Alignment controlled Graphene on hBN Substrate for Graphene Based Capacitor and Tunneling Transistor

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By

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Context

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Abbreviation

AC: Alternating Current
AFM: Atomic Force Microscope
BSCCO: Bismuth Strontium Calcium Copper Oxide
CVD: Chemical Vapor Deposition
DIC: Differential Interference Contrast
DI water: De-ionized water
FTO: Fluorine-doped Tin Oxide
hBN: hexagonal Boron Nitride
HOPG: Highly Ordered Pyrolytic Graphite
HTS: High Temperature Superconductor
IPA: IsoPropyl Alcohol
ITO: Indium Tin Oxide
LC circuit: an electronic circuit contains at least one inductor and capacitor
LED: Light Emit Diode
LLs: Landau levels
MIBK: Methyl IsoButyl Ketone
MoS₂: Molybdenum disulphide
PET: Poly-Ethylene Terephthalate
PMGI: Poly Methyl GlutarImide
PMMA: Poly Methyl MethAcrylate
QHFM: Quantum Hall Ferro-Magnetism
SiO₂: Silicon dioxide
SEM: Scanning Electron Microscope
SFM: Scanning Force Microscope
STM: Scanning Tunnelling Microscope
SdH: Shubnikov de Haas
2D: two dimensional
3D: three dimensional
TEM: Tunneling Electron Microscope
TMD: Transition Metal Dichalcogenide
WS₂: Tungsten disulphide
YBCO: Yttrium Barium Copper Oxide
Abstract

Since 2004, graphene attracts intensive attention from scientists and engineers all over the world. During the last decades, the research relates to graphene and other 2 dimensional (2D) materials are rapidly increasing. Approximately, ten thousand journal papers have been published after the discovery of graphene in relative topics widely spread. On the other hand, the simple graphene properties research is nearly completed. Researchers turn their attention to other 2D materials or Van der Waals heterostructures. By increasing the liberty and knowledge of 2D materials, the Van der Waals heterostructures can start to build something on this 2D wander land. In this thesis the Van der Waals heterostructures is based on graphene and some other well known 2D materials such as hexagonal boron nitride (hBN) to study fundamental physics and possible applications in near future.

In this thesis, three published papers which are related to Van der Waals heterostructures have been included. The electronic properties of encapsulated graphene on different 2D crystals have been investigated by the capacitance spectroscopy. Several 2D crystals have been tested as a substrate such as MoS$_2$, WS$_2$, mica, LiNbO$_3$...etc. The quality of encapsulated device is correlates the interface self-cleaning.

Follow with the fundamental physics study employed by a simple Van der Waals heterostructure. Graphene and hBN is lattice aligned within 2 degrees in difference and creates a new superlattice structure which just like moire pattern happens while two similar patterns overlapped. The basic electronic properties do not vary at near Dirac point. Away from the first generation Dirac point, the superlattice structure affects the band structure in higher carrier concentration. In this paper, aligned graphene-hBN capacitors have been demonstrated to discover more fine details of these many-body interactions in this superlattice structure.

The final part is related to twist controlled graphene-graphene resonance tunneling transistors. A Van der Waals heterostructure is constructed by two aligned graphene stripes with a thin layer of hBN as a spacer. The electrons are tunneled from one stripe to another graphene stripe while a bias voltage applied. The resonance tunneling is occurred when two graphene flakes are aligned at certain bias voltage. In this paper, we contribute the resonance tunneling to momentum conservation of tunnelling electrons. Theory simulation is highly agreed with our experiment results.

The University of Manchester; Degree of Doctor of Philosophy candidate Jhih-Sian Tu
Title: Alignment controlled Graphene on hBN Substrate for Graphene Based Capacitor and Tunneling Transistor
22/Oct/2014
Declaration

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Acknowledgment

There is always a joke for Taiwanese graduated school student as they writing acknowledgment. “Too much person to give appreciation, thank god instead.” 要感謝的人太多了，那就謝天吧! The stance was very famous in our high school text book so people use it to make fun with student who doesn’t really want to write acknowledgment. Although I am an atheist, I still understand the limitation of free will and things are not fully controlled by us. Therefore, I need to attribute my gratitude to the random walk and the great distribution of probability! Ha! I am Joking. Seriously, any success in this Ph. D degree must points to some specific person, without their contributions my project will be impossible to finish.

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Family is a large group of people who share their relation in Chinese culture. The connection although is not unbreakable but very solid between each member. There always has a position for every member even some of them are living in other place. Thus we always have a place to go back, a place we call home. Base on that, I would like to give my appreciation to every my family members especially my parents, my young sister and my wife Dr. Pei-Hua Chung. I am certainly a lucky husband, child, bother etc to be a family.

There is no an endless banquet like Chinese ancestor said. All the great time will pass like river flows to the ocean and entropy increases. Does there exist a happy ending for me and everyone I cared or I worked with? There must have one if multi-universe is true but even the idea is real I don’t know am I in it or not. However, treasuring the moment with everyone I met and doing all the best to enjoy life. Therefore, this acknowledgment is not only to return all appreciation to everyone who helped me but also to remind myself the every moment I treasured.

To everyone whom is willing to pay such attention to this thesis.
Live long and prosper!
Graphene, the world’s first discovered 2 dimensional (2D) material, is made of a single layer of carbon atoms. Materials consisting a single atomic layer were not expected to be stable or exist at room temperature but were realized in 2004, the year Sir Andre Geim and Sir Kostantin Novoselov revealed the electronic properties of atomically thick carbon films. This atomically thick carbon film, later named graphene, not only opens a new frontier for research groups, but also raises great interest from the industry. With great mobility, thermal, electric conductivity, strong mechanical properties, near fully transparent to visible light and extreme thinness, graphene has been predicted as a material that will be widely utilized in a foreseeable future. Therefore, graphene has
attracted many scientists to study its fundamental properties and its possible applications. The related researches also rapidly increased after the discovery of graphene. Statistically, graphene research has boosted the related publications by on order of magnitude since 2004, from 164 to 3671 within 6 years\(^\text{19}\). In 2010, also 6 years after graphene has been discovered, the Nobel Prize in physics was awarded to Sir Andre Geim and Sir Kostantein Novoselov for their groundbreaking discovery and continuous contribution to the investigation of 2D materials.

The surprising discovery of graphene is not only attributed to its stable existence but also to the simplicity of isolating graphene with a common and handy scotch tape\(^\text{20}\). The simple mechanical exfoliation with sticky tape was inspired by the method of clean the graphite for tunneling electron microscope (TEM) calibration. Such an exfoliation process removes several layers of graphite from the contaminated surface, leaving a suitable clean surface for calibration. With mechanical exfoliation, the lateral dimensions of the produced graphene ranges from several micrometers to a few millimeters squared, depending on the quality of graphite. In 2008, four years after graphene has been discovered, chemical vapor deposition (CVD) method has successfully been utilized to grow graphene on Ni\(^{21-23}\) or Cu\(^{24}\) surfaces. Two years later, the size of CVD grown graphene is larger than commercial silicon wafers, reaching sizes of 30 inches in diameter and can be mass produced with a roll to roll method\(^\text{25}\). The liquid exfoliation graphene\(^\text{26-28}\) is an alternate method to realize graphene mass production through use of chemicals to separate graphite into individual layers without aggregation. The graphene flakes produced as such are only sub micrometers in size but have extremely large quantities. At present, mechanically exfoliated graphene still has the best quality with higher carrier mobility and minimal chemical doping. However, some applications which do not need graphene of extremely high quality has already been implemented such as flexible touch screens which just use graphene and Polyethylene terephthalate (PET) as a replacement conducting glass (ITO or FTO)\(^\text{29}\). On other hand, single crystal CVD graphene growth and CVD graphene growth on hexagonal boron nitride (hBN) can provides better graphene quality. Therefore, high quality graphene flakes in wafer scale sizes are highly possible in the near future.

Meanwhile, other 2D materials have also attracted the attention of researchers. One of them in particular is hBN, material that possesses a hexagonal structure made up of boron and nitrogen atoms. It’s a lattice constant only differs from that of graphene by 1.8% but has huge 5.2 eV band gap due to the boron and nitrogen bonding. The wide band gap means that hBN can function as a good insulator with an atomically flat surface. When hBN is used as a substrate for graphene, the electron mobilities in graphene can easily exceed 10,000 cm\(^2\)V\(^{-1}\)s\(^{-1}\) compared to that in graphene on SiO\(_2\) surface which is only 7000 cm\(^2\)V\(^{-1}\)s\(^{-1}\). Unlike hBN, molybdenum disulphide (MoS\(_2\)) is a 2D semiconductor which bulk is widely used in dry lubrication. In 2011, Andras Kis’s group in Switzerland made the first single layer MoS\(_2\)
transistor\textsuperscript{30}. Despite the carrier mobility of MoS\textsubscript{2} is around ten to hundred cm\textsuperscript{2}V\textsuperscript{-1}s\textsuperscript{-1}, single layer MoS\textsubscript{2} still gains a lot of attraction because of its band gap. Single layer MoS\textsubscript{2} has a 1.5 eV band gap which provides better on-off ratios (>10\textsuperscript{8}) than pure graphene transistor. (Graphene has non-zero conductivity at neutrality point so pure graphene transistor switch is always leaking.) The interest in searching/investigating other 2D materials is continuously growing in recent years. From mineral mica to Transition Metal Dichalcogenides (TMD, such as WS\textsubscript{2}, MoSe\textsubscript{2}, TaS\textsubscript{2}, TiS\textsubscript{2}...etc), vast varieties of 2D materials has created a huge playground for scientists and research engineers as figure 1-1 shows\textsuperscript{31}.

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<td>MoS\textsubscript{2}, WS\textsubscript{2}, MoSe\textsubscript{2}, WSe\textsubscript{2}</td>
<td>MoO\textsubscript{3}, WO\textsubscript{3}</td>
<td>Metallic dichalcogenides: NbSe\textsubscript{2}, NbS\textsubscript{2}, TaS\textsubscript{2}, TiS\textsubscript{2}, NiSe\textsubscript{2} and so on</td>
</tr>
<tr>
<td>Fluorographene</td>
<td></td>
<td>TiO\textsubscript{2}, MnO\textsubscript{2}, VO\textsubscript{2}, TaO\textsubscript{2}, RuO\textsubscript{2} and so on</td>
<td>Layered semiconductors: GaSe, GaTe, InSe, Bi\textsubscript{2}Se\textsubscript{3} and so on</td>
</tr>
<tr>
<td>Graphene oxide</td>
<td></td>
<td></td>
<td>Hydroxides: Ni(OH)\textsubscript{2}, Eu(OH)\textsubscript{2} and so on</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Others</td>
</tr>
</tbody>
</table>

**Figure 1-1** The table of 2D material library in 2013. (Adapted from reference 31)

Formation of 2D heterostructure through combining individual 2D materials provides even more avenues for future investigation and application. Despite the basic property of “pure” graphene is nearly completed. However, this is just an opening of 2D materials research\textsuperscript{32}. Currently, researchers have begun to shift their focus to Van der Waals heterostructures which involves laying different 2D materials on each other to achieve new properties that differ from that of the original materials. These 2D heterostructure stacks are strongly held together by covalent forces in plane. In contrast, the stack is maintained in the out of plane direction by relatively weak Van der Waals like forces which are sufficient to allow influences between the layers of 2D materials. For example, placing graphene on hBN improves the electronic mobility and if the lattice of graphene is well aligned with that of hBN, self-replicas of the Dirac cones can be observed due to many-body interactions. Thus, all 2D materials can be treated as Lego blocks with atomic thickness for researchers to freely assemble. These 2D Lego materials provide an avenue for designing artificial structures with atomic precision. Imagine a structure, where graphene is stacked on a few layers of dielectric material such as mica and repeated in sequence. Such a bottom-up approach will result in structure similar to a high temperature CuO
based superconductor. Unlike conventional method which requires a furnace for its growth, the thickness of the spacing layer in these 2D heterostructures can be precisely controlled. For high temperature CuO based superconductor, the critical temperature $T_c$ is related to the thickness of dielectric layer. In this case, $T_c$ manipulation becomes simple and more detailed investigations have also become possible.

