</tbody>
</table>

the electrons travel is about several nanometers, and they contribute little to the proximity effect[125]. The forward scattering widens the exposure pattern, and is the major factor that limits e-Beam lithography’s resolution.

One concern about using e-Beam lithography is the damage from high energy electron-atoms collisions. For head-on collisions with the nucleus, the transfer of energy is given by [126]:

\[ E = E_0(1.02 + E_0/10^6)/(465.7A), \]  

(3.3)

where \( E_0 \) is the incident beam energy, and \( A \) is the atomic number of the target. If \( E \) exceeds the displacement energy \( E_d \), which is determined by atomic weight, bond strength, and crystal lattice; the electron may displace the position of the nuclei and damage the crystal structure of the substrate. \( E_d \) varies from 17 eV for aluminum to 80 eV for graphite. From this formula only when electron energy exceeds 300 \( keV \), it may damage graphite. When electron energy is below 100 \( keV \) as in our experiment, it will not affect graphite, but the heat due to scattering will modify the resist sensitivity and introduce unwanted line variations.

Another consideration is the conductivity of the substrate, which is not a problem in photolithography. When the electron beam writes on semiconducting or insulating substrate, the electrons will accumulate on surface, and electron-electron collisions will dominate the scattering effect. This is called the charging effect. The charging effect shifts the electron beam penetration direction and broadens the beam width. Spin coating a layer of conducting film on surface or using a lower writing current can reduce the charging effect.
We have used two types of SEM machines in our project: JSM 5910 and JBX 9300. For the benefit of future users in our group, the e-Beam lithography procedure are explained in detailed below. The JSM 5910 uses Design CAD LT2000 as the default structure design software. Another more popular and powerful software Auto CAD also can be used for structure design, the output *.dxf can be converted to Design CAD LT2000 file *.dc2, which is the only file recognized by JSM 5910. To reach the best result, the whole pattern can be split to several layers, each layer uses different magnification and dosage. Normally two magnification settings ×1000 and ×70 are used, ×1000 (95µm × 95µm writing area) is for fine size structure and ×70 (1.2mm × 1.2mm writing area) is for large size structure and connection pads. From ×1000 to ×70 there is a 35µm offset in X direction and 5µm offset in Y direction. The value of the offset will change after each filament replacement, thus periodic calibration is recommended. There are totally three magnification circuits for the JSM 5910. Origin offset happens at the transition point of ×500, ×5000, ×50000, a click is heard when the magnification circuit changes. In the *.dc2 file, JSM 5910 exposes the line structure with solid line and enclosed area by dashed line. After converting *.dxf to *.dc2 file, NPGS software creates a *.rf6 run file, which includes all the information for e-Beam lithography: dose, current, origin offset, and magnification.

The standard operation procedure is listed below as reference for other users of this system. First load *.rf6 into JSM 5910, mount the PMMA coated SiC sample on sample holder by the copper clip, make sure the surface is parallel to the holder. Then put the sample holder into SEM chamber, pump down to vacuum 10⁻⁴torr, turn on the e-Beam, move the e-Beam to the faraday cup to measure the beam current at different beam spot. Next set operation parameters to 30kV, 15mm WD , and ×1000 magnification, which give good lithography resolution. Then click lens reset, adjust stigma on an gold particle until the gold particle image is perfectly round, move to the sample area. Adjust the focus in sample edge, move the beam to a spot 1 mm away from designed writing area, put the magnification to ×30000, the current to 100pA; click the beam blank, turn the switch to NPGS, turn beam on, expose for 90 seconds. Decrease current back to 10pA, and take SEM images, there should be a white round contamination spot on surface due to the e-Beam.
exposure, adjust the focus on the contamination spot. If the contamination spot appears elliptical, readjust the stigma. Since HSQ is much less sensitive compared to PMMA, it is hard to get a clear contamination spot for HSQ, also longer exposure time is needed to produce HSQ contamination spot. Double check the loaded *.rf6 file, click beam blank, turn switch to NPGS, then process *.rf6 file. The current shown on the monitor is about 80% of the setting value. After the writing is finished, take sample out of chamber, develop it in the developer (one part MIBK and three part IPA mixture) for 90 seconds, rinse in IPA for 50 seconds, blow dry with N₂. Bake in a 100°C hot plate for one minute. The JSM 5910 can reach about 100 nm line width structure, for finer structures, another system the JBX 9300 is used.

The JEOL JBX 9300 100kV electron lithography system provides the capability of reproducibly achieving feature sizes below 20 nm. Additionally, multilayer EBL with less than 20 nm overlay accuracy on a wide variety of substrates is achievable. Substrate handling can range from 3 mm small pieces to 300 mm wafers and from 3 inch to 7 inch photomasks.

The JBX 9300 features an advanced electron optical column allowing it to reproducibly write sub 20 nm features as shown in Fig. 3.15. An extremely stable thermal field emission electron source operated at 100 kV is used to produce writing currents from 50 pA to 50 nA and is capable of producing a minimum spot of 4 nm. The 500 µm patterning field can be addressed on a 1 nm grid using a 20-bit deflection system, which effectively eliminates patterning defects due to grid placement errors. The precision alignment system is capable of minimizing overlay errors to less than 20 nm for multilayer lithography, and stitching accuracy of less than 20 nm can be reproducibly achieved. In spite of its complexity, the JEOL is controlled by a user friendly UNIX-based graphical interface.

Different from the JSM 5910 system, the JBX 9300 only recognizes *.v30 file format. As shown in Fig. 3.16, a pattern is designed as *.dxf file in AutoCAD software, then *.dxf is converted to *.gds format by LinkCAD software. Finally *.gds is converted to *.v30 format by JBXFILER software. The field size of the JBX 9300 is 500 µm, so it is optimal to keep the patterns smaller than 500 µm and to put the fine structure in the middle of the pattern in a *.v30 file. Use as low a current as possible, under similar condition 2nA gives 50nm
Figure 3.15: Electron optical column of JBX 9300.

In the next several paragraphs, operation procedure is discussed as reference for other users. Log into the JEOL in the main computer with Login: ebtest, Password: EBtest. Go to the EBXMENU window, if EBXMENU is closed by the previous user, open a new one by typing “ebxmenu” in a terminal window.

Wear a new pair of latex gloves, remove the HSQ resist from the sample edge to make better electrical contact between the cassette and sample. Load sample in the piece cassette window 3A, whose slit width is 3 mm. Turn the two screws below the window to adjust the edge of the sample parallel to the edge of the cassette. Place the cassette on the stage platform and make sure the door of the system is closed. Select the ALD screen to press the platform to stage exchange arrow. The loading process takes about 15 mins.

In the JOB window, edit job deck file *.jdf and schedule file *.sdf by file manager. *.jdf and *.sdf files are text files, the machine uses them to determine layout, dose, current for the exposure. It is best to edit and rename old files rather than starting new ones each time. Use command schd to compile *.jdf file and *.sdf file to *.mgn file, which is the one
to be exposed by JBX 9300.

The array check command, accessed through the analysis menu, is one of the most useful features of the JEOL software. Array check allows to view what will actually be printed on the sample by *.mgn file, the shot display option allow to view where every pixel will be written. This is particularly useful for curved features where filling and pixel dropping becomes an issue. If more than one wafer were being exposed, click the sequential number to see the next exposure in the series. Once you have the magazine file open in array check, it can be seen where every pattern is being placed, as well as the dose, wafer size, and position in the cassette.

Move the stage to 3A center (coordinate 80000,60000), turn on SEM and locate the center of metal cross marks (coordinate a, b), the origin offset in *.sdf file should be (a-80000, 60000-b). JBX 9300 is capable of automatic focus by command HEIMAP, which stands for height map. During this routine the machine will measure the height at various points of the sample, and adjust focus accordingly. For our millimeter size sample it is best to open EDS window and manually focus on surface, typically the focus values are 17390 at 2 nA current and 17550 at 100 pA current.

Once the cassette has been loaded, open the CALIB window, load the auto calibration file normal2, which will run command INITIBE, PDEFBE, SUBDEFBE, and DISTBE in order. After approximately five seconds the machine will update its parameters, press parameter save several times to ensure parameters are saved to the condition file.
Click on the EXP icon and select the *.mgn file ready to expose. Click execute and the exposure will begin. The estimated time for exposure can be get from

\[ t = \frac{(D \ast A)}{I} \]  

where \( t \) is the time (sec) estimated to finish writing, \( D \) is the exposure dose (C/cm\(^2\)), \( I \) is writing current (Amp), \( A \) is total exposure area (cm\(^2\)).

Once the exposure is done, go to the ALD screen and click the stage to platform exchange arrow. After approximately 10 minutes the cassette will be unloaded. Develop samples in 10% TMAH for 60 seconds and rinse in DI water. Fig. 3.17 shows several structures patterned by JBX 9300 from the design in Fig. 2.7.

### 3.5.3 E-Beam Resist

Two kinds of e-Beam resists are used in our fabrication process: hydrogen silsesquioxane (HSQ) and polymethyl-methacrylate (PMMA). HSQ is a high resolution negative tone inorganic e-Beam resist, which has shown sub 30nm resolution with JBX-9300 system.
HSQ has a low dielectric constant and has a cage structure before curing and a network structure after curing as in Fig. 3.18. Cured HSQ is a form of porous SiO$_2$. In the e-Beam writing process, SiH bonds, which are weaker than SiO bonds, are broken by the e-Beam. Siloxane bonds will form from the reaction of silanols and moisture. Finally a cross link network is formed and resist becomes difficult to dissolve in the developer.

After exposure, HSQ patterns are formed with high contrast by using TMAH developer. There is little thickness loss even in the lightly exposed resist, because HSQ does not contain any unstable components. Then we transfer the designed structure to graphene films by oxygen plasma etching with the HSQ resist pattern as a mask. Oxygen atoms in the plasma may diffuse into HSQ film and oxidize the films [127]. After oxygen plasma treatment, HSQ becomes hard to dissolve, and even when rinsed in HF solution for more than 10 minutes, a considerable amount of residue remains on surface. In our experiment, the HSQ pattern surface does not get rough after plasma treatment, therefore the oxygen plasma treatment does no have a negative effect on the HSQ pattern. The HSQ line width fluctuations are dominated by the granular structure of the resist film, which is made up of resist polymer aggregates. Using a fresh bottle of HSQ and performs the e-Beam lithography right after spin coating has been observed to reduce the width fluctuations.

Figure 3.18: Chemical structures of HSQ: (a) cage form, (b) network form. [127]
Another factor related to the width fluctuation is the resist film thickness. To get thin resist film, HSQ is diluted with MIBK at the ratio 1:1 and spin coated at speed of 10000 rpm, to produce a film thickness of about 40nm.

Polymethyl methacrylate (PMMA) is the positive e-Beam lithography resist we used in earlier experiments. It is formulated with 495,000 and 950,000 molecular weight resins in either chlorobenzene or anisole. The positive nature of this resist result from polymer chain scissions that are initiated by the electron beam. These chain scissions reduce the chain length of the polymer in the exposed area making it more soluble in MIBK solvent as in Fig. 3.20.
3.6 Plasma Etching

After development, graphene films are covered with patterned e-beam resist mask. ICP (inductively coupled plasma) or RIE (reactive ion etcher) in MIRC are used to transfer pattern to graphene films.

The ICP process is different from the RIE process because ICP uses two power supplies to generate plasma as shown in Fig. 3.21. One power source is used to generate a dense plasma (about ten times more reactive species than RIE), while the second power source accelerates the ions towards the etching surface. This combination increases the anisotropy of the etched feature as compared to conventional RIE.

ICP also use a Bosch process to create very high-aspect-ratio structures (∼ 20 : 1) by alternating between an etch and deposition step. The cycle begins by isotropically etching the wafer with $SF_6$, then $C_4F_8$ is used to conformably deposit a fluorinated polymer coating on both the trench’s bottom and sidewalls. The process then switches back to etching with $SF_6$, which etches the polymer off of the trench’s bottom faster than the trench’s sidewalls. Thus, the wafer is etched on the trench bottom while the sidewalls are protected by the polymer. The protective sidewall polymer layer is eventually etched away, so the
process switches back to the deposition step, and the entire process is repeated. The typical deposition time is 4 seconds, the etch time is 8 seconds; 0.5\(\mu m\) material is etched in one cycle.

The ICP etcher can be used to etch silicon, silicon carbide, silicon dioxide, silicon nitride, and some polymers. The ICP has two chambers. One is dedicated to deep silicon trench etching using the Bosch process with \(SF_6\), \(C_4F_8\), and \(Ar\). The other chamber is used for silicon dioxide, silicon nitride and polymer etching with \(Cl_2\), \(BCl_3\), \(H_2\), \(O_2\), \(CF_4\), and \(Ar\). Both chambers are pumped with turbo pumps for low-pressure operation.