Van der Waals 2D heterostructures provide the potential for future materials to be formed, investigated and applied. With flake transfer technology and an entire library of 2D materials, not only fundamental physics and electronic property research can be progressed but it also provides a method to overcome the drawbacks of individual materials by assembling them with other materials for future applications. Recently, Coulomb drag (the electron-electron interaction within few nanometer range) has been studied in graphene/hBN heterostructure. The graphene/hBN structure is made up of two graphene flakes separated by only 2-3 layers of hBN and encapsulated by thicker hBN. The quantum Hall ferromagnetism (QHFM), Hofstadter butterfly and topological insulator also have been observed in Van der Waals 2D heterostructures. In this thesis we also demonstrate several graphene based 2D heterostructures for fundamental physical study and possible future applications. Graphene-hBN aligned heterostructure capacitor provides greater details on many-body interactions. The phenomena of QHFM self-replica and suppression at rational flux values and hierarchy of Hofstadter states at higher magnetic field will be discussed in chapter 6. In chapter 7, twist graphene-graphene tunnelling transistor which is also a 2D heterostructure consisting of two aligned graphene stripes spaced by hBN flake with 3-5 layers thickness will be discussed. The resonance tunnelling between two aligned graphene stripes has been observed and also utilized to be a radio frequency oscillator as a proof of concept device.

To realize Van der Waals 2D heterostructures, flake transfer technology needs to be developed and improved with time. Before flake transfer technology has been developed, clean interfaces with atomic flatness and well-controlled stacking orientation is unimaginable. During the last 5 years, as flake transfer technology has been developed and continuously evolved\(^{33,34}\), electronic properties of graphene have also improved due to clean interfaces\(^{35}\) formed after transfer and annealing processes\(^{36}\). In chapter 3, different transfer methods will be introduced and explained in detail, beginning from the initial methods (wet transfer) to current transfer processes. The instruments involved in transfer also will be detailed in this chapter. The following chapter will show other information of fabrication such as flake selection, annealing stack, lithography and metal deposition. With these advances in transfer technologies, Van der Waals 2D heterostructures are made possible and most importantly these technologies are still evolving. For example, we have recently developed a transfer instrument situated within a gloves-box to avoid water and oxygen contamination of the 2D crystal surface. Therefore, the rise of Van der Waals 2D heterostructures is happening and will keeps growing.
To summarize, the discovery of graphene starts a brand new age for researchers and engineers. No one could imagine that graphene could be easily isolated and is stable in ambient conditions before 2004. The discovery not only reveals the existence of graphene and its novel properties but also indicates that other 2D materials are around us and waiting to be characterized. For example, BN is widely used in solid lubrication for a long time. After graphene has been discovered, hBN has also been shown to be exfoliated by a simple sticky tape method to a few layers thick, serving to be great insulator and substrate for 2D devices. At the time, we keeping investigate graphene and other 2D materials enlarge our understanding and library. The foundation is based on flake transfer, annealing, flake alignment instrument, lithography and deposition. Some of them have been widely applied in silicon industry and some of them are invented recently. With modern technology, stacking 2D materials in a specific order is now possible. Placing one 2D material on top of another 2D material in particular sequences, allows researchers to further investigate fundamental physics (e.g. many-body physics) or engineer specific properties of 2D heterostructure devices. We demonstrate both aspects for Van der Waals 2D heterostructures in this thesis. Well-aligned graphene with less than 2 degrees deviation on hBN substrates, display QHFM self-replica and hierarchy of Hofstadter states under with capacitance measurements. On the other hand, aligning two graphene strips with a thin hBN spacer in between them induces resonance tunnelling due to momentum conservation. Using resonance tunnelling, we apply this graphene-based transistor to a conventional electronic circuit and create a LC oscillator with radio frequency ranges. Van der Waals 2D heterostructures provides a promising future for next generation electronic applications as both researchers and engineers can now access this huge Lego play ground on the atomic scale.
Chapter 2

Background

An atomic layer of carbon, called graphene, opens up a brand new age for scientists and engineers. With extraordinary physical, electronic, optical and chemical properties, the discovery of graphene may imply a tempting future. A future with flexible and paper-thin touch screen, ultrafast and low energy consumption computer\textsuperscript{37-39}, long-life battery\textsuperscript{40,41}, foldable light emit diode (LED), etc. may be realized in several decades. In this chapter, the basic properties of graphene will be introduced in detail. In addition, the fundamental characteristics of other 2D materials structure will also be gone through. Utilizing graphene and other 2D materials together not only provide different way to overcome some drawbacks of
graphene, but also introduce a huge play ground for researchers. In this thesis, using 2D Van der Waals heterostructures, we research the fundamental physics and possible future applications.

2-1 Basic electronic properties of Graphene

Graphene, the first isolated 2D material, was discovered in 2004. A single layer of carbon possesses fascinating physical and electronic properties that have attracted intensive attention during the last decade. For example, elastic property of suspended graphene has been examined by nano-indentation using an atomic force microscope, revealing graphene as the strongest material with a breaking stiffness of 42 N/m.\(^1\) The electronic property of graphene was the earliest character to be uncovered and also might be the most important part for future applications\(^1\)

The unique electronic properties are based on the sp\(^2\) bonding of carbon atoms in which the 2s, 2p\(_x\) and 2p\(_y\) orbital hybridization. The sp\(^2\) carbon bonding creates an atomically flat plane with strong \(\sigma\) bonding connecting every carbon atom in the graphene flake. Furthermore, the \(\pi\) electron hopping taking place between atoms through the 2p\(_z\) orbital. The bonding angle of sp\(^2\) bonding is 120\(^\circ\) which results in the honeycomb crystal structure of graphene. The highly symmetric structure is responsible for the wonderful properties of the one atom thick carbon flake. The lattice structure of a single layer of graphene has two identical sites named A and B and each atom in one triangular sub-lattice has three nearest neighbors in the lattice which corresponds to the two K-points in the reciprocal lattices of graphene. These two identical sites have no energetic differences under normal circumstances, causing graphene to have a two-fold valley degeneracy in its electronic states. The electron spin provides an additional two more degeneracy. Therefore, the total degeneracy of graphene is four (2 valley + 2 spin).

The basic electronic structure of graphene and graphite was calculated and published in 1947 by P. R. Wallace utilizing the tight banding model to approximate the energy diagram of graphene to graphite\(^4\). Although experimental conformation comes later; near 60 years after Wallace’s paper has been published. Show in Figure 2-1 is the model that is used in the basic tight binding model calculations. We begin with the graphene lattice where two equivalent sublattices labeled a and b are indicated in Figure 2-1a. This two carbon atoms form the unit cell of graphene with unit vectors \(\vec{a}_1\) and \(\vec{a}_2\). The unit vector can be expressed with the following equations.
\[ \vec{a}_1 = \sqrt{3}a_{cc} \left( \frac{\sqrt{3}}{2}, \frac{1}{2} \right), \text{ and } \vec{a}_2 = \sqrt{3}a_{cc} \left( \frac{\sqrt{3}}{2}, -\frac{1}{2} \right) \]

\(a_{cc}\) is the length of graphene carbon-carbon bonding which is 1.42 Å. Therefore, the graphene lattice constant is given by \(|\vec{a}_1| = |\vec{a}_2| = 1.42 \times \sqrt{3} = 2.46 \text{ Å}.

Figure 2-1  Schematics of the real and reciprocal lattices of graphene. Each atom can form triangular sub-lattices \(a\) with three nearest neighbors \(b\). \(\vec{a}_1, \vec{a}_2\) are lattice unit vectors and \(\delta_1, \delta_2, \delta_3\) are vectors of atom \(a\) to the nearest atom \(b\) (a). The K and K' points in reciprocal lattice (first Brillouin zone) are also Dirac points of the electronic band structure in graphene. The existence of K and K' indicates that graphene has a two-fold valley degeneracy in zero magnetic field. Vectors \(\vec{b}_1\) and \(\vec{b}_2\) are unit vector in reciprocal lattices of graphene (b).

The Brillouin zone of graphene is also of hexagonal shape with two different K points at the corners. Figure 2-1 (b) shows the first Brillouin zone of graphene with unit reciprocal vector \(\vec{b}_1\) and \(\vec{b}_2\). If we define a basic reciprocal length (the length of two M point through \(\Gamma\) point in \(k\)-space) \(b = \frac{4\pi}{\sqrt{3}a}\) where \(a\) is the lattice constant 2.46 Å, then the unit reciprocal lattice vector \(\vec{b}_1\) and \(\vec{b}_2\) can be written as follows.
\[ \vec{b}_1 = b \left( \frac{1}{2}, \frac{\sqrt{3}}{2} \right), \text{ and } \vec{b}_2 = b \left( \frac{1}{2}, -\frac{\sqrt{3}}{2} \right) \]

As the unit reciprocal lattice vector has been determined, the \( \mathbf{K} \) and \( \mathbf{K}' \) vectors from the centre of the first Brillouin zone \( \Gamma \) can also be presented in the following equations:

\[ \mathbf{K} = b \left( \frac{1}{2}, \frac{1}{2\sqrt{3}} \right), \text{ and } \mathbf{K}' = b \left( \frac{1}{2}, \frac{1}{2\sqrt{3}} \right) \]

In real space, the three nearest-neighbor vectors are

\[ \delta_1 = a \left( \frac{1}{2}, \frac{\sqrt{3}}{2} \right), \delta_2 = a \left( \frac{1}{2}, \frac{\sqrt{3}}{2} \right), \text{ and } \delta_3 = a (1,0) . \]

The second nearest atoms are located at

\[ \delta'_1 = \pm \vec{a}_1, \delta'_2 = \pm \vec{a}_2, \text{ and } \delta'_3 = \pm (\vec{a}_1 - \vec{a}_2) \]

In the tight binding model, electron hops between nearest neighbor and second nearest neighbor atoms are taken into consideration. The electron hopping energy \( \gamma \) of the nearest neighbor atoms is around 2.7 eV, but the \( \gamma' \) (the electron hopping energy to the second nearest neighbor atoms) is still undetermined. According to the \textit{ab initio} calculations from Reich et al in 2002, the \( \gamma' \) should be between 0.2 \( \gamma \) and 0.02 \( \gamma \). In 2008 from Deacon et al, based on the tight banding fitting of cyclotron resonance experiment, the \( \gamma' \) should be around 0.1 eV\textsuperscript{43}.

\[ \text{Figure 2-2} \quad \text{Electronic dispersion of the hexagonal lattice with } \gamma=2.7 \text{ eV and } \gamma'=0.2 \gamma. \text{ Right: Zoom-in of the electronic structure at K point. (Adapted from reference 44)} \]
The tight binding Hamiltonian for electrons in graphene can be considered as in the following equation. ($\hbar$ is taken as 1.)

$$H = \gamma \sum_{<i,j>,\sigma} (a''_{i,\sigma} b_{j,\sigma}^\dagger + H.c.) + \gamma' \sum_{<i,j>,\sigma} (a''_{i,\sigma} a_{j,\sigma} + b''_{i,\sigma} b_{j,\sigma}^\dagger + H.c.)$$

Where $a''_{i,\sigma}$ is gaining an electron on ambient position $R$ at sub-lattice a and $a_{j,\sigma}$ is losing an electron on ambient $R$ at sub-lattice a with a spin $\sigma$ ($\sigma = \uparrow, \downarrow$). Same meaning as $b''_{i,\sigma}$, but the happen at sub-lattice b. The energy dispersion relation derived from the tight binding Hamiltonian can be expressed as follows:

$$E_{\pm}(k) = \pm \gamma \sqrt{3 + f(k)} - \gamma' f(k)$$

$$f(k) = 2 \cos(\sqrt{3}k_ya) + 4 \cos\left(\frac{\sqrt{3}}{2}k_ya\right) \cos\left(\frac{3}{2}k_xa\right)$$

where the $\pm$ sign indicates the conduction ($+$) or valance ($-$) band of $\pi$ electron and assuming Fermi level at charge neutrality point. Therefore, the energies at various points are: (Take the energy of an electron on the 2P$_z$ is zero. $H_{aa}=H_{bb}=0$)

$$E = -3\gamma - 6\gamma' \text{ at } \Gamma \text{ point (}k_x \text{, and } k_y = 0\rangle$$

$$E = -\gamma + 2\gamma' \text{ at } M \text{ point (}k_y = 0\rangle$$

For electronic studies, the energy dispersion at the K point is deserves greater attention. Near K point, where $(k_x = \frac{2\pi}{\sqrt{3}a}, k_y = \frac{1}{3a})$, the points $q$ with $|q| << |K|$

$$E_{\pm}(k) \approx 3\gamma' \pm \frac{\sqrt{3}ya}{2} |q| - \left(\frac{9\gamma'}{4a^2} \pm \frac{3\gamma}{8a^2 sin3\theta}\right) |q|^2 + \cdots$$

where $\theta = \tan^{-1}\left(\frac{a_x}{a_y}\right)$. The term $\frac{\sqrt{3}ya}{2}$ is Fermi velocity $v_F$ which is approximately $1 \times 10^6$ m/s. Considering that the $q$ point is very close to K then the $|q|^2$ term becomes negligibly small, together with all the terms of higher power. Furthermore, $\gamma'$ is also negligible at low charge charier densities. Therefore, the energy dispersion near K point can be approximated into a linear relation as follow.

$$E_{\pm}(q) \approx \pm v_F |q|$$

Including the constant $\hbar$ into the equation above then produces the famous energy dispersion relation of graphene.

$$E_{\pm}(k) = \pm \hbar v_F k$$
According to the energy dispersion relation of electrons in graphene near K point, graphene is a zero gap material (semi-metal). The linear relation shapes the electron energy diagram into conical-like. Moreover, electrons near K point acts as massless Dirac Fermions in this 2D system. When the electron wavevector is far from the K point, $\gamma'$ is no longer negligible, causing an electron-hole symmetry breaking which is described in figure 2-2 (at large $\gamma'$ value)\textsuperscript{44}.

2-2 Hexagonal boron nitride

Hexagonal boron nitride (hBN) is an atomically flat 2D crystal. hBN is sometimes called white graphene due to its similarity and duality. The crystal structure of hBN is similar to graphene but with boron and nitrogen atoms in the a/b sublattice position. The lattice constant of hBN is 2.52 Å which is only a 1.8 % difference from that of graphene. Although hBN is similar to graphene in crystal structure, hBN is an insulator with a 5.2 eV band gap. Strong covalent bonds between boron and nitrogen atoms makes up the honeycomb structure but no lone pair $\pi$ electrons are shared between two atoms. Therefore, in hBN, no $\pi$ electrons overlap to allow electric conduction. However, the in-plane thermal conductivity of hBN is again similar to graphene due to strong in-plane covalent bonding. Like graphene, layers of hBN are also very easily exfoliated due to relatively weak Van der Waal’s force between each layer.

Despite hBN and graphene both having hexagonal crystalline lattice with similar bond length, the layer stacking of these two materials are different. The hBN layer stacking follows an AA' rule where the top atom is exactly situated above the bottom one of a different element (i.e. top: boron, bottom: nitrogen) as figure 2-3 shows. Graphene stacks in an AB Berneel fashion where the top layer atom is not stacked directly above the bottom atom but is shifted to the position is above the honeycomb centre of the bottom layer.
Figure 2-3 Schematic of hBN monolayer and bi-layer atomic structures. The boron (yellow) and nitrogen (blue) atom sits on a/b sublattice and a distance of 1.445 Å. The vertical spacing between two hBN layers is about 3.33 Å with the layers having an AA’ stacking structure. The AA’ stacking structure is the top atom is situated above the bottom one with a different element. Therefore, one boron atom is located exactly above a nitrogen atom and vice versa.

The chemical properties of BN are corrosion-resistant (insoluble in usual acids) and thermally stable up to 900 °C in air. Additionally, cubic BN has high Mohs hardness that is very close to diamond.\textsuperscript{45,46} Therefore, initial methods of BN synthesis are similar to those of diamond and require high temperatures and pressures. As synthesis technology progress, current CVD methods require lower pressures to grow on specific catalytic substrate. The CVD synthesis of hBN was developed by Takehiko Takahashi et al in 1979. Using BCl\textsubscript{3} and NH\textsubscript{3} as source at high temperatures (900 ~ 1200 °C) in H\textsubscript{2}/Ar gas mixture, a 100 μm thickness hBN film can be grown on carbon steel\textsuperscript{47,48}. Fine grain hBN is widely used in solid lubrication, cosmetics, paints, dental cements, and pencil leads. Although the great chemical stability hBN film can be corrosion-resistant layer, hBN is also very soft just like graphite. BN film was expected to be used in metal-insulator-semiconductor memory diodes\textsuperscript{46} but turns out to be much more complex than simple and effective metal–oxide–semiconductor field-effect transistors. However, after discovery of graphene, hBN is widely used as a substrate or spacer due to its atomically flat surface and wide band gap for electronic insulation. Hexagonal BN become an equally important 2D material as graphene itself. With hBN as a substrate and encapsulating layer, the mobility of graphene can reach 500,000 cm\textsuperscript{2}V\textsuperscript{−1}s\textsuperscript{−1} comparable with suspended graphene but more stable for applications and without any possible contamination from environment. Recently, Wei Yang et al has grown graphene directly on hBN with lower carrier mobility which is only 5000 cm\textsuperscript{2}V\textsuperscript{−1}s\textsuperscript{−1} but still provides some possibilities for future application\textsuperscript{49}.\textsuperscript{31}
2-3 Other 2D materials

Since the discovery of graphene, research involving 2D material is rapidly increasing. These expansive studies not only just focus on hunting of new 2D materials, but also on revealing more 2D electronic properties of those materials. Scientists and engineers can utilize the unique properties of individual 2D crystal to examine electronic properties in greater details (ex: many-body electron interaction) or realize desired electronic properties on new artificial materials. Before we put atomic Lego engineering in practice, we need to first understand the basic properties of these 2D materials.

With mechanic exfoliation, the materials with layered structures are easy to isolate on different substrates such as MoS$_2$, mica, WS$_2$, etc. However, not every 2D material can be simply isolated in an ambient environment which is full of oxygen and water molecules. As materials become thinner, the melting point decrease and chemical interactions with air become severe. Those 2D crystals have to be prepared in an inert gas environment for example in a glove box. Before such related technology is fully developed, the 2D library only includes air-stable 2D flakes in discussion. In this section, three 2D materials (MoS$_2$, mica, and bismuth strontium calcium copper oxide) will be introduced.

*Molybdenum disulphide (MoS$_2$)*

Molybdenum disulphide (MoS$_2$) is a silver colored transition-metal-dichalcogenide (TMD) material. The crystal structure of MoS$_2$ consists of vertically stacked layer with an inter-layer distance of 6.5 Å, as shown in figure 2-4 (a). The stack of MoS$_2$ layers is held by Van der Waals force which can be easily broken by the tape exfoliation method or through intercalation of Li or K atoms to isolate monolayer MoS$_2$. MoS$_2$ is a semiconductor. Single layer MoS$_2$ has a direct band gap of 1.8 eV at the K point which is distinct from the bulk which has an indirect band gap of 1.2 eV as described in figure 2-4 (b)$^{50}$. The presence of an energy gap provides better on-off ratios ($>10^8$ at 500 mV excitation) for conventional field effect transistors. Unlike gapless graphene which has a minimal conductivity limit hinders “switch off” of graphene based devices. However, the charge carrier mobility of MoS$_2$ is limited by the absence of $\pi$-conjugate free electron cloud. The mobility of MoS$_2$ for a typical device is only about $0.1-10$ cm$^2$V$^{-1}$s$^{-1}$. $^{30}$
Figure 2-4 Schematic of MoS$_2$ structure. Sulfur atom colored with yellow and Molybdenum colored with black. The layer distance is 0.65 nm (a). (Adapted from reference 30) The band structure of mono-, bi- layer and bulk MoS$_2$ by screened hybrid density functional theory (blue line) and tight-binding fitting (red line) (b). (Adapted from reference 50)

Since Andras Kis’s group published the single layer MoS$_2$ transistor$^{30}$, 2D TMD materials have attracted lots of attention$^{51}$. TMD crystals such as WS$_2$, WSe$_2$, MoSe$_2$ has similar structures to MoS$_2$ but with different band structures and chemical stabilities. Most importantly, TMD materials have an electronic band gap. Therefore, the related 2D crystals not only provide a higher on-off ratio for conventional transistors, but also illuminate the possibility of 2D light emitting diodes (LED) and photo detectors$^{52,53}$. L. Britnell et al combined multilayer layers TMD crystals with graphene to form Van der Waals heterostructures for used as a flexible LED as well as a light detector$^{54}$. The strong light-matter interaction occurs from Van Hove singularities in the electronic density of states of the TMD material. The interaction enhances the photon absorption and electron-hole pair creation in graphene/TMD/graphene. Moreover, the high transparency of the graphene electrodes allows passages of enough light for these interactions. The quantum efficiency at low power laser illumination is nearly 30%.
Figure 2-5  Wavelength dependence of external quantum efficiency of graphene/MoS$_2$/graphene/hBN device on different laser power (A); Photocurrent of the devices on SiO$_2$ or flexible substrates at different laser power (B); Schematic of devices with gold nano-particles (C); Photocurrent maps of same device before (D) and after (E) gold particle sputtering. The x-y axis respects to spatial position of the device and color respects to the intensity of photocurrent. (Adapted from reference 54)

*Figure 2-5*

Mica

Mica is a group of sheet silicate minerals which can be easily cleaved along the [001] planes. The group includes biotite, muscovite, lepidolite, phlogopite, and zinnwaldite. The word mica usually indicates muscovite mica and also in this thesis. Muscovite mica is an aluminum and silicate oxide based material $\text{KAl}_2(\text{Si}_{3\text{a}}\text{Al})\text{O}_{10}(\text{OH}_2)$. The muscovite mica crystal basically consists of tri-levels of aluminum or silicon atom surrounded by 12 oxygen atoms with potassium atoms located at the top/bottom level as figure 2-6 shows$^{55}$. As a substrate, micas have been known
for its atomically flat surface and large band gap (7.85 eV)$^{56}$. Muscovite mica is a good insulator and thermal conductor, which is widely utilized in electronics such as capacitors. The dielectric constant of mica is nearly two times higher (6.4-9.3) than SiO$_2$ (3.9) and hBN (2-4). Therefore, micas are expected to be a great substrate and spacer for graphene-based or 2D electronic materials.