The ICP system does not have a cleaning process, and it accepts 4” wafers only. Smaller samples must be mounted on a 4” carrier wafer.

RIE is the most used etcher for our project. A plasma thermal RIE produces reaction gas plasma in RF (radio frequency 13.56 MHz) electrical field to etch materials. The RIE system has two chambers, the right chamber is used for etching of nonmetallic materials such as \(Si\), \(SiC\), \(SiO_2\), \(Si_3N_4\) with gas \(O_2\), \(CHF_3\), and \(SF_6\), and the left chamber is for etching metals with gas \(BCl_3\), \(Cl_2\), \(CHCl_3\), and \(SiCl_4\). The bottom electrode (where the samples are placed) is called the plate, and the upper electrode (where the gases enter the chamber) is called the showerhead. The plasma generates free ions that are accelerated towards the surface to be etched as shown in Fig. 3.22. Through chemical reactions and bombardment of the wafer with the reactive ions, etching is accomplished. In a typical run, the plasma thermal RIE can process a wide range of sample sizes, from several millimeter to 4 inches.

After oxygen plasma etching, the HSQ mask can be removed using a HF solution. As shown below, electric transport is mainly dominated by the interface layer, so the contamination on the surface will not affect the transport properties. Then sample is mounted on home made sample holders by wire bonding as in Fig. 3.23.

### 3.7 Dielectric Film Deposition

After etching, we may deposit a layer of \(SiN\) by Unaxis PECVD (plasma enhanced chemical vapor deposition) on the sample surface to protect the structures.
Figure 3.22: Figure of RIE (reactive ion etcher), 13.56 MHz RF energy is applied on the two parallel plates to produce plasma and etch wafers.

Figure 3.23: A sample after package and ready for measurement.
A PECVD system reacts gases in a RF induced plasma to deposit materials such as $SiO_2$ and $Si_xN_y$, stress of deposited films is adjusted by the ratio of $H_e : N_2$. The PECVD system has only one chamber for all depositions.

The Unaxis PECVD can process a wide range of sample sizes. A typical run can process up to four 4” wafers, and deposition will be uniform regardless of any through-wafer or through-sample holes. PECVD can deposit silicon dioxide, silicon carbide, and thin layers of amorphous silicon. Typical deposition rates range from 80 Å/min to 400 Å/min, depending mainly on power and temperature. We use this system primarily for depositing low-stress silicon nitride films.

During process, the value of reflect power represents the chamber condition. The larger the reflect power, the dirtier of the chamber is. The reflect power should be below 1W, otherwise a cleaning process should be performed.

### 3.8 Transport Measurement

A Janis SuperVariTemp (SVT) cryostat is used for transport measurements, the lowest temperature is 2 K and highest magnetic field is 9 Tesla. This system consists of an outer liquid nitrogen reservoir, an inner liquid helium reservoir, a superconducting magnet, and an insert as shown in Fig. 3.24. The insert provides a sample tube that is isolated from the main reservoir by an isolation tube with the space between the two evacuated tube. The insert draws helium form the main reservoir through a needle flow control valve and a capillary tube. The helium enters the bottom of the sample tube through a special vaporizer. The helium vapor travels up the sample tube and cools the sample mount and any sample attached to the mount. Temperatures between 4.2k and 300k can now be obtained by passing appropriate current through the vaporizer heater, to counter the cooling power of the helium. A LabView program has been developed to interface the instruments via GPIB boards and control the measurements at different temperatures. Operating below 4.2k is achieved by filling the sample tube with liquid helium, closing the needle valve and the vent outlet, and then using roughing pump to reduce the pressure on top of the helium. This provide 1.5k temperature at the sample.
The temperatures of 70 K is reached by filling the liquid nitrogen reservoir with liquid nitrogen and allowing it to pre-cool overnight. For lower temperature measurement, liquid helium is then transferred into the helium reservoir and a Lakeshore electronically controlled heater mounted on the sample stage is used to maintain the sample temperature at a certain value. A Lakeshore thermometer mounted on the sample stage is used to monitor the actual sample temperature. Conductance measurements in this work are performed using a Stanford Research Systems SR830 lock-in amplifier.

Figure 3.24: Figure of Janis cryostat [129].
CHAPTER IV

ELECTRONIC TRANSPORT IN TWO DIMENSIONAL SYSTEMS

4.1 Introduction to 2D Electron Gas

As discussed in the previous chapter, we have grown ultra thin graphite films on SiC wafers with the thermal decomposition method. In transport measurement, ultra thin graphite films show spectacular two-dimensional electron gas (2DEG) properties different that are different from bulk graphite. In a 2DEG system, charge carriers move in a plane and are tightly confined in the perpendicular direction, which leads to momentum quantization [130, 131]. While in bulk metal and semiconductors, the charge carriers can move freely in all three spatial directions. 2DEG systems are produced in several ways discussed below.

In a MOSFET device, with the gate potential applied, an accumulation or inversion layer is formed to connect the source and drain. In this way the carriers are trapped at the surface in an approximately triangular potential well and form a 2DEG as shown in Fig. 4.1. [132, 133]

Another type of 2DEG is formed in the heterostructures of two semiconductors, usually AlGaAs and GaAs. By using MBE (Molecular Beam Epitaxy) or MOCVD (Metalorganic Chemical Vapor Deposition), AlGaAs and GaAs alternatively are grown sequently to form a sandwich like structure, where each semiconductor layer is several nanometers thick to produce a superlatice. [135, 136]

Since the Fermi energy in the wide gap AlGaAs layer is higher than that in the narrow gap GaAs layer as shown in Fig. 4.2, electrons spill over from AlGaAs to GaAs. AlGaAs is positively charged donor and GaAs is negatively charged accepter. The space charge gives rise to an electrostatic potential that causes band bending as shown in Fig. 4.2. In equilibrium, the Fermi energy is constant everywhere, since electrons flow from a high Fermi
Figure 4.1: Band diagram showing a conductance band $E_C$, a valence band $E_V$, and Fermi level $E_F$. A 2DEG is formed at the interface between the oxide ($SiO_2$) and silicon substrate as a consequence of the gate voltage $V_g$. 
Figure 4.2: Band structure of the interface between AlGaAs and GaAs, before and after the charge transfer.[134]
energy region to a low Fermi energy region until they reach equilibrium. At the interface, the Fermi energy is inside conduction band, and a thin conduction layer is formed, this is the 2DEG [137]. This structure resembles to a standard MOSFET, where the 2DEG is formed in the Si instead of the GaAs, and SiO₂ takes the role of the wide gap AlGaAs[138].

4.2 Density of States of 2DEG

Electric transport in a 2DES is different from 3D and 1D systems. The dispersion relation of the free conduction electrons in 2DEG is [139, 140]

\[ E = E_0 + \frac{\hbar^2}{2m}(k_x^2 + k_y^2), \]  

(4.1)

where \( E_0 \) is the bottom of the conduction band, and \( m \) is the effective mass of quasi-electrons. The periodic boundary conditions require \( k_x, k_y \) to take quantized values

\[ k_x = n_x(2\pi/L_x), k_y = n_y(2\pi/L_y), \]  

(4.2)

where \( L_x, L_y \) are dimensions of the sample and \( n_x, n_y \) are integers. In the \( k_x, k_y \) plane, each individual state occupies the area:

\[ \frac{2\pi}{L_x} \times \frac{2\pi}{L_y} = \frac{4\pi^2}{S}, \]  

(4.3)

where \( S \) is the area of the sample. The total number of states in the area of \( k \) space \( \pi k^2 \) is

\[ N_T = 2 \times \frac{\pi k^2}{4\pi^2/S} = \frac{mS}{\pi \hbar^2}(E - E_0). \]  

(4.4)

\( 2 \) is for spin, and the density of state of 2DEG per unit area per unit energy is

\[ N_{2d}(E) = \frac{m}{\pi \hbar^2} \vartheta(E - E_0), \]  

(4.5)

where \( \vartheta \) is unit step function. From here we get the result that the density of states is independent of the energy in 2DEG [134]

\[ N_{s(2d)} = \frac{m}{\pi \hbar^2}. \]  

(4.6)

This is different than that of 1D and 3D systems as shown in Fig. 4.3. In a 3D system, the number of states with energy less than \( E \) is

\[ n = \frac{1}{3\pi^2} \left( \frac{2m(E - E_0)}{\hbar^2} \right)^{3/2}. \]  

(4.7)
Figure 4.3: Densities of states versus energy for free electrons in one, two, and three dimensions.

The density of states becomes \([141]\)

\[
N_{3d}(E) = \frac{dn}{dE} = \frac{1}{2\pi^2} \left( \frac{2m}{\hbar^2} \right)^{3/2} \sqrt{(E - E_0)} \quad (4.8)
\]

The density of states in a 1D system is \([141]\)

\[
N_{1d}(E) = \frac{\pi}{2} \left( \frac{dE(k)}{dk} \right)^{-1} = \frac{2m}{\pi\hbar^2} \left( \frac{\hbar^2}{2m(E - E_0)} \right)^{1/2}. \quad (4.9)
\]

By the Pauli exclusion principle, the electrons will fill all the available energy levels up to the top of that Fermi sea of electrons at the Fermi energy or Fermi level. In equilibrium the conduction electron population is calculated from the integral of the product of the Fermi distribution function and electron density of states over the energy: \([141]\)

\[
n_s = \int N(E)f_0(E)dE, \quad (4.10)
\]

where

\[
f_0(E) = \frac{1}{1 + \exp[(E - E_f)/(k_B T)]}. \quad (4.11)
\]

For a degenerate 2DEG

\[
n_s = N_s(E_F - E_0), \quad (4.12)
\]

where \(n_s\) is the electron sheet density, and \(N_s = m/\pi\hbar^2\). At low temperature \(T \ll E_F/k_B\), all states are filled up to the Fermi level, \(E_F - E_0 = \hbar^2 k_F^2 / 2m\). The Fermi wave number is \([134]\)

\[
k_F = \sqrt{2m(E_F - E_0)}/\hbar, \quad k_F = (2\pi n_s)^{1/2}, \quad (4.13)
\]
and the corresponding Fermi velocity is [139]

\[ v_F = \frac{\hbar k_F}{m}. \]  

(4.14)

### 4.3 Transport Parameters of 2DEG

Applying an electric field \( E \) parallel to the 2DEG plane, a drift velocity \( v_d \) of the carriers in the direction of the force \( eE \) is produced [139]

\[ \frac{mv_d}{\tau_m} = eE, \quad v_d = \frac{e\tau_m}{m} E, \]  

(4.15)

where \( \tau_m \) is the momentum relaxation time, which is the period between successive collisions.

The mobility is defined as the ratio of the drift velocity to the electric field [139]

\[ \mu = \frac{|v_d|}{E} = \frac{|e|\tau_m}{m}. \]  

(4.16)

From Eq. 4.16, it is clear that the fewer defects and smaller carrier masses give higher mobilities. The mobility increases with decreasing temperature due to the suppression of phonon scattering. The value of mobility will saturate at low temperature when phonon scattering become small enough and impurity scattering becomes the dominate mechanism.

The conductivity of the 2DEG is expressed as [142]

\[ \sigma = n_s e^2 \tau/m = g_s g_v \frac{e^2 k_F l_e}{\hbar}, \]  

(4.17)

where \( n_s \) is the electron density, \( g_s \) is the spin degeneracy, \( g_v \) valley degeneracy, \( \tau \) is the transport time, \( m \) is the effective mass. This formula is valid when electron wavelength \( \lambda_F = 2\pi/k_F \) is much smaller than the mean free path \( l_e = v_F \tau_m \); that is \( k_F l_e \gg 1 \) or \( E_F \tau_m \gg \hbar \).[143, 134]

In a closed circuit with applied electrical field \( E \), a current \( I \) due to carriers flowing is produced. In 2DEG without considering thickness, current density is expressed as \( J = I/W \), where \( W \) is the width of the conductor. The equation [139]

\[ J = e n_s v_d, \]  

(4.18)
relates the current density to carrier density $n_s$ and drifty velocity $v_d$. Comparing $J = -eD\nabla n = e^2 D n_s E$ with $J = \sigma E$, we obtain the expression for conductivity as [134]

$$\sigma = e^2 N_s D$$

(4.19)

where $D$ is the diffusion constant. This is Einstein relation for degenerate conductors. Since $\sigma = |e| n_s \mu$, we get $|e| D \mu = n_s N_s = E_F = k_B T$, so [134]

$$D = \frac{E_F \mu}{|e|}, D = l_e v_F / 2.$$  

(4.20)

In this way we derive the mean free path of 2DEG from conductivity measurements.

## 4.4 Characteristic Lengths of Mesoscopic System

In a mesoscopic system, there are four key characteristic lengths: the momentum relaxation length (or mean free path), the phase relaxation length, thermal dephasing length, and the Fermi wave length.