![Figure 2-6](image)

**Figure 2-6** Schematic of muscovite mica in top view (a), and side view (b). The solid black line indicates the size of a unit cell in muscovite mica. The purple spheres are potassium atom and the grey spheres are sites for extra potassium in case of electropositive surface. (Adapted from reference 55)

Scientific research on related electronic properties of graphene on mica is much less extensive than those of graphene on hBN. Possibly, the reason for such is not only due to the extra chemical doping from non-uniform distribution of potassium atom$^{57}$, but also low charge carrier mobility of graphene on mica for unknown reasons. The surface character of mica may provide a hint for such low mobility. Mica has a hydrophilic surface which absorbs water molecules when exposed in air$^{58,59}$. The layer of water on mica surface will be encapsulated in the interface when flake transfer is performed in ambient environment. Many related studies have revealed an atomic layer of water present on mica, resulting in graphene/water/mica structures, as shown by scanning force microscope (SFM)$^{60,61}$ or scanning tunnelling microscope (STM)$^{62}$. These layers of contamination will gather into pockets due to strong adhesion of two hydrophobic 2D materials (such as hBN and graphene). However, mica is a hydrophilic surface, resulting in a well distributed layer of water molecule which may halt the gathering process and leave a relatively rough interface. Therefore, the surface of mica as graphene on it may not be
atomically flat, causing the low carrier mobility. In this thesis, more details will be discussed in chapter 5.

To overcome this limitation, graphene can be grown on mica substrate in an ultra-high vacuum chamber. Gunther Lippert et al have successfully grown monolayer graphene on mica using molecular beam but no transport data has been revealed. On the other hand, preparation and transfer of mica substrate Flake in water free environment may also be an alternate solution.

_Bismuth strontium calcium copper oxide (BSCCO)_

Bismuth strontium calcium copper oxide (BSCCO) is a high temperature superconductor (HTS) which is discovered in 1988. The critical temperature of the BSCCO family HTS ranges from 2 K to 108 K, depending on the proportion of calcium and copper atoms in structure. The elemental proportions present in BSCCO vary with doping and the composition is usually presented as $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4+x}$ where $n = 0, 1, 2,$ and 3. The $\text{Bi}_2\text{Sr}_2\text{CuO}_6$ (Bi-2201, meaning $n = 0$) has the lowest $T_c$ of this family at 2 K while the $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$ (Bi-2223, $n=2$) has a higher $T_c$ at 108 K, above the boiling point of liquid nitrogen. The polycrystalline Bi-2223 also has a large critical current density ($J_c$) 30,000 - 40,000 A/cm² at 77K. The epitaxial film can even reach $10^6$ A/cm² at 77K. BSCCO is a cuprate superconductor with a 2D layered perovskite structure in which superconducting phenomenon is happening at the Cu-O plane, just like Yttrium barium copper oxide (YBCO, the first HTS material). BSCCO is the first commercialized HTS material (BSCCO HTS wire and tape) due to its weak interlayer bonding. The structure of BSCCO can be cleaved easily along the double bismuth oxide layer as figure 2-7 revealed. The micaceous property provides self-aligned behavior in the exfoliated BSCCO grain for growth and deformation. Based on these properties, the electrical connection between each BSCCO grain can be enhanced and the super conducting current in electrical transport can be extended longer.

BSCCO is a 2D material due to its micaceous property. The basic physical characteristic was fully studied decades ago as a 3D material, although the principle of HTS is still arguable. However the lasagna-like structure may inspire the idea of Van der Waals heterostructure to investigate HTS or other electronic/physical properties. Exfoliation of BSCCO can also be done by the sticky tape method. The thinnest layer consists of a layer of BSCCO structure which breaks into half (15 nm thick) at the double bismuth oxide site. Despite the popularity of this
material a few decades ago; there is less related graphene/BSCCO research than that of graphene/MoS\textsubscript{2} or graphene/mica. In fact, only one publication has tested such a graphene/BSCCO structure which is performed by L. A. Ponomarenko \textit{et al} in 2009\textsuperscript{69}. The transport measurement has concluded that the carrier mobility in graphene on a BSCCO substrate is around 4000 cm\textsuperscript{2}V\textsuperscript{−1}s\textsuperscript{−1}, having the same magnitude as SiO\textsubscript{2}. Interestingly, BSCCO like mica is an atomically flat surface after crystal cleavage but mobility is the supported graphene is not improved. The Dirac point of graphene on mica and BSCCO is also shifted which indicates chemical doping from the substrate surface. In this thesis, more detailed information on the electronic properties of the graphene/BSCCO structure will be provided in chapter 5.

![Schematic of the BSCCO (Bi-2212) structure.](image)

**Figure 2-7** Schematic of the BSCCO (Bi-2212) structure. The color of sphere respects to different elements (left). Three oxide planes plus one calcium plane are basic floor for BSCCO unit cell (center). A unit cell structure of BSCCO. The unit cell can be cleaved along the bismuth oxide layer and creates a half-layer structure. The thickness of monolayer BSCCO is around 2.44 nm and the length at in-plain direction is 0.54 nm (right).
2-4 Van der Waals heterostructure

Van der Waals force is the sum of interactions (attraction/repulsion) between molecules. Unlike electrostatic forces, Van der Waals forces are due to permanent or induced dipoles. Therefore, for two point molecules, the interaction range \( F \propto r^{-6} \) is much shorter than that for two point charges \( F \propto r^{-2} \). The strength of the Van der Waals force also correlates with the material polarizability which is reflected from the dielectric constants and refractive indices. To quantify it, Hamaker has introduced a constant which is defined in following equation:

\[
A = C \pi^2 \rho_1 \rho_2
\]

where \( \rho_1 \rho_2 \) are the number of atoms per unit volume and \( C \) is the particle-particle pair interaction coefficient\(^{70}\). For material in the condensed phase, the Hamaker constant is about \( 10^{-19} \) J for interaction in a vacuum. In 2D system, we take the surface to be of infinite area to simplify calculations and the interaction energy of two flakes separated by a distance \( D \) can be expressed as follow:

\[
W(D) = -\frac{2\pi C \rho^2}{(n-2)(n-3)} \int_0^\infty \frac{dz}{z^{n-3}} = -\frac{2\pi C \rho^2}{(n-2)(n-3)(n-4)D^{n-4}}
\]

where \( n = 6 \) (Van der Waals force\(^{70}\); energy between two induced dipoles) becomes

\[
W(D) = -\frac{C\pi \rho^2}{12D^2}
\]

per unit area. The interaction energy is only proportional to the distance square of two flakes.

**Table 2-1** Non-retarded Hamaker constants for two identical media interacting in vacuum at room temperature\(^{70}\). (partly adapted from reference 70)

<table>
<thead>
<tr>
<th>Medium</th>
<th>Dielectric Constant</th>
<th>Refractive index</th>
<th>Hamaker Constant ((10^{-20} \text{ J}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diamond</td>
<td>5.66</td>
<td>2.375</td>
<td>28.9</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>2.55</td>
<td>1.557</td>
<td>6.5</td>
</tr>
<tr>
<td>SiO(_2)</td>
<td>3.8</td>
<td>1.448</td>
<td>6.3</td>
</tr>
<tr>
<td>Mica</td>
<td>5.4-7.0</td>
<td>1.6</td>
<td>10</td>
</tr>
<tr>
<td>Si(_3)N(_4)</td>
<td>8</td>
<td>1.98</td>
<td>17</td>
</tr>
<tr>
<td>Al(_2)O(_3)</td>
<td>10.1-11.6</td>
<td>1.75</td>
<td>15</td>
</tr>
</tbody>
</table>
Van der Waals heterostructure is a structure comprising different materials held together by Van der Waals forces. Fabricating Van der Waals heterostructure is done by simply layering one material on top of another material. Van der Waals forces keep the stack intact. For example, the energy required to separate a stack of two 1 mm$^2$ mica flakes in contact the stack is about $10^8$ J in vacuum. Both flakes are assumed to be atomically flat (surface contamination and roughness reduces Van der Waals adhesion force). The force required to separate the stack depends on the methods used. For vertical lift off, $F = A x \text{area} / 6\pi D^3 \approx 10^{2}$ N when peeling is performed the force requirement is only about $F = W/d \approx 10^{-6}$ N in vacuum. The force required differs by eight orders of magnitude between peeling and planar separation which answers why we can easily peel 2D materials but stack them firmly.

In 1984, A. Koma et al. has grown sub-nanometer TMD films by Van der Waals epitaxy method successfully. Van der Waals epitaxy is a method by using molecule beam epitaxy to grow thin films on cleaved single crystalline atomically flat surfaces in ultra-high vacuum. Furthermore, K. Saiki et al. grew TMD thin film on heterogeneous substrates (nature mica) using similar Van der Waals epitaxy method in 1989. The method circumvents the lattice matching restriction of the growing layer and substrate. In other words, the growing layer has no bonding with the substrate as only Van der Waals forces hold the film and substrate together. It is commonly believed that Van der Waals epitaxial film growth may play a principle role directing 2D material growing. However, Van der Waals epitaxial growth are still limited on specific substrates such as mica, graphite and TMDs while only TMD crystals has been grown successfully at the time. Until recently, T. Sasaki et al. revealed Van der Waals epitaxy-like methods to grow SrTiO$_3$, anatase TiO$_2$ and ZnO on glass or plastic substrates by an inducing seed layer. On the other hand, as monolayer 2D materials have been isolated by mechanical exfoliation, Van der Waals heterostructures now do not need to be grown in vacuum but rather by simply stacking flacks.