The mean free path $l_e$ is the average distance that an electron travels before its initial momentum is changed [141]

$$l_e = v_f \tau_m,$$

(4.21)

where $v_f$ is the Fermi velocity, and $\tau_m$ is the momentum relaxation time. The mean free path is not affected by electron-electron scattering processes since the electron-electron interaction does not affect the total momentum. (Consider all the electrons as a system, the momentum is conserved by electron-electron scattering.)

Comparing the mean free path with characteristic dimensions of the system, $L$, one can discriminate between diffusive, quasi-ballistic, and ballistic transport. The situation is illustrated in Fig. 4.4, for the case where the length $L$ of the sample is much larger than its width $W$ [144].

The phase relaxation length $l_\varphi$ is the length that an electron retains its coherence as a wave, which is a quantum mechanical relaxation length and has no analogs in classical physics. Then

$$l_\varphi = v_f \tau_\varphi,$$

(4.22)
Figure 4.4: Electron trajectories for (a) the diffusive ($l < W; L$), (b) quasi-ballistic ($W < l < L$) and, (c) ballistic ($l > W; L$) transport regimes.[144]

when the phase relaxation length is smaller than the mean free path, where $\tau_\varphi$ is the phase relaxation time, which describes the relaxation period of the phase memory. The electrons can be characterized as propagating waves that have phases. If the phases of the waves are not destroyed, specific quantum interference phenomena can be observed, such as weak localization, conductance universal fluctuation as we will discuss later.

Phase relaxation length is similar to mean free path, but the scattering mechanism is different. Scattering against any static potential, where the equations of motion are time-reversible, will not lead to the phase relaxation. The only processes that are responsible for phase relaxation are the ones that break the symmetry of time-reversal, such as inelastic scattering by phonons, electron-electron collisions, spin-flip processes [145]. When an electron suffers many elastic collisions during the phase relaxation time, it moves diffusively, a proper way to estimate the $l_\varphi$ is [141]

$$L_\varphi = \sqrt{D\tau_\varphi}, \tau_\varphi \leq \tau_m,$$  \hspace{1cm} (4.23)

where $D = l_e v_F / 2$ is from Eq. 4.20.

Besides the interference of a single electron state wave function, two electrons having
Figure 4.5: Random walk of a conduction electron. Two complementary partial waves propagating in opposite direction interfere at the origin and create a coherent echo.

similar energy may interfere with each other. Electrons will travel coherently during time $\frac{\hbar}{kT}$, when the energy difference between them is less than $kT$. The estimated characteristic length is the thermal dephasing length \cite{146}

$$l_T = \sqrt{\frac{\hbar D}{kT}}.$$ \hspace{1cm} (4.24)

The Fermi wavelength (the de Broglie wavelength for electrons at the Fermi energy) is expressed by \cite{139}

$$\lambda_F = \frac{2\pi}{k_f} = \sqrt{\frac{2\pi}{n_s}}.$$ \hspace{1cm} (4.25)

4.5 Weak Localization

Weak localization is a quantum-mechanical effect, which occurs in disordered electronic systems at low temperatures. In such a system, the electron motion is diffusive rather than ballistic, and an electron does not move along a straight line, but rather experiences a series of random scattering off impurities, which results in a random walk.

As in Fig. 4.5, the electron wave can propagate from 0 to 1, 2, 3, ..., 8, 0, this loop is generally called Feynman path. Being a wave with a defined phase, the electron also can propagate from 0, via 8, 7, ..., 1, back to 0 in the reversed path at the same time.
These two partial electron waves return to 0 and interference with the same amplitude $A$. The combined return probability of the two waves is $|2A|^2 = 4|A|^2$. Return probability for two uncorrelated electron waves is $|A|^2 + |A|^2 = 2|A|^2$, thus there is $2|A|^2$ difference due to coherence correlation. So the transport probability or conductance is related to the coherence correlation. [147, 148]

The weak localization happens when the phase coherence length is much larger than the mean free path, $l_\varphi \gg l_e$. When $l_\varphi < l_e$, the electron loses its phase memory before finishing the Feynman path, the conductor resistance is linear to the conductor length $L$, unless $L$ is comparable to $l_\varphi$.

When the phase-coherent conductor’s conductance is larger than $2e^2/h$, and its phase coherent length is smaller than the localization length $L_c$, the conductor is in the regime of weak localization.

$$L_c = Ml_e,$$

where $l_e$ is the mean free path, $M$ is the number of conduction channels. The decrease of conductance is

$$\Delta G = <G_Q> - G_{CL} \approx -\frac{e^2}{h},$$

where $<G_Q>$ is the average quantum conductance, $G_{CL}$ is the classical conductance. This result is independent of material and background conductance. [134, 149]

On the other hand, when conductance is smaller than $2e^2/h$, and the length of a phase coherent conductor is much larger than the localization length $L_\varphi \gg L_c$, the conductor is in the strong localization regime.

## 4.6 Universal Conductance Fluctuations

UCF (Universal Conductance Fluctuations) may be seen as repeatable noise like fluctuation structures in conductance measurements. It is another electron interference effect similar to weak localization. The characteristic fluctuation amplitude is independent of the details of the elastic scattering centers, of the value of the Fermi energy, or of the strength of an external magnetic field. The conductance fluctuation is

$$\sqrt{\langle \delta G^2 \rangle} \approx 2e^2/h,$$
Figure 4.6: A schematic drawing illustrates the difference between the types of diffusing trajectory that give rise to weak localization (left) and universal conductance fluctuations (right).

where $\sqrt{\langle \delta G^2 \rangle}$ is defined by $\sqrt{\langle \delta G^2 \rangle} = \sqrt{\langle G^2 \rangle - \langle G \rangle^2}$, and $\langle G \rangle$ denotes the average conductance of the sample. Thus the fluctuation is on the order of quantum conductance $2e^2/h$ and does not relate to the sample material. [150, 151, 152]

The UCF are observed when the phase coherence length $L_\phi$ is comparable to the sample size $L$. The fluctuation will become small and even be smoothed out when the sample size $L$ is larger than $L_\phi$. [145, 134]

4.7 Comparing Weak Localization and UCF

Both weak localization and UCF originate from the electron coherent interferences, as illustrated in Fig. 4.6, weak localization results from the interference of time-reversed pairs of paths that start from a initial point A and diffuse back to the same point by undergoing a series of elastic scattering events. On the other hand UCF results from interference involving weak-localization-like trajectories, as well as interference between electron partial waves that propagate between different points of the sample, A and B, along distinct paths. [150, 145]

While UCF are not sensitive to a small magnetic field, weak localization vanishes rapidly
when magnetic field $B_c$ is applied \cite{134,153}

$$B_c \approx \frac{h}{eL_\phi^2}. \quad (4.29)$$

$B_c$ is about 40 G when $L_\phi = 1\mu m$. In an electron waveguide with a width $W$, which is much less than the phase relaxation length, the $B_c$ is different

$$B_c \approx \frac{h}{eWL_\phi}. \quad (4.30)$$

$B_c$ is about 140 G when $W = 280$ nm and $L_\phi = 1\mu m$. When the width of the wave guide is less than the mean free path, the $B_c$ gets even larger. Under some conditions a positive, instead of a negative, magnetoresistance resulting from spin orbit scattering is observed. \cite{142}

### 4.8 Landau Levels

When placing a 2DEG in a high magnetic field, the Lorentz force causes the electrons to perform a cyclotron motion, where $\omega_c = eB/m$ is the cyclotron frequency, $mv^2/r = evB$, $r = mv/eB$. In quantum mechanics, the circumference must be an integer number of de Broglie wavelength, so the radius can not vary continuously, but takes quantized values $r = n\lambda/2\pi$, $n$ is integer. The energies of an electron can only take discrete values, $E = E_0 + (n + 1/2)\hbar\omega$, the carrier densities start to degenerate and form Landau level. Each Landau level contains the same number of states as in the original 2D bands over a range of $\hbar\omega$, which is the separation of the Landau levels \cite{154}. The total number of states will not change after applying magnetic field. As the magnetic field rises, the separation between two Landau levels increases, and so does the states each Landau level holds. The number of states per unit area in each Landau level are $2eB/h$, number of occupied Landau levels is \cite{142}

$$\nu = \frac{n_s}{2eB/h}. \quad (4.31)$$

where $\nu$ is called filling factor. Generally, $\nu$ is not an integer, such as if $\nu = n + \frac{1}{2}$, there will be $n$ full Landau level that will not contribute to conduction and a half filled top level. Raising the magnetic field causes $\nu$ to decrease and the number of states in each level to
grow, so that fewer electrons occupy the top level. When \( B = \frac{hn_s}{2ne} \), there are exactly \( n \) Landau levels, and no states at Fermi level, and hence no free charge carriers. As the magnetic field continues to rise, the next Landau level starts to empty. Eventually when \( B \) is above \( \frac{hn_s}{2e} \), all the electrons lie in the lowest Landau level, which is called magnetic quantum limit [155, 142].

Landau levels exist only when an electron can complete a few orbits before losing its momentum due to scattering, \( \omega_c^{-1} \ll \tau_m \), or when the spacing \( \hbar \omega_c \) is much bigger than the broadening by scattering, \( \hbar \omega_c \gg \hbar/\tau_m \). From \( \omega_c = \frac{|e|B}{m}, \mu = \frac{|e|\tau_m}{m} \), it is derived that \( B \gg \mu^{-1} \) is the requirement for carrier densities to split into Landau levels [134, 156].

### 4.9 Shubnikov-de Haas Oscillations

When carrier densities degenerate to Landau levels, the longitude magnetoresistance will oscillate with the increasing the magnetic field. These are Shubnikov-de Haas Oscillations (SdH) [157, 158], the minimum can reach almost zero resistivity during oscillations. The low resistivity does not coincide with extended states of Landau levels, instead it happens when Fermi level lies between the Landau levels, which are localized states as in Fig. 4.7.

From the period of the SdH oscillations, we can obtain the carrier density. At zero temperature, the density of stats of 2DEG per unit area per unit energy is

\[
N_{2d}(E) = \frac{m}{\pi \hbar^2} \vartheta(E - E_0). \tag{4.32}
\]

As shown in last section, the density of states breaks into a sequence of peaks spaced by \( \hbar \omega_c \) in a high magnetic field, where \( \omega_c = \frac{eB}{m} \) is the cyclotron frequency.

The degeneracy in each Landau level is \( 2eB/\hbar \). If we know the carrier density \( n_s \), we can determine the number of Landau levels occupied [141]

\[
v = \frac{n_s}{2eB/\hbar}. \tag{4.33}
\]

When we sweep the magnetic field to get two successive peaks at \( B_1, B_2 \), so that

\[
\frac{n_s}{2eB_1/\hbar} - \frac{n_s}{2eB_2/\hbar} = 1. \tag{4.34}
\]
Figure 4.7: Landau quantization of a spinless 2DEG. The continuum of states that exists in zero field (left side) becomes quantized in Landau levels when the magnetic flux density is turned on (central part). When disorder is added to the system, the Landau levels are broadened in localized and extended states (right side). The region of the localized states is called the mobility gap. [159]
We obtain the carrier density value from

\[ n_s = \frac{2e}{\hbar} \frac{1}{(1/B_1) - (1/B_2)}. \]  

(4.35)

The usual procedure to extract \( n_s \) is plotting peak index versus \( 1/B \). This produces a straight line and the slope of the line gives the carrier density [160, 161].

In Fig. 5.6 inset, the Landau plot demonstrate the linear dependence of the measured magnetoresistance peak position \( 1/B \) versus the peak index \( n \), when the cyclotron diameter is smaller than the sample width. While the observed deviations from linearity occur when confinement becomes important, that is when the cyclotron diameter is larger than the sample width.

The formation of Landau levels \( (B \gg \mu^{-1}) \) [134] is a prerequisite for SdH oscillations, SdH oscillations may be observed in low magnetic fields with high mobility samples. For example, a graphene sample with mobility of 10,000 cm\(^2\)/V s or 1 m\(^2\)/V s, the magnetic field needs to exceed 1 T to show SdH oscillations.

### 4.10 Quantum Hall Effect

One spectacular phenomena is that a 2DEG can exhibit the quantum Hall effect (QHE) when placed under a strong perpendicular magnetic field. Although two dimensionality is the prerequisite, QHE is a universal effect, which do not have sample dependence. QHE has been observed in Si, GaAs and other semiconductor 2DEGs. von Klitzing was the first to demonstrate that the Hall resistance is quantized in units of \( h/2e^2 \approx 12.9 \Omega \) with accuracy of parts per million [130, 131]. The QHE has been adopted as resistance standard \( R_k = h/e^2 \) for its accuracy. The impressive accuracy comes from almost complete suppression of momentum relaxation (electron scattering) and true ballistic conduction in the sample.