Stacking 2D crystals directly to form a Van der Waals heterostructures reveals an appealing idea for studying and engineering 2D materials. The idea involves regarding all 2D crystals as Lego bricks to be used for building a new artificial materials from the bottom side up. At present, the field of Van der Waals heterostructures is just starting to develop. Beginning with graphene/hBN structures, graphene are encapsulated by hBN flakes which provide much greater surface flatness than SiO$_2$. Due to the flatness, charge mobility of graphene encapsulated by hBN flakes can reach 1,000,000 cm$^2$V$^{-1}$s$^{-1}$ having the same charge mobility level as suspended graphene. Graphene/hBN heterostructures also reveals Moire’s pattern due to graphene and hBN having similar honeycomb structures with a slightly 1.8 % lattice difference. The Moire’s pattern presents a larger periodic electronic structure that generates a secondary charge neutrality point. The extra Dirac points, also like the original Dirac point, opens a gap in the DoS under the presence of a magnetic field. Those DoS interacts as
they cross each other to generate a self-replicating diagram of a charge carrier DoS pattern which is called the Hofstadter’s butterfly\textsuperscript{77,78}. 2D TMD materials (MoS\textsubscript{2}, WS\textsubscript{2})/graphene/hBN heterostructures can be an ultra-thin and flexible transparent LED or light sensor\textsuperscript{51,52,54}. This development would not be possible if conventional materials such as gold contacts or ITO glass were employed. Thus, graphene/hBN and 2D TMD materials (MoS\textsubscript{2}, WS\textsubscript{2})/graphene/hBN heterostructures are great examples to demonstrate the potential of engineering functional 2D materials as well as possible fundamental researches that can be achieved through Van der Waals heterostructure\textsuperscript{51,53,79-81}.

2-5 Hofstadter’s butterfly

In 1976, Douglas Hofstader demonstrated the energy level of Bloch electron in a uniform magnetic field\textsuperscript{82}. He modeled a 2D square crystal lattice with lattice constant ‘\(a\)’ immersed in a uniform magnetic field \(\mathbf{H}\) which is perpendicular to the 2D crystal surface. The energy dispersion is constructed from the tight-binding theory of Bloch bond by altering the operator \(\hbar \mathbf{k}\) into \(\mathbf{p} - e\mathbf{A}/c\) where A is vector potential. The effective Hamiltonian then contains the translation operator \(\exp(a \mathbf{p}_x/\hbar)\) and \(\exp(a \mathbf{p}_y/\hbar)\). In addition, selecting a Landau gauge \(-\mathbf{A} = \mathbf{H}(0,x,0)\) which limits the translation along \(y\) direction and can be multiplied by phase. Inducing this effective Hamiltonian into the time independent Schrodinger equation with 2D wave functions results in the following eigenvalue equation:

\[
E_0[\psi(x + a, y) + \psi(x - a, y) + e^{\frac{-ieHax}{\hbar c}}\psi(x, y + a) + e^{\frac{ieHax}{\hbar c}}\psi(x, y - a)] = E\psi(x, y)
\]

where the equation is now linked with four nearest neighbor atoms. Crystalline atoms are periodically located in position which allow us substitute \(x\) to \(ma\) and \(y\) to \(na\) where \(m\) and \(n\) is integer. Moreover, assuming plane wave behavior at \(y\) direction, the variable in eigenvalue equation is only \(x\). Therefore, the wave function \(\psi(x, y)\) can be expressed as \(e^{iy\beta}f(m)\) and \(\alpha\) (the ratio of magnetic flex through 2D crystal) is set as such:

\[
\alpha = \frac{Ha^2}{\hbar c} = \frac{\phi}{\phi_0}
\]
Thus the eigenvalue equation can be written as:

\[ f(m + 1) + f(m - 1) + 2 \cos(2\pi m \alpha - \gamma) f(m) = \epsilon f(m) \]

Or in matrix form:

\[
\begin{bmatrix}
  f(m + 1) \\
  f(m)
\end{bmatrix}
= \begin{bmatrix}
  \epsilon - 2 \cos(2\pi m \alpha - \gamma) & -1 \\
  1 & 0
\end{bmatrix}
\begin{bmatrix}
  f(m) \\
  f(m - 1)
\end{bmatrix}
\]

where \( \epsilon \) is defined from \( E/E_0 \). The 2x2 matrix is the translation matrices \( A(m) \) from vector \([f(m), f(m-1)]\) to \([f(m+1), f(m)]\). In this case, the matrices \( A(m) \) are constantly repeated with \( m \) periods with a condition. For a periodic function, with period \( m \), there is also another period \( q \) which should coexist with an integer \( p \) in matrices \( A(m) \), where both \( p \) and \( q \) are integer if the matrices \( A(m) \) are truly a translation matrix.

\[ 2\pi \alpha (m + q) - \gamma = 2\pi m \alpha - \gamma + 2\pi p \rightarrow \alpha = \frac{p}{q} = \frac{\phi}{\phi_0} \]

The condition on \( \alpha \) is its rationality. (\( \alpha \) also allows irrational number as Bloch and Landau states are incommensurate) Here, if we limit the energy and magnetic flex diagram in \( \emptyset = 1 \) (for currently reachable magnetic fields) and \( |\epsilon| \leq 4 \), we gain a complex spectrum shown in figure 2-8 which reveals a seemingly endless self-replicating pattern. In other words, the magnificent complex structure is caused from the competition of Bloch and Landau states. This results in a recursive structure which resembles a butterfly with a large gap in the middle. The figure is named Hofstadter’s butterfly.

The Hofstadter’s model was experimentally realized in 1996 by T. Schlosser et al. A GaAs/AlGaAs heterostructure has been made to create 2D electron gas. In the heterostructure, electrons are confined in a 2D plane with gates having 100 nm in periodicity. The experiments reveals the great details in Hofstadter’s model prediction by observing splits of Shubnikov de Haas (SdH) oscillation in the fractal energy spectrum, identifying the gaps between Landau bands or internal mini-gaps within Landau gaps and matching the prediction of Hall conductance behavior when Fermi energy passing through a Landau bands with mini-gaps. In this system, the density of charge carrier needs to fulfill each fractal sub-band. Therefore, the butterfly diagram (energy) translates to density versus magnetic field. The electron energy gaps become linear trajectories (Wannier’s diagram). The Wannier’s diagram can be described by a linear relation call Diophantine relation as following shows:

\[
\left( \frac{n}{n_0} \right) = t \left( \frac{\phi}{\phi_0} \right) + s
\]
where \( t \) and \( s \) both are integer, \((\eta/\eta_0)\) and \((\phi/\phi_0)\) are charge carrier density and magnetic flux. The quantum number \( t \) associates the quantum Hall conductance \( \sigma_{xy} \) and minigap in the fractal spectrum with relation \( \sigma_{xy}=te^2/h \). The second quantum number \( s \) is connected to the Bloch band filling index in spectrum\(^{77}\). However, due to restrictions in the ability to tune the charge carrier density, it is difficult to complete the entire spectrum using GaAs/AlGaAs heterostructure. Although, some experiments not based on solid-state systems also tried to explore the physics in Hofstadter’s butterfly but large parts of the spectrum remains unknown\(^{86,87}\).

**Figure 2-8** The Hofstadter’s butterfly spectrum has \( \varepsilon \) as x-axis and \( \phi/\phi_0 \) as y-axis. The whole unit cell is ranged in \( |\varepsilon|\leq4 \) and \( 0\leq\alpha\leq1 \). The DoS of electron split while magnetic flux changed. The splitting creates a self-replica pattern which is named Hofstadter butterfly. (Adapted from Reference 82)
In 2013, two groups (Andre Geim’s and Philip Kim’s group) independently observed Hofstadter’s butterfly spectrum on lattice aligned graphene/hBN heterostructures\textsuperscript{77,78}. Tuning the charge carrier density of graphene-based device involves simply applying a gate voltage which allows scientist to reproduce the diagram in detail rather than only observing SdH oscillations. For hexagonal lattice, the unit cell area is $\sqrt{3}a^2/2$ so after normalizing $\alpha = \frac{e\sqrt{3}Ha^2}{2}\phi/\phi_0$ and $n_0 = 2/\sqrt{3}a^2$. Despite the exciting results of first observation of Hofstadter’s butterfly diagram being a great progress for researcher, the experimental results do not having high enough resolution to express the fine structure of the butterfly. Therefore, in this thesis, we demonstrate finer structure of the Hofstadter’s butterfly spectrum based on lattice aligned hBN/graphene/hBN capacitor. The capacitance measurement only observes the static electron on two electrodes, which directly correlates with the DoS without any translation\textsuperscript{88}. For high quality devices, not only single particle behavior can be clearly observed, but also many body interactions are revealed in the magnetocapacitance spectrum.

Figure 2-9 The Hofstadter’s butterfly spectrum in energy verses magnetic flux (left) and charge carrier density verses magnetic flux. The color line indicates the different constant chemical potential. (Adapted from Reference 77 supporting information)
2-6 Future electronic application

Graphene, a novel material, opens new area of physics research in 2D electronics while also rolling out possible applications in the near future based on its amazing properties. At the time, as silicon-based technology starts to approach its physical limits such as lithography or leakage current when devices are smaller than few nanometers\textsuperscript{17}, scientists and engineers start to look for new materials for further progress. Graphene and other 2D materials seem to be possible candidates to transform the silicon-based into a carbon-based industry. After graphene can be produced in massive amount by CVD method, companies such as Intel, IBM, Samsung have focused on developing this graphene-based electronics. Graphene has high charge carrier mobility even at high carrier concentrations and is only mildly affected by chemical doping. Moreover, room temperature ballistic transportation on sub-micrometer scale can be realized in graphene\textsuperscript{89}. Such high charge carrier mobility makes graphene suitable as a great material for transistors in the THz frequency. To exceed the high carrier mobility, graphene has to be on another atomically flat substrate forming a heterostructure\textsuperscript{5} or be suspended\textsuperscript{4}. However, suspended graphene is hard for device fabrication. Thus graphene-based heterostructures provide a better alternative to realize future applications.

For logic electronics, graphene does not seem to be a suitable material as it has no electronic energy band gap. The relative on-off ratio for pure graphene-based transistor is only about 10-100 because graphene has a minimum conductivity at neutrality point that cannot be switched off. In theory, graphene can have an energy band gap through quantum confinement if graphene as narrow as a nano-ribbon (<10 nm)\textsuperscript{90,91}. The energy gap of graphene is nearly equal to the inverse of the width of graphene ribbon $\Delta E$ (eV) = 1/w (nm)$\textsuperscript{92}$. In an ideal case, pure graphene-based transistor can simply copy current silicon technology if the energy gap can be opened. However, the edge of graphene strongly affects electronic properties of graphene as the graphene ribbon gets narrower\textsuperscript{93}. At present, graphene etching is not anisotropic and terminating graphene at crystallographically defined faces such as armchair, zigzag edges. In 2008, both theory and experiment data indicate the charge carrier mobility drops from 1000 (theory)\textsuperscript{94} to 100 (experiment)\textsuperscript{95} cm$^2$V$^{-1}$s$^{-1}$ as the width of graphene ribbon is around 2 nm. Furthermore, in 2009, C. Stampfer et al. etched graphene into 40 nm ribbon and revealed that the energy gap is only about the order of 10 meV which is nearly less than one order of magnitude compare to theoretical expectation\textsuperscript{96}. The random edge of graphene nano ribbon leads to extra scattering and cancels all the advantages of graphene-based devices such as energy consumption, switching speed etc. Despite simple etching methods not working, more scientists turn their focus to fabricating graphene ribbons such as sonochemical methods, nanoscale cutting of graphene, and unzipping of carbon nanotubes. Recently, Timothy H. Vo, et al. has successfully fabricated graphene nano ribbon with less than 2 nm in width and >100 nm.
in length by chemical solution synthesis\textsuperscript{97}. The chemical synthesis ensures that graphene terminated with armchair edges and a 1.57 eV energy gap is opened. However the graphene nano ribbon is not straight or requires other branches to be stable for the entire ribbon to be straight. The length of the nano ribbon is also required to be longer for future applications.