The large mean free path is not from the high purity of the sample as normally supposed, but from suppression of back scattering. At certain magnetic field \( B = h n_s/2ne \), \( n \) is integer, there are no free charge carriers in the center of the sample. The current only flows along the edges of the sample [159]. And current in one direction is confined in one side of the sample, while the current in opposite direction is confined on the other side. Since the currents are divided, the wave functions of forward and backward going current do not
Figure 4.8: Experimental measurements of the Hall resistance $R_H$ and of the longitudinal resistance $R_{xx}$ for a Si-MOSFET ($B = 13.8$ T) and a GaAs/AlGaAs heterostructure at a temperature of 0.3 K. [159]

overlap and hence there will be no scattering. This result in an unusually long mean path of several millimeters. [162, 163]

The mobility and carrier density can be easily obtained from Hall effect measurements. In a Hall bar structure as in Fig. 4.9, it is clear that $V_x = V_1 - V_2$, $V_h = V_2 - V_3$, the current density along x-direction is $J_x$, along y-direction is $J_y = 0$, and resistivity tensor is defined by $E_x = \rho_{xx} J_x$, $E_y = \rho_{xy} J_x$. Since $I = J_x W$, $V_x = E_x L$, and $V_H = E_y W$ we find

$$\rho_{xx} = \frac{V_x}{I \frac{W}{L}}$$

From these simple formulas, we can get longitude resistivity and Hall resistivity from the measurement of sample potential. Furthermore [134, 142]

$$n_s = \left| e \right| \frac{d\rho_{yx}}{dB}^{-1} = \frac{I/|e|}{dV_H/dB},$$

$$\mu = \frac{1}{|e| n_s \rho_{xx}} = \frac{I/|e|}{n_s V_2 W/L},$$

$\mu$ is the mobility and $n_s$ is the carrier density. The Hall measurement is a powerful characterization method for 2DEG.

When the magnetic field rises, the key features of the QHE are that magnetoresistance vanishes when the plateaus of Hall resistance reach $\hbar/2ne^2$. This happens when Fermi level lies exactly between two Landau levels, almost no free charge carriers in center of the sample, and the conductance is from the current on the edge. As shown in Fig. 4.7, the
density of states (DOS) is very low between bulk Landau levels. As a result Fermi energy should not be located in such regions, since a slight change in electron density will cause a large shift in the Fermi energy. If this is true, the Fermi energy should only stay inside Landau levels where the DOS is high and QHE plateaus can not be observed: the gap between two Landau levels in DOS corresponds to the QHE plateau \[142, 164\].

The explanation of the QHE is that potential fluctuations inside the sample form localized cyclotron orbits. These localized states do not contribute to the current but provide a certain amount of DOS between Landau levels that helps stabilize the Fermi energy in these regions. It is similar to the fact that the pure crystals do not give the strongest QHE, because defects in the sample are prerequisite for plateaus. Defects provide a background potential well that some electrons are localized to by cyclone motion. Without these defects, all electrons are in extended states, electrons can travel across the sample to destroy the divided current. Thus lower temperature and more defects give wider QHE plateaus, while high mobilities give narrower plateaus. \[142, 164\]

As we discussed above, it seems that in the condition of magnetic quantum limit, all electrons have the same kinetic energy and there will be no Hall plateau any more. In 1982, Daniel Tsui and Horst Stormer observed the fractional quantum Hall effect \(\nu = \)
Figure 4.10: A demonstration of the fractional quantum Hall effect discovered by Tsui and Stormer. Plotted are the diagonal (R) and Hall \( R_H \) resistances of a two-dimensional electron gas at the interface of two semiconductors, as a function of magnetic field applied normal to the plane. [165]

\[ 2/7, 1/3, 2/5, 3/5, 5/2 \text{ etc.} \) in experiments performed on extremely pure gallium arsenide heterostructures as shown in Fig.4.10. The fractional QHE is caused by the electron electron Coulomb interaction, which is different from integer quantum effect.[165, 166]

### 4.11 The Aharonov Bohm Effect

The Aharonov Bohm effect (AB) is another interference experiment of correlated electron waves (Fig. 4.10). Electron waves travel through both the upper arm and lower arm of the conducting ring and interfere with each other. The phase difference between the two paths can be adjusted by applying a magnetic field perpendicular to the ring. Even in the case that the magnetic field is confined to the interior of the ring and does not affect the electron in the arms directly, the phase difference still depends on the magnetic flux inside the ring.
Figure 4.11: Illustration of Aharonov-Bohm effect in a ring geometry. (a) Trajectories responsible for \( \hbar/e \) periodicity, (b) trajectories of the pair of time-reversed states leading to \( \hbar/2e \) periodicity.

\[
R(B) \approx \cos^2 \left( \frac{2\pi B}{B_0} \right) = \frac{1}{2} + \frac{1}{2} \cos \left( \frac{4\pi B}{B_0} \right). \tag{4.39}
\]

The period \( \Delta B \) of the resistance oscillations is half of \( B_0 \), \( B_0 = \hbar/e(\pi r^2) \),

\[
\Delta B = \frac{h}{2e(\pi r^2)} = \frac{\Phi_0}{A}, \tag{4.40}
\]

where \( A = \pi r^2 \), \( \Phi_0 = \hbar/e \) is the quantum flux. The flux enclosed by the ring changes by \( \hbar/2e \) for one oscillation cycle, this effect is refereed to as \( \hbar/2e \) Aharonov Bohm effect. For a ring radius \( r = 100 \text{nm} \), period \( \Delta B \) is about 700 G. There is another type of fluctuation with flux changing by \( \hbar/e \) for one oscillation cycle, this is refereed to as \( \hbar/e \) Aharonov Bohm effect as shown in Fig. 4.11. [134, 169] \( \hbar/e \) Aharonov-Bohm effect can be observed in a individual small ring, but it disappears when average over many rings [134]. That is why \( \hbar/e \) Aharonov-Bohm effect is not observed in cylinders, which can be viewed as many parallel rings.
CHAPTER V

EXPERIMENTAL RESULTS

5.1 Introduction

As we discussed in previous chapters, the exceptional electronic transport properties of low dimensional graphitic structures have been amply demonstrated in carbon nanotubes and nanotube-based transistors. Ballistic transport has been observed up to room temperature [25, 170, 171], and quantum interference effects at cryogenic temperatures [52, 168, 172]. Simple nanotube transistors [55, 60], and interconnected logic gates [28] have been demonstrated, which rely on the ability to control the nanotube conductance via an electrostatic gate. The basic transport parameters of these devices are so compelling that nanotubes are considered to be a candidate material system to eventually supplant silicon in many electronic devices.

An under-appreciated fact is that most electronic properties of carbon nanotubes are shared by other low-dimensional graphitic structures. For example, planar nanoscopic graphene ribbons (ribbons of a single sheet of graphite) have been studied theoretically [91, 92], and they exhibit properties that are similar to nanotubes. Graphene ribbons with either metallic or semiconducting electronic structure are possible, depending on the crystallographic direction of the ribbon axis [91]. Thus, if suitable methods were developed to support and align graphene sheets, it would be possible to combine the advantages of nanotube-like electronic properties with high-resolution planar lithography to achieve large-scale integration of ballistic devices. An essential difference between nanotubes and planar graphene ribbons is the presence of dangling bonds at the edges. Normally these would be hydrogen-terminated, with little influence on the valence electronic properties. However, edge atoms could be passivated with donor or acceptor molecules, thus tuning the electronic properties without affecting the graphitic backbone of the device.
5.2 2D Electron Gas Properties of Graphene Films

As presented below, our first epitaxial graphene films were produced on 6H-SiC wafer purchased from Cree company. The wafer was conducting at room temperature with resistivity is 0.053 Ω · cm due to intentionally N doping. 6H-SiC is a large band gap (3 eV) semiconductor, which provides an insulating substrate at temperatures below 50 K. We used magnetoconductance measurements and the physics of weak localization to determine transport parameters of the graphite 2D electron gas (2DEG). We show that the character of the magnetotransport localization spans a wide range of behaviors, depending on the amount of disorder in the film or substrate. Quantum oscillations in the magnetoconductance and in the Hall resistance are found for the most ordered samples. The character of these features suggests that the quantum Hall effect could be observed at lower temperatures, higher fields, or in ultrathin graphite films of only slightly higher mobility. To our knowledge, these are the first transport measurements on oriented and patterned graphite films of only a few monolayers thickness (hence graphene films), although related transport experiments have been done on thicker (65-100 graphene layers) free-standing graphite microdisks, which were nanopatterned by focused-ion-beam lithography [173]. Given the large mean free paths measured in high-quality graphites [174], the unusual electronic dispersion of graphene, and the fact that the carriers lie near an air-exposed surface, this unique 2DEG system holds great scientific potential. Furthermore, with sufficiently high-quality material, ballistic and coherent devices analogous to nanotube designs [175] would be possible. This goal requires that the epitaxial graphene can survive the processing necessary for creation of submicron ribbons [91, 92], and that the 2DEG can be gated electrostatically.

Figures (5.1a-d) show low energy electron diffraction patterns (LEED) at different stages during the growth of a 2.5 monolayer (ML) graphite film grown in situ. Figure (5.1e) displays an STM image from the sample obtained after stage (d). The image reveals a distinct 6 × 6 corrugation of the overlayer [176] and a raised region along a step on the surface. This modulation has been previously attributed to variations of the interlayer interaction arising from Moiré coincidences between the graphite and SiC lattices within a fundamental $6\sqrt{3} \times 6\sqrt{3}$ surface unit cell[176, 107, 177]. LEED confirms that the graphene...
Figure 5.1: (a-d) LEED patterns from graphite/SiC(0001). The sample was heated several times to successively higher temperatures. (a) 1050°C for 10 min. Immediately after oxide removal, showing SiC $1 \times 1$ pattern at 177 eV. AES C:Si ratio 1:2. (b) 1100°C, 3 min. The $\sqrt{3} \times \sqrt{3}$ reconstruction is seen at 171 eV. AES ratio 1:1.9. (c) 1250°C, 20 min. 109 eV pattern showing diffracted beams from the $6\sqrt{3} \times 6\sqrt{3}$ unit cell. Examples of first-order SiC and graphite spots are marked. Note the surrounding hexagons of $6 \times 6$ spots. AES C:Si ratio 2:1 (1 ML graphite). (d) 1400°C, 8 min. 98 eV LEED pattern. AES ratio 7.5:1 (∼2.5 ML graphite). (e) STM image of a surface region of the sample described in Figure d. Inset: Atomically resolved region (different sample, similar preparation). (f): dI/dV spectra (log scale) acquired from the regions marked with corresponding line types in the image at top. The solid line is an average of 396 spectra at different positions, the dashed line an average of 105. With a few “glitchy” exceptions, individual spectra in each region showed negligible variation from the average dI/dV shown.
sheets register epitaxially with the underlying SiC, as shown in Figure (5.1c) and (5.1d). The mean height difference between terraces (0.25 nm), indicates that the step in Figure (5.1e) is a bilayer step in the SiC substrate. Terrace sizes (corresponding to a single $6 \times 6$ domain) are found by STM to be up to several hundred nanometers in extent. Preliminary high resolution LEED studies indicate that the graphene layers are strained in-plane by 0.3-0.5 %, with a mean structural coherence length of greater than 20 nm.

Also shown in Figure (5.1f) are derivative tunnelling spectra ($dI/dV$ vs $V$) acquired within the respective boxed regions of the image. The $dI/dV$ spectrum obtained from the lower terrace (solid line) is similar to that of a zero-gap semiconductor, as found typically for bulk graphite. On the upper terrace, the $6 \times 6$ domain images and the $dI/dV$ spectrum (dashed line) displays a region of constant, finite conductance around the Fermi energy (zero bias). Spectral shapes are very uniform within each $6 \times 6$ domain. The $dI/dV$ curves show that the electronic properties of the film are not entirely homogeneous. This may relate to differing lateral registry (i.e. not orientational) of the graphite on the SiC substrate, or electron confinement within $6 \times 6$ domains. $dI/dV$ spectra acquired over the buckled region at the step edge are nearly identical to those found on the upper terrace, suggesting that the graphite layer remains continuous over the step.

DC and low-frequency AC conductance measurements were made for temperatures $T = 0.3 - 50K$ and for magnetic fields $H$ from $0 - 8T$ on graphite films with thicknesses of typically 3 graphene sheets (Table 5.1). For Hall-effect measurements, samples were defined using standard photo lithography (photoresist coating, plasma etching, photoresist removal via solvents). Four contacts were painted with silver paste directly on the surface or on evaporated Pd-Au pads on mm-sized samples. For samples B, C, and E, the voltage probe distance $d_V$ is 2 mm. For the Hall bar samples A and D, $d_V=600$ and 300 $\mu m$ respectively (see photo inset, Figure 5.2a). Reported values below are the square conductance $G$.

The 2D nature of electrical transport in the film is vividly demonstrated in Figure 5.2a by the large anisotropy in the magnetoconductance $|MC | = G(H)$: For sample E, for $H$ perpendicular to the graphene plane the differential magnetoconductance ($dMC = dG/dH$) is large and positive ($3.0 \mu S/T$ at 4 K), whereas there is essentially no response when $H$ lies
in the plane (in-plane MC was measured with H transverse to the current direction). This anisotropy is found in all of our samples and indicates that the motion of charge carriers is confined to the graphene planes. The observed positive dMC is in contrast to bulk graphite[157], which shows negative dMC for well-ordered single-crystals, and also a large anisotropy. However, carbon foils fabricated from exfoliated graphite [178] and partially graphitic carbons [179] have positive dMCs initially, which become negative at large fields. This behavior is a consequence of disorder-induced localization in the sample.

Fig. 5.2 shows systematic changes in the perpendicular MC for samples of successively larger zero-field conductance (i.e., decreasing disorder). For sample C the initial 4 K slope is larger, at 30 µS/T, and the MC attains an approximately temperature independent maximum of 185 µS at H ≈3.5 T. Sample A shows even more structure. Following a large initial dMC (180µS/T at 4 K), the MC maximizes near 1.5 T, then decreases, followed by a series of (Shubnikov-de Haas) oscillations. A temperature independent “fixed point” at G=680 µS and H=7.4 T is also observed.

As a function of temperature, the conductance increases proportional to \( \ln T \) at low T, as shown in Figure 5.2b for samples A-C. This is quite characteristic of a 2D electron gas in the weak localization regime [180, 181]. The least conductive samples (D and E; \( G < \frac{e^2}{h} = 38.8\mu S \)) deviate slightly from the \( \ln T \) dependence, which is indicative of a transition to strong localization. In a 2D system, carriers will localize at low temperature due to constructive quantum interference of time-reversed paths for carriers scattered elastically from static disorder [180]. The interference is reduced (conductance increased) by breaking time reversal symmetry through the application of a magnetic field, or by increasing temperature. These coherent effects are manifest when the elastic mean free path \( l_e \) is smaller than the inelastic mean free path \( l_i(T) \). For \( k_F l_e \gg 1 \) (\( k_F \) is the Fermi wave vector), the system is in the weak localization regime. Strong localization occurs for smaller \( k_F l_e \) [152].

Shown in the center panel inset of Fig. 5.2a are the perpendicular MC of sample B for five different temperatures (circles) and fits to the data according to 2D weak localization theory (lines) [181]. The entire family of MC curves is fit by a single temperature-dependent
Figure 5.2: (a) Magnetoconductance $G(H)$ for samples E, C, and A in perpendicular field for temperatures as indicated. Also shown for samples E and C, the in-plane magnetoconductance at 5 K. Note the strong anisotropy between the perpendicular and in-plane field configuration. In sample C, the conductance goes through a maximum at about the same value of field and conductance for all T. In sample A Shubnikov-de Haas oscillations develop at high magnetic field. Center-panel inset: $G(H) - G(H = 0)$ for sample B. Solid curve are fits to the weak localization theory with no spin-orbit, yielding elastic scattering length $l_e \approx 15$ nm and inelastic scattering length $l_i(4K) \approx 100$ nm. Lower-panel inset: Hall resistance $R_{xy} = V_{xy}/i$ and magnetoresistance $R_{xx}$ as a function of magnetic field at 4 K for sample A. Below 4.5 T, $R_{xy}$ is remarkably linear, indicative of n-type carriers. At high magnetic field, the oscillations coincide with the oscillations in the magnetoresistance. (b) Square conductance as a function of temperature for samples of various conductance (samples A, B, C, D, and E from top to bottom). Note that the conductance scale is $\times 4$ for samples D and E, compared to the scale for sample A-C. Samples A, B, and C show a $\ln T$ form in this decade of temperature, characteristic of 2D weak localization.
Table 5.1: Ratio of intensities in the C (271 eV) and Si (92 eV) AES peaks, calculated thickness in graphene monolayers, square resistance at 4 K, and mobility.

<table>
<thead>
<tr>
<th>Sample</th>
<th>C:Si</th>
<th>Thickness</th>
<th>$R_{4K}$</th>
<th>Mobility</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>10</td>
<td>3 ML</td>
<td>1.5 kΩ</td>
<td>1100 cm²/Vs</td>
</tr>
<tr>
<td>B</td>
<td>∞</td>
<td>&gt; 5</td>
<td>2.2</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>9</td>
<td>3</td>
<td>22</td>
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<tr>
<td>D</td>
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<td>E</td>
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<td>F</td>
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parameter, $l_i(T)$. Note that for transport in two dimensions, the mean free paths are obtained from the modelling without knowledge of either the Fermi velocity or the carrier effective mass. For sample B, we find $l_c = 15 \text{nm}$ and $l_i = 100 \text{nm}$ at $T=4\text{K}$. Weak localization effects are observed over a much smaller range of magnetic field for sample A, but a similar estimate gives $l_c = 20 - 30 \text{nm}$ and a much larger inelastic mean free path $l_i(4\text{K}) \approx 300 \text{nm}$. From the carrier density $n = 10^{12} \text{cm}^{-2}$ per graphene sheet (see below), we find for sample A $k_F l_c \approx 5$, in agreement with the weak localization regime. In two cases we have observed a reversal of the dMC.

At the maximum MC for sample C (Fig. 5.2a), the conductance per graphene sheet (Table 5.1) is $1.5 e^2/h$, i.e., comparable to the conductance quantum. This behavior, and the large change in MC of this sample (320%) are reminiscent of disordered 2DEGs, which have been explained in terms of a transition from an Anderson insulator to a quantum Hall liquid [182]. The second case is that of sample A, which underwent an improved substrate preparation. For this sample, we also observe an initial maximum in the MC, but at much lower field (1.5 T). Apparently, weak localization dominates the MC behavior of sample A in the low-field region, but the longer scattering paths are dephased by a smaller magnetic field. The subsequent appearance of Shubnikov-de Haas oscillations indicates quantization of the electron energy spectrum and wave function coherence on a scale comparable to the cyclotron radius ($\sim 30\text{nm at 5 T}$), which is consistent with the elastic scattering lengths estimated above. The significance of the quasi-temperature independent fixed point at 680 µS and a field of 7.4 T is not yet fully understood. Note that $1/H$ at the crossing point is equal
to the mobility obtained from Hall measurements (see below). This correspondence would be an expected consequence of electron-electron interactions under weak localization, but the observed quantum oscillations show that at high fields the system is beyond this regime.

The Hall resistance $R_{xy}$ was measured for samples D and A in the Hall bar configuration (photo inset, Figure 5.2a) at a bias current of 100 nA. For sample D at 4 K, $R_{xy}$ versus $H$ is linear from 0 to 8 T, with the slope corresponding to a density $n = 10^{13} \text{cm}^{-2}$ n-type charge carriers, and a mobility of $15 \text{cm}^2/\text{V} \cdot \text{s}$. The Hall voltage is also linear up to 4.5 T in sample A, from which we determine $n = 3.6 \times 10^{12} \text{cm}^{-2}$ (n-type), and an enhanced mobility of $1100 \text{cm}^2/\text{V} \cdot \text{s}$. The observation of a linear Hall effect is particularly remarkable, since single-crystal graphite samples display a substantial quadratic component at small fields [183, 184, 185], due to three subbands (one electron, two hole). Apparently, our samples cannot be thus described. The carrier densities found here are comparable to those of other 2DEG systems, although the density per graphene sheet ($\sim 10^{12} \text{cm}^{-2}$) is higher than that found in high-quality graphite [157, 184, 185]. It remains to be determined what effect substrate doping has on the carrier density and mobility in the graphite films.

For the case of sample A, a carrier density can be obtained from the period (in $1/H$) of the Shubnikov-de Haas oscillations. Assuming a circular 2D Fermi surface, we estimate $n = 10^{12} \text{cm}^{-2}$ ($k_F = 2.5 \times 10^6 \text{cm}^{-1}$). The carrier density determined by the Hall effect is very nearly a factor 3 larger, which is the number of graphene layers measured via AES. Clearly, the simplest explanation would be that each graphene sheet supports a 2D electron gas which remains confined within the sheet. This would be consistent with the large anisotropy in conductivity for bulk graphite [157]. The temperature dependencies of samples A-C also support this interpretation: $dG/d(lnT)$ falls between $2.5e^2/\pi h$ and $3.5e^2/\pi h$, about a factor 3 larger than the predicted weak localization contribution to the conductance, of the order of $(e^2/\pi h)lnT$.

Above 4.5 T in sample A, we observe nonlinearities in $R_{xy}$ vs $H$, as shown in Figure 5.2a (lower-panel inset) for $T = 4K$. These coincide with the Shubnikov-de Haas oscillations in the magnetoconductance, showing that they have the same origin: either broadened quantum Hall plateaus or bulk magnetoquantum oscillations in a metallic system. If the
Hall conductance. Sample at the location of the local maximum (≈ 5.5T) is normalized with respect to the number of sheets, one obtains a conductance ≈ 4e^2/h, which suggests a quantum Hall effect (see also predictions in ref [186]). Experiments at lower temperatures and higher fields will be necessary to verify this conjecture.

At 0.3 K, we also observe a pronounced zero-bias anomaly in the highly resistive sample D. The conductance is found to increase by about a factor 10 as the bias voltage is increased from 0 to 25 mV. Samples were carefully mounted with the connecting wires thermally connected by stycast epoxy to the cooled copper plate. This mounting provided more than sufficient thermal coupling to ensure that the maximum power into the sample (10 nW) did not cause significant heating. For weak electron-electron interactions it can be understood in terms of enhanced scattering of carriers near the Fermi energy: the wavelengths of these carriers are commensurate with the Friedel oscillations surrounding impurities, thus they scatter strongly. The coherence is lost at higher bias (higher kinetic energies). Zero-bias anomalies have also been observed in carbon nanotubes [187, 188].

It should be noted that the samples are remarkably stable over time. For instance, measurements in Figures 5.2a and 2b were made four months earlier than those in the lower-panel inset of Figure 5.2a, with no particular storage precautions. The features observed are essentially the same, except for a slight decrease in conductance and carrier density. The results presented above for sample A also show that the multisheet epitaxial graphene films survives conventional lithographic processing extraordinarily well.

Finally, as a preliminary demonstration of the device potential of this new 2DEG system, a large-area gated graphite channel field effect transistor (FET) structure was assembled. A schematic of the “device” is shown in Figure 5.3, as well as the measured source-drain resistance as a function of gate voltage. The top-gate structure consisted of a conductive coating on a 100-nm-thick insulating aluminum oxide layer. The gate covered only a portion of the graphite films between the source and drain electrodes, leaving large ungated leakage paths (see inset, Figure 5.3). Consequently, the resistance modulation is rather small (2%), but these results show clearly that multisheet epitaxial graphene films can be gated, in distinct contrast to thicker samples [189]. Thus we anticipate that FET-type devices will
Figure 5.3: Conductance as a function of gate voltage for sample F at 4 K. Inset, sketch of the sample showing the contacts and top-gate geometry (S, D, G) = source, drain, gate). The top gate is only partially effective due to the open geometry. Nevertheless, a 2% change in conductance is observed.
be possible, particularly when the channel electronic structure is controlled by patterning the graphite into a narrow strip [190].

The experimental results presented here demonstrate the rich scientific promise of ultra-thin epitaxial graphite (“graphene”) films. Several points should be appreciated. First, the production method allows graphitic films to be grown epitaxially, as evidenced by LEED and STM measurements. From Auger spectroscopy we further conclude that the layers involve only a few graphene sheets. Remarkably, the films are electrically continuous over several mm. Magnetoconductance measurements clearly reveal 2D electron gas properties, including large anisotropy, high mobility, and 2D localization, in samples patterned by conventional lithography. Quantum oscillations observed in both the magnetoconductance and the Hall resistance indicate a potential new quantum Hall system. Finally, control of the 2D electron gas carrier density via electrostatic gating was also demonstrated.

Considered with prior research in graphitic systems, these results provide ample evidence that the graphite/SiC system could provide a platform for a new breed of seamlessly integrated ballistic carrier devices based on nanopatterned epitaxial graphene. Such an architecture could have many advantages for nanoelectronics, including potentially coherent devices, energy efficiency, and facile integration with molecular devices.

5.3 Electronic Confinement and Coherence

Ultrathin graphite films grown on doped 6H-SiC samples can only be measured below temperature of 50 K. For higher temperature measurement, we switched to undoped 4H-SiC samples. 4H-SiC wafers were polished on both sides and transparent with resistivity larger than $10^5 \, \Omega \cdot cm$. The ultra thin graphite films grown on the C face of 4H-SiC show much higher mobility than on 6H-SiC.