Figure 2- 10 The cross section schematic of graphene/TMD/graphene/hBN heterostructure transistor (a), the band diagram of transistor without bias and gate voltage applied (b), and the band diagram of transistor with bias and gated applied to have on-current (c).

On the other hand, some researchers move their attention to other 2D materials to bypass the major drawback of graphene. In 2012, L. Britnell et al. demonstrate field effect transistors based on vertical graphene/hBN heterostructure\textsuperscript{98}. The heterostructure involves alternate placing of graphene and hBN on top of each other and a hBN spacer between two graphene flakes which is thinner than the bottom and top hBN (only around 3-5 atomic layers of hBN). Electron in graphene starts to tunnel through hBN spacer and creates a tunneling current when a bias voltage is applied. With this graphene/hBN heterostructure tunnelling transistor, the on-off ratio can reach $10^4$ to $10^6$. About a year later, Woo Jong Yu et al. made a MoS\textsubscript{2}/graphene\textsuperscript{80} and Thanasis Georgiou et al\textsuperscript{81} made graphene/WS\textsubscript{2}/graphene/hBN heterostructure tunnelling transistor to have a high on-off ratio devices and large current at “on” state. The idea of using TMD as a barrier is for a large on-current while still keeping a high on-off ratio. The band gap of hBN is 5.7 eV which is an insulator but WS\textsubscript{2} has indirect band gap 1.4 eV and direct band gap 2.1 eV which is a semiconductor. By applying gate and bias voltage, the Fermi level of graphene can exceeds the energy gap of TMD materials which results in conduction between two graphene flakes instead of depending on electron tunneling. For heterostructure tunnelling transistor
using hBN as spacer, the on-current at 0.2 V is 0.005 A/cm$^2$, for WS$_2$ spacer is 200 A/cm$^2$ and for MoS$_2$ spacer is near 2600 A/cm$^2$ at 0.5 V. The on-off ratio for heterostructure tunnelling transistor using MoS$_2$ spacer is $>10^3$ and WS$_2$ spacer exceeds $10^5$. With reasonable on-off ratio and tunneling current, the vertical tunnelling transistors may provide new way to realize graphene based logic electronics.

By engineering graphene and other 2D materials into a heterostructure with proper properties, other graphene-based electronics applications such as LED$^{54}$, light sensor$^{52}$, and flash memory etc$^{79}$ have begun to be developed. For example, Augustin J. Hong et al. used CVD graphene with Al$_2$O$_3$ as spacer and Ti/Al/Au contacts on top created graphene-based flash memory in 2011$^{39}$. The information stored in this memory is estimated to last for more than 10 years. The cell to cell interaction is also minimal. In 2013, Simone Bertolazzi et al. revealed the single layer MoS$_2$/graphene based flash memory (HfO$_2$ spacer) with multilayer graphene as a floating gate$^{99}$. The single layer MoS$_2$/graphene based flash memory reached in factor of $10^4$ differences for writing and erasing. Recently, Soong Sin Joo et al. realize graphene-based flash memory with graphene quantum dot which is an emerging technology for flash memory$^{100}$.

To realize the future application of graphene-based electronics, fabrication has undergone a great progress during last decade. At present, single crystalline graphene has been grown on hydrogen terminated germanium on the wafer scale$^{101}$. The single crystalline graphene membrane can be free from substrate etching and transferred to other substrates. In other words, higher quality synthesis graphene will be possible in near future. Other researchers Wei Yang et al grew graphene directly on hBN substrate using epitaxial growth in 2013$^{49}$. For future commercial graphene-based heterostructure products, even substrate transfer of different 2D materials may not be necessary. However, before these can be realized, for developing future graphene-based heterostructure applications, flake exfoliation and transfer is still the fundamental technology. Therefore, the modern techniques will be fully introduced in the following two chapters.
Chapter 3

Flake preparation & transfer

In this chapter, the method of flake preparation and transfer will be introduced in detail. To start research and future application, graphene based devices have been manually made in clean room. With modern technology such as atomic force microscope (AFM), water solvable tape, monitor camera etc, help researcher to prepare better materials, correct layering and clearer surface. It’s a fundamental in condensed material research and 2D material industry.
3-1 Mechanical exfoliation

As Geim et al\(^1\) discovered graphene by using scotch tape technique. The mechanical exfoliate is the first and easiest processes to obtain graphene flakes. Within five years, CVD method has been fully studied to create wafer size graphene on copper foil and can even be mass produced with roll to roll factory line\(^{22,25,34}\). However, the quality of the CVD graphene is not as good as exfoliated one due to contamination from copper etcher and relative smaller crystal domain\(^{102,103}\).

For example, graphene flake should be high carrier mobility (>50,000 cm\(^2\)/Vs) and low contamination\(^5\). Therefore, the mechanical exfoliation is a better option to produce high quality device.

Natural graphite has been used in all experiments to cleave on to different substrates. Different from highly ordered pyrolytic graphite (HOPG), natural graphite has large crystal domains\(^{102}\) provided larger graphene/graphite flake when exfoliated. The cleaving process has been carried out in class 100 clean room to decrease dust or other possible contaminations typical for normal environment like figure 3-1 presents. The natural graphite sometime contains small rocks or quartz crystals so it has been cleaned by repeating sticky tape cleavage to reveal metal colour face and relatively flat surface before usage. To gain larger graphene flake, the cleaved face should be large and flat without cracks and wrinkles.

![Photo image of natural graphene exfoliated on water solvable tape.](image)

**Figure 3-1** Photo image of natural graphene exfoliated on water solvable tape.
The hBN has been synthesis by Takashi Taniguchi’s group with Ni solvent and high pressure for all experiments mentioned in this thesis. The hBN exfoliation method is exactly same as graphite. The hBN crystal is much smaller and thinner than natural graphite. Therefore the cleavage of hBN has to be more careful than graphite to gain target thickness (for mono/few layer hBN or hBN substrates).

For different purposes the tape with cleaved graphite will be attached on different substrates, usually on SiO₂/Si substrate or plain Si substrate spin-coated with Poly methyl methacrylate (PMMA)/Poly methyl glutarimide (PMGI). For general purpose or wet transfer, the prepared flake would be exfoliated on SiO₂/Si substrate, which has been clean in acetone, isopropyl alcohol (IPA) ultrasonic bath for 10 minutes each and went through 10 minutes of oxygen plasma cleaning. For dry transfer, graphene would be exfoliated onto plain Si substrate cleaned in acetone, isopropyl alcohol (IPA) ultrasonic bath for 10 minutes each and spin-coated with PMMA/PMGI bilayer.

Giving an evenly press when the tape on the target substrate to increase flake contact with target surface. Peel the tape off for the final cleavage gently.
3-2 Observing Flakes

The technique of observing 2D material such as graphene or hBN has been developed. Though very convenient for visualizing otherwise invisible flakes, the technique based on the interference enhanced contrast is heavily dependent on the relative thickness of substrate layers as figure 3-2 reveals. That is why a great deal of experience is needed to distinguish different flake thickness in this technique. Fortunately, other methods such as AFM and Raman spectroscopy can provide an independent verification of the flake thickness.

Figure 3-2 The images of a graphene flake from one to six monolayers on 290 nm SiO₂ wafer with white light (a). Same graphene flake in (a) with 590 nm wavelength filter (b) and 470 nm wavelength filter (c). The number in figure (a) respects the layer number of graphene. By using filter, the contrast of flake can be increase or decrease which depends on the thickness of substrate layer.

Graphene on SiO₂/Si surface

Graphene on 290 nm and 90 nm thickness oxide layer can be easily observed using optical microscope without any colour filter, differential interference contrast (DIC) or dark field. On 90 nm thickness SiO₂ layer, graphene flake have higher contrast than on 290 nm SiO₂ layer. However due to transfer process, scratch on thinner oxide layer will induce higher chance to backgate leakage. Therefore, graphene and few layers of graphite on 290 nm thickness SiO₂ are taken as a standard contrast for all flakes hunting.

The size of graphene flakes on SiO₂ substrate can be as large as near few millimeters depending on cleavage and flatness of graphite like figure 3-3 shows.
Figure 3-3 The image of a millimeter size graphene on SiO$_2$/Si surface produced by mechanic exfoliation. The scale bar is 1 mm.
Graphene on PMMA/PMGI surface

The contrast of graphene flake under white light strongly depends on the thickness of resist layer. With a proper color filter one can increase the contrast of flake. To choose the proper color filter (from 700 ~ 400 nm wavelength), highest contrast will be used to search flakes. The reason of color to filter help contrast improvement is same as graphene on SiO₂/Si surface. The incident light is refracted between each layer (PMMA/PMGI). The contrast is fully depending on the refraction light intensity as the light adsorption of graphene is constant at constant incident light intensity. For specific color of light would be enhanced due to the phase of light is the ratio of thickness per wavelength. Therefore, we can select a color filter to gain better contrast of graphene flake when the thickness of spin-coated PMMA/PMGI is slightly different every time.

Figure 3-4 The optical image of a 200 μm size graphene on PMMA/PMGI surface produced by mechanic exfoliation. This optical image was filtered with 470 nm wavelength filter and the contrast of image is strongly increased with computer. The edge of flake has been label by the red broken line. The scale bar is 100 μm
**hBN on SiO$_2$/Si surface**

Hexagonal BN has an energy band gap large than 5 eV which is a zero opacity material. The visible light will pass through thin flake nearly without any absorption due to the energy of light (1.7 – 3 eV) is much smaller than the energy gap of hBN (5.2 eV). Therefore the optical contrast of monolayer hBN is much lower than graphene$^{105}$. Hunting few layer hBN flakes need to be prepared on 90 nm or 70 nm SiO$_2$ thickness to increase contrast (contrast is about 2.5% per layer) but still need 590 nm wavelength filter or differential interference contrast (DIC) microscope to further increase contrast or other optical information.

![Figure 3-5](image)

**Figure 3-5** The optical images of a monolayer hBN flake on 90 nm SiO$_2$ wafer. Under white light (a), 590 nm wavelength filter (b), dark field (c) and 50x objective in DIC microscope (d). The monolayer hBN flake is not visible under whiter light but slightly visible with 590 nm wavelength filter as green broken line labeled. The dark field and DIC microscope can provide more information to identify monolayer hBN flake. The scale bar in (a)-(c) are 20 µm and (d) is 40 µm.
For device fabrication, hBN provide an atomically flat surface to support graphene flake\textsuperscript{5,107}. Hunting a proper thickness (~20 nm) of hBN can be easily done even on 290 nm thickness SiO\textsubscript{2} surface without filter. Selecting the flake with light blue colour which thickness will be around 20~30 nm. In this thickness, the SiO\textsubscript{2} surface roughness will be smoothed by the thickness of hBN.