The electronic properties of $sp^2$ bonded carbon structures (i.e. bulk graphite, graphene ribbons, carbon nanotubes, aromatic molecules) result from the overlap of the $p_z$ atomic orbitals of neighboring carbon atoms. Recall that in graphene, $\pi$ bands are formed, with electronic energy dispersion[81]

$$E(p) = v_0|p|,$$  \hspace{1cm} (5.1)
where $p$ is the carrier momentum $p = \hbar \sqrt{(k_x^2 + k_y^2)}$ [81, 191] $v_0$ is the velocity, and $\hbar$ is Planck’s constant divided by $2\pi$.

Consequently, like photons, the velocity of electrons is independent of their energy. The predicted velocity $v_0 = 3a_0\gamma_0/2\hbar \approx 10^6 m/s$, where $\gamma_0 \approx 3eV$ is the interatomic overlap energy and $a_0 = 1.42\AA$ is the interatomic spacing. The Fermi surface of neutral graphene (Fermi energy $E_F = 0$) shrinks to a point, so that it is a zero band gap semiconductor. As for 2D electron gases in general, when graphene is confined its properties depend on geometry.

In contrast to other 2D electron gases however, epitaxial graphene [192, 103, 193] is a robust and defined material that in principle can be shaped at the atomic level, thereby providing access to molecular electronics properties.

We present production methods and focus on the transport properties of a simple representative patterned structure to demonstrate the confinement and coherence properties of epitaxial graphene (EG). From the measured transport properties we show the following. The interface material is graphene with Berry phase $\Phi_B = \pi$, Fermi temperature $T_F = 2490K$, and Fermi velocity $v_0 = 1.0 \times 10^6 m/s$. The mobility $\mu = 2.7m^2/Vs$ and the diffusion constant $D = 0.3m^2/s$; The (elastic) mean free path $l_e = 600nm$ and the phase coherence length $l_\varphi = 1.1\mu m$ at 4 K and 500 nm at 58 K. Furthermore, quantum-confined states are observed.

The production of EG on diced (3 mm by 4 mm) commercial 4H-SiC wafers is illustrated in (Fig. 5.4). In summary, the steps are (i) hydrogen etching to produce atomically flat surfaces [194], (ii) vacuum graphitization to produce an ultrathin epitaxial graphite layer, (iii) application of metal contacts (Pd, Au), (iv) electron-beam patterning and development, (v) oxygen plasma etch to define graphite structures, and (vi) wire bonding. To date, more than 200 SiC samples have been processed, of which 22 have been patterned and measured in detail. The structural order has been characterized by low-energy electron diffraction (LEED), Auger electron spectroscopy, x-ray diffraction, and scanning tunnelling microscopy (STM) [192]. The electronic structure has been characterized by angle resolved photoelectron spectroscopy (ARPES), scanning tunnelling spectroscopy (STS) [192], and electronic transport. Patterned surfaces are routinely measured by atomic force microscopy.
Figure 5.4: Production and characterization of EG. (A) LEED pattern (71 eV) of three mono layers of EG on 4H-SiC(0001) (C-terminated face). The outermost hexagon (spots aligned on the vertical) is graphene $1 \times 1$ diffraction. Bright sixfold spots aligned on the horizontal are SiC $1 \times 1$. The smallest hexagon is the result of a $\sqrt{3} \times \sqrt{3}$ reconstruction of the interfacial layer, as are the spots lying just inside the graphene pattern. Graphene thickness is determined via Auger spectroscopy (attenuation of Si peaks). (B) AFM image of graphitized 4H-SiC, showing extended terraces. STM studies indicate that the graphite is continuous over the steps. (C) STM image of one monolayer of EG on SiC(0001). Tunnelling conditions (tip bias -0.8 V, current 100 pA) preferentially image structure beneath the graphene layer. Two interface corrugations are apparent, with periods $6 \times 6$ (1.8-nm triangular superlattice) and $\sqrt{3} \times \sqrt{3}$ (smaller spots with 0.54-nm spacing) relative to the SiC surface unit cell. (D) STM image of interface reconstruction beneath one monolayer of graphene on SiC(0001) obtained after lithography. General features are as seen in (C). (E) SEM of patterned EG. Dark regions are the EG (still coated with electron-beam resist). (F) EFM of another patterned EG sample, showing a horizontal ribbon (bright contrast) with tapered voltage contacts left and right, which is flanked by diagonally oriented side gates above and below the ribbon. Contrast is obtained through electrostatic forces between the probe and the graphene structure to which potentials are applied, thus allowing functioning devices to be measured.
(AFM) and electrostatic force microscopy (EFM) under ambient conditions. The results are summarized in Fig. 5.4. As evident from LEED, an ultrathin graphite layer grows epitaxially on the SiC(0001) surface. X-ray diffraction shows that graphene grown on the 0001 face has a structural coherence of at least 90 nm. On the Si-terminated SiC(0001) surface, LEED and STM measurements reveal a \((6\sqrt{3} \times 6\sqrt{3})R30^\circ\) interface reconstruction. STS measurements reveal the graphitic band structure, and STM and STS together suggest that graphene layers can remain continuous over steps on the SiC surface. The ARPES data (for two EG layers on 0001 SiC) suggest a Dirac electronic dispersion and a Fermi temperature of 2700 K. This relatively large energy indicates that the interface layer is charged, with a charge density \(\sigma \sim 10^{12} \text{ electrons/cm}^2\) (see below). As usual for such interfaces, the electric field caused by the surface charge compensates the work function difference between the materials. Only the interface layer is expected to be highly charged \([137, 195]\); the (few) other layers are essentially neutral. Thus, the interface layer should dominate the transport properties, which are essentially identical to those of isolated graphene (see below). The interface layer is further distinguished from any others by a weak superlattice structure imposed by the epitaxial match to SiC.

We briefly summarize some relevant properties of confined Dirac electrons in graphene. For a graphene ribbon of width \(W\), the boundaries impose a constraint on the transverse motion so that (for not too small \(n\)) \(k_y\) is quantized: \(k_y = n\pi/W\), where \(n\) is an integer \([97]\). Hence, the energy of the \(n\)th electronic subband is

\[
E_n(p_x) = v_0 |p| = \hbar v_0 \sqrt{k_x^2 + k_y^2} = \sqrt{E_x^2 + n^2 \Delta E^2},
\]

where \(\Delta E = \Delta E(W) = \pi \hbar v_0/W \sim (2eV\text{nm})/W\), and \(E_x = \hbar v_0 k_x\). Hence, these electrons propagate like electromagnetic waves in waveguides. A more detailed analysis shows that undoped graphene (i.e., \(E_F = 0\)) can be tuned to be either a metal or a semiconductor with a band gap on the order of \(\Delta E(W)\) \([92, 91]\). This is an important property that undoped graphene ribbons share with undoped carbon nanotubes.

For any 2D electron system \([142, 196]\), a perpendicular magnetic field \(B\) creates a discrete energy spectrum (Landau levels) due to quantization of the cyclotron orbits (radius \(R_c = \)
p/eB). The energy states for Dirac electrons are given by [197]

\[ E_n(B) = \sqrt{(2neBv_0^2\hbar)} \] (5.3)

where \( n \) is the integer Landau level index [by contrast, \( E^*_n(B) = (n + 1/2)heB/m^* \) for normal electrons, where \( m^* \) is the effective mass]. Shubnikov-de Haas (SdH) MR maxima were observed at magnetic fields \( B_n \) such that \( E_n(B_n) = E_F \). Hence, \( B_n = B_0/n \), where [157, 198]

\[ B_0 = E_F^2/(2ev_0^2\hbar) = \hbar k_F^2/2e \] (5.4)

Next, consider a graphene ribbon of width \( W \) in a magnetic field. It is intuitively clear that for low magnetic fields, when \( W < 2R_c \) the ribbon cannot support a cyclotron orbit, so the above picture needs to be modified. For graphene, \( 2R_c = 4n/k_F \), which is 260 nm for \( n = 20 \). Quantitatively, Berggren et al. [199] found that for a normal 2D electron system confined to a strip of width \( W \),

\[ E_n(B, W) \approx \sqrt{E_n(W)^2 + E_n(B)^2} \] (5.5)

\[ E_n(W) = (n\pi\hbar/W)^2/2m^*. \] (5.6)

Analogously, for graphene ribbons,

\[ E_n(W) = n\pi hv_0/W, \] (5.7)

and an approximate expression for the energy levels can be obtained:

\[ E_n(B, W) \approx [E_n(W)^4 + E_n(B)^4]^{1/4} = [(n\pi hv_0/W)^4 + (2neBv_0^2\hbar)^2]^{1/4} \] (5.8)

Recent numerical results agree very well with this analytical form. As for normal electrons, SdH peaks are expected when \( E_n(B_n, W) = E_F \). Consequently \( B_n = B_0/n \) for small \( n \), whereas for large \( n \sim n_{max} \) the peak spacing becomes more regular: \( B_n - B_{n+1} \sim B_0/n_{max} \), where \( n_{max} = E_F/\Delta E(W) \) is the number of populated transverse modes. To illustrate the properties of carrier confinement and coherence, we next present magnetotransport data from a representative patterned EG structure. The sample is a Hall bar (ribbon) of width \( W = 500 \) nm created on the graphitized 0001 face of a high-quality semiconducting 4H-SiC
substrate (Fig. 5.5A, lower inset). Contacts are bonded on Pd/Au deposited pads. Four-point measurements were made using standard lock-in methods, with excitation currents through the ribbon limited to 100 nA. Voltages were measured over a 6-mm length L of the ribbon. MR and Hall effect data were acquired at six temperatures from 4 to 58 K and in magnetic fields from −9 to +9 T. Field sweeps were repeated to verify reproducibility.

Figure 5.5 A shows that $\rho_{xx} = R_{xx} W^*/L$ (where $\rho_{xx}$ is the resistivity and $W^*$ the effective ribbon width), and the Hall resistance $R_{xy} = \rho_{xy}$ of the sample. $\rho_{xx}$ increases approximately linearly with increasing field. At high fields, SdH oscillations are clearly seen in the $\rho_{xx}$ curves and step-like features are observed in $\rho_{xy}$. Subtracting a common smooth curve from the MR data reveals a rich, reproducible, and temperature-dependent structure (Fig. 5.5B). Pronounced, regularly spaced SdH maxima are distinguished clearly at high fields, whereas at low fields MR peaks are visible but are less well defined. Increasing the temperature decreases the amplitude of the peaks, with the high-field peaks decreasing more slowly than the low-field peaks. At a given temperature the amplitudes are relatively constant for $B < 2T$ and increase uniformly for $B > 2T$. Positions of 29 distinct SdH peaks $B_n$ have been identified and are indicated in Fig. 5.5B. Features are identified as SdH peaks when they present a clear maximum, and they are present at all of the measured temperatures. A complication is the reproducible fine structure observed throughout the MR spectra, which can obscure the SdH peaks for small fields. These are (universal) conductance fluctuations. As discussed below, the temperature dependence of universal conductance fluctuations (UCFs) and SdH oscillations are well understood and quite distinct. Incorporating this information results in an ambiguity of less than 10% in the number of peaks assigned according to the above criteria.