**hBN on PMMA/PMGI surface**

The monolayer hBN flake is difficult to find on resist due to the thickness variation of spin-coated PMMA/PMGI layer. The flake contrast is also strongly depended on the thickness of the resist. The thickness of resist may not locate in the range which can provide high contrast. Normally, hunting monolayer will required the use of a SiO\textsubscript{2}/Si substrate. However it is still possible to search monolayer hBN on PMMA/PMGI resist spin-coated Si substrate.

For few layers hBN flake (3-5 layers), the contrast is lower than for graphene but still visible with color filter as figure 3-6 shows. The selection of proper color filter is still based on the one which provides better contrast like graphene on resist case. The contrast of few layers hBN flake is also similar with graphene on resist under proper color filter. For capacitor spacer, thicker hBN flake (3-10 nm) can be easily observed even without filter.
Figure 3-6 The image of few layers hBN (3-5 layer) in 20x objective lens at white light (a), in 50x objective lens at 530 nm wavelength filter (b), in 100x objective lens at dark field mode (c). The few layers hBN flake is not visible under white light while flake is located on PMMA/PMGI. With color filter, the hBN flake can be visualized and with dark field mode provide more information about the edge of flake. All images have been increased with contrast by computer for better presentation on printed paper.
3-3 Wet transfer method

As 2D materials have been prepared on SiO$_2$/Si surface, wet transfer method can move flake from SiO$_2$/Si substrate to other substrate such as SiN, Quartz, BN or other surfaces. The Wet transfer method is the earliest method to transfer flakes from one substrate to another or layering flake on top of each other. The interface will contact the liquid; it was so named ‘wet transfer’. Although later dry transfer has been developed, which provides a cleaner interface, the wet transfer still has some advantages such as the possibility of larger flakes (up to millimeter in size) transfer or the transfer of a whole stack of flakes needed on a different substrates.

![Image](image.png)

**Figure 3- 7** The image of a tape window (a), and PMMA-tape windows floating on di-ionized water (DI water) surface (b).

To start transfer, first spin PMMA (3% in Anisole at 4000 rpm; thickness is about 100 nm) on substrate which already has flakes to be transferred. Then the baking of the substrate follows on a hot plate at 130°C for 5 minutes. Second, place tape window (a piece of tape with a 1x1 mm$^2$ hole) on the substrate aiming the center of the hole to the flake selected for transfer. Third, scratch out skirt of the tape to disconnect PMMA with the part prepared for transfer shown in figure 3-8 (d). Prepare 3 % (w/w) potassium hydroxide (KOH) solution for etching SiO$_2$ layer. Leave the substrate in KOH solution for 6 hours at room temperature. The SiO$_2$ will be etched by KOH solution and makes the tape window attached to PMMA to lift off on the solution. Finally, leave the PMMA-tape window pairs floating on the surface of fresh de-ion water (DI water) for cleaning the residue of KOH for 2 hours.
Figure 3-8 Schematics of wet transfer processes. First exfoliate and find graphene flake on SiO2/Si surface (a). Spin coating a layer of PMMA (A3) on substrate and bake the substrate at 130°C for 5 min (b). Place tape window on transferring graphene flake (c). Scratch the PMMA following the outskirt of the tape window (d). Dive whole substrate into 3% (w/w) KOH solution for 6 hours at room temperature (e). Transfer floated PMMA-tape window onto fresh DI water for 2 hours (f).
3-4 Dry transfer method

As the last section reveals, dry transfer provided a cleaner interface for 2D material layering. The wet transfer assumes that the flake was in direct contact with KOH and DI water. On the contrary, the dry transfer can be done without any solvent contacting the interface of flake. The interface is freshly exfoliated from low residue tape then directly transfers on the target. By reducing source of contamination, the graphene flake with dry transfer produces higher carrier mobility and less chemical doping\textsuperscript{108}.

Dry transfer is very different from the wet transfer. The flake exfoliated on the PMMA/PMGI bilayer spun onto a plain Si substrate (each layer backed at 130 °C for 5 minutes). Different concentration of the PMMA will change the strength of the membrane due to the thickness of membrane varying. Here, 8% (w/w) PMMA has been used to provide a stronger support (compare to 2% or 3% for normal electron beam lithography) during fishing and drying the membrane. After flake hunting, scratch resist layer around the flake going to transfer. The scratch follows the edge of the view field at 5x objective lens (about 2.5 mm in diameter). The cutting must done through the bi-layer resist and complete the circle without any PMMA connection. Using metallic tweezers to hold a droplet of Microposit MF 319 developer (MF319) solution and drop the solution on the scratching edge. The PMGI layer will be dissolve by MF 319 then the upper PMMA layer and flake will float on MF 319 liquid surface.

As the membrane completely floats on MF 319 surface, dip the substrate in DI water with a shallow angle. The membrane should slip onto DI water ready for fishing. To fish the floating membrane, tape window, metallic washer or tape window plus metallic washer has been used for carrying the membrane. Tape window has an advantage of good handling the membrane, but also has a major drawback that the tape is too flexible, which may damage membrane fixed on a holder. On the contrary, metallic washer is hard to handle especially during drying the residue water at the window area and has to handle it very carefully. Combination of the tape window and metallic washer provides a good holding place for handling, easy to dry water with clean room wiper and a firm structure without shape change if any stress is applied. The metallic washer should dip in PMMA and baked dry on a hotplate to increase adhesion between washer and membrane. Pick up the membrane from the water surface with the tape window, washer or combination of both keeping the membrane in the centre of the hole of the tape window or washer.
Figure 3-9 Schematics of dry transfer processes. Spin coat PMMA/PMGI on plain Si wafer and bake at 130 °C for 5 min each layer (a). Exfoliate and hunt graphene flake on bi-layer resist surface (b). Scratch a circle on the bi-layer resist surface (about 2.5 mm in diameter) around the transferring flake and carefully add MF 319 droplets at the edge of scratched circle (c). The PMMA layer and transferring flake floats on MF 319 solution after PMGI layer is fully dissolved by MF 319 (d). Slip the Graphene/PMMA membrane onto DI water and fish the membrane out by tape window, washer or the combination of both of them (e).
3-5 Flake transfer

In this section the transfer instrument and processes will be described. To transfer the flake as precisely as possible, the flake transfer has been manipulated under microscope with micro-positioning instrument. Before the particular transfer equipment has been built, mask aligner had been used for precise transfer. The mask aligner is designed for pattern exposure of optical resist by UV light and pattern mask. To align the substrate with the mask, the mask aligner has microscope and micro-positioning stage which also fits the basic requirements for the flake transfer. The requirements are able to observe the transfer flake/substrate under microscope and manipulate xyz axis motion in micrometer precision. Therefore, the MJB4 mask aligner has been used as transfer instrument before the homemade transferor machine was built. However, some minor modifications had been made on this standard mask aligner for flake transferring. In our case the substrate chuck was placed with a small copper heater stage, and a simple adapter was made to attach a washer or tape window to the mask holder. Despite the improvements, there still have some main drawbacks of using mask aligner as a transfer machine. For a mask aligner, the stage should not be contacts with mask. Therefore, for the needs of transfer the copper stage is supported by two glass slides. In this case, the copper stage not only isn’t fully flat, but also the extra wire for stage heating also move stage position as operator touch the wire.

To start flake transfer processes, place washer or tape window on sample adapter. The sample adapter has two strips of double side tape for holding washer or tape window position during transfer. As the membrane placed on the adapter, put the adapter on mask holder which provides vacuum to hold it at facing down position. Leave target substrate on the substrate chuck and warm the copper stage. The substrate is distant with membrane around few centimeters after the mask holder has place in the track. Lift the stage to several hundred micrometers, start to align flake and target substrate. Changing focus level of microscope to observe flake position and then manipulating target substrate for adjustment by x-y axis micro-positioning stage. As flake aligned with target, lifting z axis micro-positioning stage and keeping the position alignment. Depending on the flatness of the membrane, the approaching distance is varying from each transfer. Therefore, always keep the alignment in the correct position is critical. When membrane contacts with substrate, the stage adjust will be rough to manipulate. Use a sharp scratcher to tick the corner of the membrane which helps PMMA membrane attach with substrate faster. Rise the substrate temperature also helps PMMA membrane attachment. Scratch PMMA membrane around the hole of washer or window. Finally lower the stage to separate the un-cut membrane and substrate.
Figure 3-10 The photograph and description of MJB4 musk aligner for flake transfer.

Figure 3-11 The photograph and description of the home made transfer instrument.
The home made flake transfer instrument combines together a commercial microscope (Nikon Eclipse LV100) and two micro-positioning stages together. The transfer instrument improves drawbacks of using mask aligner for flake transfer such as more firm structure of the substrate stage, better visibility provided by the commercial microscope and computer. For transfer instrument, the heating stage is firmly fixed on the table and the sample is held by the vacuum. The heater power supply is controlled by the LabView PID controller, which ensures the stage temperature stable with 0.1 °C. The commercial microscope provides a more flexible choice to use filters and different objective lenses. Moreover, the computer offers better teaching and learning opportunity for user. The trainer and operator can observe the transfer action at the same time. The computer also helps the operator to judge the flake position and alignment by screen drawing. After the transfer instrument has been built, the precise flake transfer (position error <2 μm) becomes easier and more users can do precise transfer with less training time.

Figure 3-12 Schematics of transfer processes. Aligning and approaching (a), membrane contact and cutting (b) and separation (c).

The transfer processes using the home made transfer instrument are very similar to MJB4. Start from placing double side tape on washer/ tape window holder and fix wash/ tape window on it. Put the target substrate on stage then turn on vacuum to hold the substrate. Match the washer/ tape window holder on 3 axis (xyz) adjustment stage then turn on vacuum to hold the holder. Roughly align the flake and target substrate first and then lower the membrane (equal to lifting the target substrate in MJB4) until the distance between them is about 1 mm. Drawing shape of the flake and the flake near it then check position in the computer (or using small tapes marked on monitor in MJB4) and alignment are correct against the target. Keep the image position of the flake in the screen drawing by using xy adjustment in 3 axis adjustment stage when lowering the membrane. As the membrane contacts the substrate the xy adjustment will be difficult to manipulate. Use a sharp scratcher to contact the corner of the membrane to help the membrane to come in full contact with the target substrate. Cut the
edge of the membrane from the washer/tape window to finish the flake transfer. Finally lift the holder to separate membrane and substrate.

3-6 Stamp (peel off) method and flakes picking

The stamp (peel off) method is still follow normal transfer procedure but differs at the last step. Normally, to release the transferred flake the PMMA membrane is cut off from the washer/tape window and dissolved in acetone. In the stamp method the PMMA membrane is peeled off from the target substrate. The transfer flake and target flake will stick together because of the strong interface adhesion (Van der Waals force), and it is stronger than the adhesion between the transferred flake and PMMA. Therefore, the transfer flake can stay on top of target flake. However, the adhesion between target flake and substrate sometime is not sufficient, and in some cases the transferred flake picks up the target flake on PMMA membrane, and becomes the techniques of flakes picking. In other cases, the peeling processes apply too much tension and cause the transfer flake to scroll at the edge or break.

![Schematic of transfer processes with stamp method](image)

**Figure 3-13** Schematics of transfer processes with stamp method. Aligning and approaching (a), membrane contact (b) and separation (c).