A Landau plot of the peaks [i.e., $B_n^{-1}$ versus $n$ [142, 157]] is shown in the inset of Fig. 5.6. The low index peaks ($n = 4$ to 12) define a straight line: $B_n^{-1} = (n + \gamma)B_0^{-1}$ with $B_0 = 35.1 \pm 0.8T$ and $\gamma = -0.05 \pm 0.14$. This value of $\gamma$ is consistent with a Berry phase $\Phi_B = \pi$, as expected for Dirac fermions and previously observed in graphene. It is specifically not consistent with $\gamma = \pm 0.5$ , as would be the case for normal electrons. Note that the same result was found for various subsets of peaks in the interval n= 4 to 12. For
Figure 5.5: Magnetotransport of a lithographically patterned graphene Hall bar (SEM micrograph, lower inset) measured at temperatures $T = 4, 6, 9, 15, 35, \text{ and } 58 \text{ K}$, and magnetic fields $-9 \text{ T} \leq B \leq 9 \text{ T}$. (A) Components of the resistivity tensor $\rho$ are shown (inset; $\rho_{xx} = \rho_{xx} W^*/L$, $\rho_{xy} = R_{xy}$). $\rho^*$ is derived from $\rho$: $(\rho^*)^{-1} = \rho^{-1} - (\rho^0)^{-1}$, where $\rho_{xx}^0 = 1125 \text{ ohms}$ and $\rho_{xy}^0 = 0$. Hence, the slight slope in $\rho_{xx}$ appears to be caused by a conducting layer $\rho^0$ on top of the graphene layer. The graphene mobility is $\mu^* = 2.7m^2/\text{Vs}$. (B) $\Delta R_{xx}$ obtained from the measured $R_{xx}$ by subtracting a smooth background. Peak positions are indicated (peak 11 is missing). The peak character changes near $B = 4.5 \text{ T}$. The peak amplitudes are essentially constant below 2 T and increase above 2 T. Inset: Detail of the oscillations near $B = 1 \text{ T}$. The amplitude of the universal conductance fluctuations (noise-like structures) increases with decreasing temperature.
Figure 5.6: Demonstration of confinement. Inset: Landau plot demonstrating the linear dependence of the measured inverse MR peak positions $1/B_n$ on the peak index $n$ when the cyclotron diameter is smaller than the ribbon width. The linear fit for small $n$ (bold line) intercepts the ordinate at $n = 0.05$, consistent with the graphene value $\gamma = 0$ and Berry’s phase $\Phi_B = \pi$ (the slope of the fit corresponds to $B_0$, which determines $k_F$). The observed deviations from linearity occur for larger $n$ when confinement becomes important; these correspond well with Eq. 5.8 predictions. The confinement is further illustrated by plotting $\Delta R_{xx}$ in terms of the variable $n(B)$ from Eq. 5.8, which shows that the peak positions approximately coincide with integers.
a 2D electron gas in general, we have

\[ k_F = \sqrt{\frac{2eB_0}{\hbar}} \]  

(5.9)

From \( B_0 \) we find \( k_F = 3.3 \times 10^8/m \), and the carrier density \( n_s = g_sg_v k_F^2/4\pi = 3.4 \times 10^{16} \) electrons/m\(^2\) (where \( g_s = 2 \) and \( g_v = 2 \) are the spin and valley degeneracies). The deviation from linearity for the larger index peaks \( (n > 14; B < 2.5T; 2R_c > 170nm) \) indicates confinement, as explained below.

We next analyze the individual SdH peaks. The amplitudes of SdH peaks decrease with increasing temperature because higher Landau levels are thermally populated. The temperature dependence of the peak amplitudes is given by the Lifshitz-Kosevich (LK) equation [200]:

\[ \frac{A_n(T)}{A_n(0)} = \frac{u}{sinh(u)}, \]  

(5.10)

where \( A_n(T) \) is the peak amplitude (or peak area) of the \( n \)th SdH peak at temperature \( T \), and

\[ u = 2\pi^2 k_B T/\Delta E(B), \]  

(5.11)

where \( \Delta E(B) = E_{n+1}(B) - E_n(B) \). Experimental values for \( \Delta E(B) \) were determined by fitting SdH peaks to the LK equation for six different temperatures. In Fig. 5.7 the results are plotted as solid circles; values of \( \Delta E(B) \) calculated from Eq. 5.8 are shown as open circles. A nearly linear increase for \( B > 4 \) T and saturation at low fields is observed in both theory and experiment. For large \( B \), \( \Delta E(B) \sim E_F B/2B_0 = E_F/2n \); for small \( B \), \( \Delta E(B) = \hbar \pi v_0/W \). Consequently, the data in Fig. 5.7 can be used to find \( E_F/k_B = 2490 \pm 80K \) and \( v_0 = E_F/\hbar k_F = E_F/\hbar \sqrt{2eB_0}/\hbar = (1.00 \pm 0.03) \times 10^6 \) m/s. Our experimental \( v_0 \) agrees remarkably well with the accepted value for graphene. Furthermore, \( E_F \) is also consistent with recent ARPES measurements on two layer EG grown on SiC(0001), which found \( E_F/k_B = 2700 \) K. Hence, experimental evidence (measured \( \Phi_B, v_0, E_F \)) strongly supports the conclusion that the material is indeed graphene.

For small \( B \), the saturation of \( \Delta E_n(B)/k_B \) at \( 80 \pm 10K \) indicates quantum confinement. The number of confined subbands should be \( n_{max} \sim E_F/\Delta E(B \rightarrow 0) = 31 \pm 3 \), consistent with the observed \( n_{max} = 29 \pm 3 \). However the hard wall boundary condition would predict
Figure 5.7: Landau level excitation energies $\Delta E(B)$. Inset: Normalized MR amplitudes $\Delta R_{xx}(B,T)/\Delta R_{xx}(B,T=4 \text{ K})$ are fitted to Eq. 5.8; fit examples are shown for $B=7 \text{ T}$ ($n=5$), $5 \text{ T}$ ($n=7$), and $1 \text{ T}$ ($n=23,24$). Note that $\Delta E(B)$ increases approximately linearly for $B \geq 2$ as predicted theoretically (open circles from Eq. 5.8). In this region $\Delta E(B_n) \sim E_F/2n$. For smaller fields $\Delta E(B_n) \rightarrow E_F/n_{max}$, where $n_{max}$ is the number of subbands in zero field. Good correspondence with theory is found for $W^* = 270 \text{ nm}$. 
that \( n_{\text{max}} = \frac{W k_F}{\pi} = 52 \). This discrepancy suggests that the carrier confinement width of the ribbon is less than the lithographic width \( W = 500 \text{ nm} \) (subsequent AFM and EFM studies confirmed that the physical width of the ribbon is compatible with the lithographic width; this does not preclude edge roughness effects). In fact, the best fit to the data using Eq. 5.8 is for \( W^* = 270 \text{ nm} \), as shown in Fig. 5.7 (see below for further evidence of reduced width). Similar discrepancies have been observed in several ribbons. The smaller effective width may be related to carrier scattering from steps on the substrate (Fig. 5.4 steps tend to run parallel to the ribbon) or to a stronger confinement potential caused by charge transfer to states at the ribbon edges (edge roughness, chemisorbed molecules, and intrinsic edge states could contribute), or it may have a more fundamental origin. In Fig. 5.6 the MR data are presented with the Landau index \( n(B) \) as the abscissa, obtained by inversion of Eq. 5.8 (for \( E_n = E_F \)), where the experimental values \( v_0 = 1.0 \times 10^6 \text{ m/s} \), \( E_F = 2490k_B \), and \( W^* = 270\text{ nm} \) were used. If Eq. 5.8 is correct, the measured SdH peaks should coincide with integers. The correspondences up to \( n = 22 \) are remarkable (note that the \( n = 11 \) peak is missing at low \( T \)), providing additional support for our conclusion that the SdH peaks are determined by both Landau orbital quantization and transverse quantum confinement.

The overall linear increase in the MR (Fig. 5.4A, inset) may result from a conducting layer on top of the graphene [i.e., a thin graphite layer, consistent with independent x-ray measurements on similar samples]. The slope is removed completely by subtracting from the measurement the conductivity of a layer with resistivity \( \rho_{xx}^0 = 1125 \text{ ohms/square} \), and with negligible Hall coefficient. This procedure results in \( \rho_{xx}^* \) and \( \rho_{xy}^* \) values that are similar to those reported for isolated graphene. Hence, the resistivity of the graphene layer is \( \rho_{xx}^* = 68 \text{ ohms/square} \), versus 63 ohms/square for the sample before correction. The integrated carrier density derived from the Hall resistance is \( n_{\text{Hall}} = 6.5 \times 10^{16}/\text{m}^2 \), compared with \( n_s = 3.4 \times 10^{16}/\text{m}^2 \) found for the graphene layer (see above). The difference can be attributed to the integrated carrier density of the conducting (presumably neutral graphite) layer. Hence, we find the graphene mobility \( \mu^* = (n_s e \rho_{xx}^*)^{-1} = 2.7 \text{ m}^2/\text{V} \cdot \text{s} \), and carrier diffusion constant \( D = E_F/2n_s e^2 \rho_{xx}^* = 0.30 \text{ m}^2/\text{s} \). From \( D = l^* v_0/2 \), we obtain \( l^* = 600 \text{ nm} \), where \( l^* \) is the carrier mean free path in the graphene. This value is in
excellent agreement with the limiting value \( l^* = 3\pi W^* / 4 = 635 \text{ nm} \) for a ribbon 270 nm wide with only diffuse elastic boundary scattering, which implies that the resistance is determined primarily by the confining geometry and not by defect scattering in the material. Alternatively, the conductance of a graphene ribbon can be estimated from the Landauer equation:

\[
G = \frac{e^2}{h} g_s g_v \Sigma T_n, \tag{5.12}
\]

where \( \Sigma T_n \) is the sum over transmission coefficients of the nth modes \((0 \leq T \leq 1)\). The \( T_n \) values are obtained approximately as \( T_n = l_n / L \), where \( l_n \) is the mean free path of the nth mode. If we assume elastic scattering at the boundaries without mode mixing, then \( l_n \) is the distance along the wire between scattering events for the nth mode that is,

\[
l_n = k_x / k_n W = W\left( (k_F W / n\pi)^2 - 1 \right)^{1/2}.
\]

Hence,

\[
G = \frac{e^2}{h} (g_s g_v W^* / L) \Sigma [(n_{max} / n)^2 - 1]^{1/2}. \tag{5.13}
\]

With \( W^* = 270 \text{ nm} \), \( L = 6 \text{ mm} \), and \( n_{max} = 29 \), we find \( R = 1 / G = 1430 \text{ ohms} \), or \( \rho_g = RW^* / L = 64 \text{ ohms/square} \), in remarkable agreement with experiment. The sample resistance decreased uniformly from 1490 ohms at \( T = 180 \text{ K} \) to a minimum of 1410 \( \Omega \) at \( T = 30 \text{ K} \), below which it increased (Fig. 5.8, inset). From 300 to 30 K, the resistance decreased only 13\%, which indicates \[ from Matthiessen’s rule [142] \] that the electron phonon-scattering time is about \( 4 \times 10^{-12} \text{ s} \) at 300 K. The increase of resistance below 30 K is caused by the increasing phase coherence length \( l_\varphi \). The resistance increase is a manifestation of constructive quantum interference between time-reversed trajectories, which enhances the probability for an electron to be localized at a scattering site. This well understood weak localization (WL) effect is undone in a magnetic field because time reversal symmetry is lifted. The pronounced peak in the low-field MR at \( B = 0 \) shows this WL effect (Fig. 5.8). Clear universal conductance fluctuations flank the peak. The reproducible UCFs are caused by quantum interference from elastic scatterers \( \text{e.g., at the ribbon edges} \). For all fields, the widths of UCF features are similar to the WL peak width, in contrast to the SdH peaks, which are much wider. The WL peak saturates at low temperatures \( \text{peaks for 4, 6, and 9 K are similar} \), whereas the amplitude of the UCFs increases very rapidly.
Figure 5.8: Electronic coherence determined from weak localization and conductance fluctuations. The weak localization peak observed in the MR near $B = 0$ results from electronic coherent backscattering effects. The temperature dependence of the absolute amplitudes and the widths depend on the phase coherence length $l_{\phi}(T)$ and the geometry [note the low-temperature saturation of $l_{\phi}(T) \sim 1.1 \, \mu\text{m}$]. The UCF structures have widths that are similar to the WL peak ($\sim 0.03$ T, considerably narrower than the SdH peaks). The theoretical fits (bold lines, plotted only for $B=0$), using only $l_{\phi}(T)$ as a parameter, describe reasonably well both the WL peaks and the UCF amplitudes (bold horizontal lines). Inset: sample resistance as a function of temperature for $B=0$. 

\[ R_{xx} \, (\text{OHm}) \]

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure5.8.png}
\caption{Electronic coherence determined from weak localization and conductance fluctuations. The weak localization peak observed in the MR near $B = 0$ results from electronic coherent backscattering effects. The temperature dependence of the absolute amplitudes and the widths depend on the phase coherence length $l_{\phi}(T)$ and the geometry [note the low-temperature saturation of $l_{\phi}(T) \sim 1.1 \, \mu\text{m}$]. The UCF structures have widths that are similar to the WL peak ($\sim 0.03$ T, considerably narrower than the SdH peaks). The theoretical fits (bold lines, plotted only for $B=0$), using only $l_{\phi}(T)$ as a parameter, describe reasonably well both the WL peaks and the UCF amplitudes (bold horizontal lines). Inset: sample resistance as a function of temperature for $B=0$.}
\end{figure}
with decreasing temperature (which also distinguishes UCFs from SdH peaks).

Weak localization and UCFs have been exhaustively investigated in 2D electron systems. Before saturation below 9 K, the observed decrease of the WL peak with increasing T fits a $T^{2/3}$ dependence, which indicates that electron-electron scattering is the primary dephasing mechanism. The decrease in amplitude of the UCFs with increasing T is caused by a reduction of $l_\varphi$ combined with thermal smearing, which is characterized by the thermal length $l_T = \sqrt{\hbar D/k_B T}$.

On the other hand, the WL is not sensitive to $l_T$. Its width $\Delta B$ is essentially determined by the field for which an electron trajectory of length $l_\varphi$ encloses one flux quantum (for this sample $l_\varphi \gg W$, so that flux cancellation effects also need to be taken into account). Following the thorough development reviewed by Beenakker and van Houten [142], the field is parameterized in terms of

$$l_B = \sqrt{D \tau_B}, \quad (5.14)$$

where $\tau_B = 3m^* l_\varphi / (W^2 v_0)(4\pi l_m^2 / 3WL^* + 1)$, and $l_m = (\hbar/eB)^{1/2}$ is the magnetic length. The WL contribution to the conductance (for $l_\varphi \gg l^* \gg W$) is

$$\Delta G_{WL} = -4(G_0/L)[(l_{\varphi}^{-2} + l_B^{-2})^{-1/2} - (l_{\varphi}^{-2} + l_B^{-2} + l^*^{-2})^{-1/2}] \quad (5.15)$$

and the root mean square amplitude of the UCFs is given by

$$\Delta G_{UCF} = \sqrt{24G_0(l_\varphi/L)^{3/2}}[1 + (9/2\pi)(l_\varphi/l_T)^2]^{-1/2} \quad (5.16)$$

The only free parameter in these expressions is $l_\varphi(T)$. The origin of the commonly observed low-temperature saturation of the WL is still debated intensely. Here we assume that it is caused by a physical limitation to $l_\varphi$, which appears to length. The effective phase coherence length $l^*_\varphi = [l_\varphi(T)^{-2} + (L_{sat}/2\pi)^{-2}]^{-1/2}$ saturates at $L_{sat}/2\pi$. The fit shown in Fig. 5.8 correspond to $L_{sat} = 7 \mu m$ and $l_\varphi(T) = (7 \mu m)T^{-2/3}$ [at 4 K, $l_\varphi^* = 1.1 \mu m$, and $\tau_\varphi = (l_\varphi^*)^2/D = 4 \times 10^{-12}$ s; at 58 K, $l_\varphi^* = 430$ s; at 58 K, $l_\varphi^* = 430 \mu m$, and $\tau_\varphi = 6 \times 10^{13}$ s].

This analysis clearly shows that the resistance of the graphene ribbon is determined primarily by boundary scattering, with a coherence boundary scattering, with a coherence length far larger than the effective ribbon width, even at 58 K. Therefore, as also shown in
our analysis of SdH oscillations, the low-field resistance depends directly on the eigenmodes of laterally confined carriers in the graphene ribbon. Other samples indicate that the width dependence of resistance can persist up to room temperature. Because electron-phonon scattering is weak even at room temperature (see above), electron-electron scattering should continue to be the dominant dephasing mechanism under ambient conditions (such scattering affects the resistance only through phase-breaking, i.e., by limiting $l_\phi$). Accordingly, on the basis of the measurements presented here, we expect to see quantum interference effects over distances exceeding 100 nm at room temperature (and beyond 400 nm at liquid nitrogen temperature). Moreover, quantum confinement should be observable at room temperature in ribbons as wide as 50 nm. In this context, we also note that a ribbon 100 nm wide has been observed to sustain a current of 9100 mA at room temperature, and that, like nanotubes, the conductance of graphene ribbons increases approximately linearly with bias voltage at high bias. These results raise new possibilities for coherent EG electronics on an attractive size scale and at relatively high temperatures. The demonstrated material and transport properties of EG could allow electronic devices and interconnects to be designed that rely on the wave properties of electrons and holes, so that interference-based electronic switches can be envisioned. Nanotubes, on the other hand, require metallic interconnects that destroy phase coherence. Furthermore, graphene is an extremely robust material that has the potential to be patterned with atomic precision down to the molecular level. Such precision might be achieved through a combination of standard lithographic and chemical methods, enabling a wide variety of coherently connected molecular structures. Finally, we note that it has been previously determined that the carrier density can be controlled electrostatically and that chemical doping of the edges also is feasible. Consequently, epitaxial graphene provides a platform for the science and technology of coherent graphene molecular electronics.

5.4 Conclusion and Future Work

We have produced ultrathin epitaxial graphite films on single-crystal silicon carbide by vacuum graphitization, which show remarkable 2D electron gas (2DEG) behavior. The most
highly ordered sample exhibits Shubnikov-de Haas oscillations that correspond to nonlinear-

ities observed in the Hall resistance, indicating a potential new quantum Hall system. The
transport properties, which are closely related to those of carbon nanotubes, are dominated
by the single epitaxial graphene layer at the silicon carbide interface and reveal the Dirac
nature of the charge carriers. Patterned structures show quantum confinement of electrons
and phase coherence lengths beyond 1 micrometer at 4 kelvin with mobilities exceeding 2.5
square meters per volt-second.

We show that the high-mobility films can be patterned via conventional lithographic
techniques, and we demonstrate modulation of the film conductance using a top-gate elec-
trode. These key elements suggest electronic device applications based on nanopatterned
epitaxial graphene (NPEG), with the potential for large-scale integration. Patterned struc-
tures exhibit extraordinary two-dimensional electron-gas properties, previously seen only
in semiconductor inversion layers, demonstrating its fundamental science potential. The
research created a foundation for graphene science and technology and established a path
toward graphene-based nanoelectronics. Specifically, we have succeeded in producing ex-
tended defect free EG, developing patterning methods, establishing the 2D character of
electrical transport in EG, and electrostatic gating of simple NPEG devices at room tem-
perature. Additionally, recent results strongly indicate that quantum-size-effects determine
the room-temperature transport properties of NPEG structures.

The success of the NPEG project is relies on the quality of graphene films. Preparation
of highly-perfect graphene layers will depend on the quality of the SiC substrate. Until
recently, the defects (screw dislocations in Fig. 3.6(a) and micropipes) that result from the
bulk growth process are the main reasons for quality fluctuations of the graphene films.
After hydrogen etching, the steps like terraces on SiC surface as shown in Fig. 3.5 also
affect the the uniformity of the graphene films. We are working on improving the qualities
of both the SiC substrates and the graphene films by fine tuning the growing conditions
and developing new growth methods.

Neudeck and collaborators at NASA Glenn [201, 202, 203] have reported a CVD tech-
nique to grow atomically-flat SiC mesas of size 400 $\mu m \times 400 \mu m$. As shown schematically
in Fig. 5.9, the SiC substrate is optically-patterned into raised mesas, followed by high-temperature (1600°C - 1700°C) CVD growth using silane and propane precursors. The defect density on the surface is low enough that more than 50% of mesas contain no extended defects. Under CVD step-flow growth, all of the steps flow off the edge of the mesa, leaving an atomically flat surface. We expect that the mesa CVD substrates ultimately will be the path to large-scale patterns and high-mobility material, the very highest quality graphene ribbons would likely utilize a thin CVD overgrowth after lithographic patterning in the future work.

With an eye on future integration with Si technology, our collaborators have invested alternative low temperature production methods of SiC on Si. One attempt is to use electron beam-stimulated CVD (EB-CVD) to grow SiC on Si.

A film of silicon carbide nanocrystallites may grow on n-Si(111) with an acetylene background pressure of 10^{-5} Torr for 30 minutes under UHV. During growth, 5 - 11 eV electrons irradiated the substrate stimulating film growth via low energy electron scattering processes such as dissociative electron attachments and the negative ion resonances of acetylene and silicon carbide. The substrate temperature of 650°C is much lower than typically reported for good film growth. By using diffraction electron stimulated desorption (DESD), we ultimately intend to impose a nanoscale pattern of SiC growth on the surface. In this method a surface electron standing wave is created by the incident and diffracted electron waves. Electron stimulated growth occurs preferentially at the antinodes of the standing wave pattern. We aim to create short defect-free pillars of SiC on the Si surface that could serve as a strain-accommodating layer between Si and a CVD-grown SiC film. With properly chosen pillar spacing, which is adjustable via e-beam energy and angle, a similar technique (done as incoherent EB-CVD to keep the temperature below the melting point of Si) could result in a strain-free single-crystal SiC film on top of the pillars.

SiC wafers are much more expensive than Si wafters, a research grade three inch SiC wafer costs up to five thousand dollars. It is certain that a new low temperature, low cost, CVD related graphene films growth method should be developed before graphene films are introduced to commercial applications.
Figure 5.9: Diagram illustrating the growth of step-free mesas. (a) Before growth, initial mesa surface parallel to bottom of wafer surface contains steps due to tilt of basal plane with respect to polished wafer surface. (b) After growth, steps have been grown out of existence, leaving a step-free mesa surface parallel to the basal plane, tilted with respect to the initial surface. [201]
The research presented here is actually only a small step in this direction. As we show, the patterned graphite structures which we already have built, demonstrate remarkable (and possibly size dependent) two dimensional electron gas properties. The work will be successful when we succeed in demonstrating the fundamental properties of the material as well as simple prototype device structures. All graphene electronically coherent devices and device architectures are envisaged.
APPENDIX A

LANDAUER FORMULA

The conductance of large samples follows the ohmic scaling law: \( G = \sigma W/L \). But the ohmic law does not apply to mesoscopic systems, there are two corrections to this law:

The interface resistance is independent of the sample length \( L \) and the conductance does not decrease linearly with the width \( W \). As shown in Fig. A.1, an ideal ballistic wire with a constant transversal confining potential connects to two macroscopic electrodes. The quantum mechanical solution for such a wire gives plane waves electron states along the wire axis and standing waves electron states in the transversal direction. The energy dispersion is: \( E_n(k) = E_n + \hbar^2 k^2/2m \); where \( k \) is the wave vector in the axis direction and \( E_n \) is the energy of the \( nth \) transversal wave function. Each transversal wave function defines a conductance channel, in which the electrons are propagating with a velocity of \( v_k = \partial E/\partial k = \hbar k/m \). The macroscopic electrodes are ideal electron reservoirs with well defined chemical potential (\( \mu \)) and temperature (\( T \)), which inject electrons corresponding to their distribution function and absorb the entering electrons without reflection. The chemical potential of the electrodes is shifted by the applied voltage \( \mu_1 - \mu_2 = eV \). The occupation of the electron states in the wire is presented in Fig. . The imbalance between the occupation of the right and left moving states results in a net current through the wire.

The current \( I^+ \) carried by each transverse mode in \(+k\) states is [134]

\[
I^+ = \frac{e}{L} \sum_k v f^+(E) = \frac{e}{L} \sum_k \frac{1}{\hbar} \frac{\partial E}{\partial k} f^+(E)
\]

(A.1)

where \( L \) is the length of the conductor, \( v \) is the electron velocity, \( f^+(E) \) is the Fermi function in the \(+k\) state. Assuming periodic boundary conditions and converting the sum over \( k \) into an integral, the current is given as [134]

\[
I^+ = \frac{2e}{\hbar} \int_{-\infty}^{+\infty} f^+(E)d(E)
\]

(A.2)
Figure A.1: (a) Ballistic wire connecting to two wide electrodes, which emit electrons to the channel with the distribution functions corresponding to chemical potentials $\mu_1$ and $\mu_2$. The energy dispersion and occupation of the states are shown. In the electrodes the quasi-continuous transversal modes are filled up to their chemical potential. Due to the small transversal dimension in the ballistic conductor only a few modes are occupied; and the $+k/-k$ states have depending on which electrode they arrive from.
Extend this result to multi-modes waveguides as in Fig. A.1, current $I_1^+$ flowing entirely in the energy range between $\mu_1$ and $\mu_2$ from electrode 1 is given [134]

$$I_1^+ = \frac{2e}{h} \int_{-\infty}^{+\infty} f^+(E)M(E)d(E) = \frac{2e}{h} M(\mu_1 - \mu_2). \quad (A.3)$$

The current from electrode 2 is current from electrode 1 times the transmission probability $T$:

$$I_2^+ = \frac{2e}{h} M T(\mu_1 - \mu_2). \quad (A.4)$$

The rest of the current is reflected back to contact 1

$$I_1^- = \frac{2e}{h} M (1 - T)(\mu_1 - \mu_2). \quad (A.5)$$

The net current $I$ flowing at any point in the device is given by

$$I = I_1^+ - I_1^- = \frac{2e}{h} M (1 - T)(\mu_1 - \mu_2). \quad (A.6)$$

Hence the conductance is given by landauer formula [142]

$$G = \frac{I}{(\mu_1 - \mu_2)/|e|} = \frac{2e^2}{h} M T = G_0 MT \quad (A.7)$$

where $M$ is the number of transverse modes, $T$ is the average probability that an electron injected at one end of the conductor will transmit to the other end. So the conductance depends on the number of transverse modes in the conductor and goes down in discrete steps. The Landauer formula is a model which does not take into account the inelastic processes or the electron-electron interaction, but it has been very powerful to explain mesoscopic phenomena, and it also helps to understand the nature of conductance at atomic level.
REFERENCES