The flake on the PMMA membrane is essential to create heterostructure without any solvent during flake layering. To increase the efficiency of picking, the target flake should be made on a PMGI coated substrate (gives poorer adhesion between target flake and PMGI). In this method, the heterostructure can be assembled on one PMMA membrane which decreases the time of fabrication but still has some limitations. The flake picking can only be done in atomic flat flakes and the dimension of two flakes cannot be different too much (less than 1.5 times). If
the flatness is poor or the surface affinity to water such as mica is a hydrophilic material, which adsorb water molecule on surface the flake cannot be picked up\textsuperscript{109}. The surface adhesion force will be screened by those un-even surfaces or the water molecule interlayer. Furthermore, the dimension difference of the flakes is also important. For example, a 10 x10 µm flake on PMMA cannot pick up a 5 x20 µm flake on substrate. The bottom flake will break, usually at the edge of top flake, during the flake picking. In this case, the bottom flake stay partially on the top flake, and become the flake of 5x10 um in size.

\textbf{Figure 3-14} Images of stamp processes (a)-(h), the scale bars are 20 µm for (a)-(g) and 200 µm for (h). graphene flake on PMMA membrane which marked with red line (a). Aiming the wanted MoS\textsubscript{2} flake on PMGI coated Si substrate. The PMGI coated substrate provides poor adhesion to MoS\textsubscript{2} for better lift off (b). Membrane approaching (c), contact (d), picking up the bottom MoS\textsubscript{2} on membrane (e). Aiming the target substrate (f), contact with target substrate (here is hBN) (g), release flakes on hBN substrate by scribing the membrane (h). All images have been increased with contrast by computer for better presentation on printed paper.
The advantage of stamp method is not only the fast device fabrication, but also better device quality. With less PMMA residue and solvent cleaning, the quantity of bubbles can be reduced and creates some area which is completely flat. For example, the mobility of graphene flake transfer on hBN with stamp method can achieve $1 \times 10^6 \text{ cm}^2/\text{Vs}$. In normal dry transfer graphene on hBN flake, the mobility is only around $1 \times 10^5 \text{ cm}^2/\text{Vs}$. The reason of bubble formation is an important issue of fabricating 2D heterostructure by Lego method. Further detail has been discussed in this thesis at chapter 5 and published in journal$^{35,109}$. 
Chapter 4

Device Fabrication Method

In this chapter, the fabrication and characterization of two major graphene based devices (capacitor and tunneling transistor) will be introduced. Based on the techniques which have been revealed in chapter 3, the 2D heterostructure assembling is possible. On this foundation, proper flake selection, alignment, annealing, lithography and contact deposition are also important for device fabrication. For different purposes, different procedures will be used with different considerations.
4-1 Flake selection and arrangement

To investigate the physics of 2D materials and its electronic properties, the graphene based heterostructures have been made. For characterization, high quality devices are needed where the quality of the flakes and interface cleanness is crucial. In our experiment, the high quality graphene and hBN flake has been made by mechanic exfoliation method. The flake transfers were done with normal dry transfer procedures.

In this section, the flake selection and arrangement will be discussed. Unlike CVD synthesized graphene, mechanically exfoliated graphene flake has its unique shape that is arbitrate decided during exfoliation. The hBN crystal is synthesized but is limited by its thickness and size. For proper thicknesses of the hBN flake, exfoliation is also used and the shape of flake is arbitrary as well. Therefore, flake choosing and arrangement is the first step of device fabrication. Planning the flake’s arrangement not only increases the chance of producing high quality device by reducing processes, but also improve quality of device fabrication by reducing flake etching or extra transfer and cleaning.

As the flake has been cleaved, several types of flake shape can be classified. At first, whether the flake is isolated or non-isolated is of importance. An isolated flake without any thicker flake attached is easier to use than a non-isolated one. In some cases, the non-isolated flake is can still be used but it needs more planning for flake arrangement. Beside the flake isolation, the shape of flake can be classified into fine stripe (width < 5 μm and length >> width), stripe (width > 5 μm and length >> width), small flake (length ~ width; width and length < 30 μm) and large flake (length ~ width; width and length > 30 μm). By distinguishing types of flake, it allows us to plan flake layering before device fabrication and select proper shape of flakes for assembling 2D heterostructures.

The fault and uneven area also need to be taken into consideration. By using dark field and DIC function in optical microscope, these can easily detected. For a graphene flake having a fault may result in having no contacts on both sides. For a hBN flake, having a fault may result in an unstable measurement when used it as a substrate or current leakage when employed as a spacer. The uneven area will not affect measurement as the uneven area is not situated at the core of the device which comprises the gating site of the capacitor and the tunneling section of the tunneling transistor. However, in practice, the uneven flake will not be used for device making because the un-even area is difficult to be observed when under the transferring instrument and it decreases the error of margin during fabrication.
Figure 4-1 The images of a graphene with different shapes on PMMA/PMGI coated Si substrate (a)-(d). A fine stripe graphene is one micrometer in width and 50 μm long under 530 nm wavelength filter (a). A stripe graphene is about 10 mm in width and large than 70 mm long under 470 nm wavelength filter (b). A large graphene flake is large than 50 mm in both dimensions under 470 nm wavelength filter (c). A non-isolated flake connects with flakes thicker than one layer under 590 nm wavelength filter (d).
4-2 Align the edge of flake

To study Hofstadter states and their replicas together with quantum Hall ferromagnetism and resonance tunneling, the transfer flake needs to be aligned with the target flake to match the lattice structures. Two flakes with long edges are suitable for fabrication of this kind of device. With longer edges the alignment will be more accurate. However, atomic lattice structure cannot be observed by optical microscope. Distinguishing zigzag from armchair edges is impossible without the help of STM or Raman\textsuperscript{110}. Therefore, in the early stage of our experiments large amounts of edge aligned device are fabricated to obtain a few lattice matched device.

![Graphene Lattice with Armchair and Zigzag Edge](image)

**Figure 4-2** The schematic of graphene lattice with armchair and zigzag edge.
To align the edge of a flake, the washer/tape window holder (for MJB4 mask aligner) or substrate stage (for home made transfer instrument) can be rotated to match the line of edge. With naked eye and assistance from the computer, the error of misalignment is less than 2 degrees. However, aligning the edge of a flake is aligned doesn’t guarantee that the lattice is also aligned. The long edge of both flakes can be zigzag or armchair. In some cases the angle of two edges (same flake) isn’t 30° or 60°, which decrease the chance of lattice alignment. Therefore, only the long edge which has a 30° angle (or integral proportional to 30°) with another edge will be used for alignment as figure 4-3 shows.

**Figure 4-3** The image of hBN flake (thickness is about 30 nm) on quartz substrate with edge angled at 150° and 60°. These edges not only provide a straight line for flake alignment, but also guarantee the edges are its crystalline edges (armchair or zigzag for red broken line in figure) due to the angle between them. The green scale bar is 25 μm.
4-3 H$_2$/Ar annealing

The 2D heterostructure during fabrication has been annealed in H$_2$/Ar (H$_2$:Ar = 10:90) environment after each flake transfer. The H$_2$/Ar annealing improves the flake interface cleanliness$^{36,111,112}$. The high temperature hydrogen argon environment can remove hydrocarbon and PMMA residue. For 2D heterostructure, the interface decides the quality of the device and also affects the performed measurements$^{35}$. Therefore, after each flake transfer, the heterostructure has to be annealed if the substrate can endure the H$_2$/Ar annealing environment.

![Temperature vs. Time Diagram](image)

Figure 4-4 The diagram of temperature against time for H$_2$/Ar (H$_2$:Ar = 10:90) annealing.

In this section, the annealing details in our experiment will be discussed. After the flake is transferred onto the substrate, the PMMA membrane is removed by warm acetone (60 °C). Although, the PMMA membrane has been removed, several nanometers of PMMA residue can still remain on the transferred flake surface. For higher quality devices, further cleaning is needed. Thus, in our experiments the heterostructure will be annealed in H$_2$/Ar environment at 300 °C. The whole annealing procedure is done in a commercial furnace. The sample will be placed in a quartz boat at the center of the furnace tube while H$_2$/Ar gas purging is carried out.
for 10 minutes. At the same time, the lid and the connection is checked for gas leakage and then heating begins once the purge is done. The heating rate is 10 °C per minute and remains at step temperature for 1 hour for it to stabilize. Two step temperatures, 100°C and 200°C are used in this process. The target temperature is 300 °C and maintained for 3 hours. Three hours later, power supply of the heater is turned off and the furnace allows cooling naturally. During the process, the H₂/Ar gas flow should be adjusted by gas valve to be within 0.6 sccm.

4-4 Optical lithography

After the 2D heterostructures are stacked, lithography is needed to pattern the area for contacts or for preventing electrical shorting. The basic idea of optical lithography is to cover sample with a layer of optical resist. Following which it is patterned with optical light on the resist and resultant product is developed, only the part of resist which is exposed to optical light will be lost (with negative resist) or remained (with positive resist). With this pattern, the electric contacts or mesa can be done precisely.

Optical lithography is convenient and faster than electron-beam (e-beam) lithography for patterning a sub millimeter size device. However, optical lithography has two major drawbacks, the optical resist residue and accuracy. Base on the reason, our major experiment is done by e-beam lithography. Optical lithography is only for test samples or materials that cannot be treated by e-beam.

The optical lithography has to be performed in a yellow room to avoid exposure from white light.

Preparation

Before optical lithography begins, photo resists are first spin coated on top of the substrate (with 2D heterostructure). Here, bi-layer resist (S1805/PMGI) has been used. The S1805 (From Microposit Company) is a negative resist which is sensitive to UV and near-UV light exposure. The PMGI is only sensitive to UV light but the developer (MF319 also from Microposit Company) for S1805 resist can fully dissolve it. The PMGI later is sandwiched by substrate and S1805 to thicken the resist for better lift off after metal deposition processes or to avoid the hardened resist from attaching after mesa processes.
To dehydrate the substrate, improve the adhesion between PMGI and substrate, prebaking the substrate at 170 °C for 10 minutes. Spin coating of PMGI on the substrate is done at 4000 rpm for 1 minute (the layer thickness is around 1.5 µm) and the substrate is backed at 170 °C for 5 minutes. The substrate is then cooled in air for 1 minute before spin coating another layer of resist S1805 on it at 4000 rpm for 1 minute. Finally the substrate is backed at 110 °C for 1 minute.

Table 4-1 The spin coating and baking parameters of bi-layer photo resists.

<table>
<thead>
<tr>
<th>Resists</th>
<th>Revolution (rpm)</th>
<th>Time (min)</th>
<th>Baking time and temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMGI</td>
<td>4000</td>
<td>1</td>
<td>170 °C for 5 minutes</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(prebaking for 10 minutes before putting PR on)</td>
</tr>
<tr>
<td>S1805</td>
<td>4000</td>
<td>1</td>
<td>110 °C for 1 minute</td>
</tr>
</tbody>
</table>

**Exposure and development**

By using laser writer, the exposure for every specific device can be done. Compared with the traditional optical lithography which is done by mask aligner, laser writer has greater freedom to change specific designs to fit the needs of experiment. Contacts or etch masks are first designed using the software and the laser writer then exposes the areas according to the design.

A 405 nm wavelength GaN semiconductor laser has been used for exposure light and limits the resolution around half micrometer due to diffraction limit of laser wavelength. The exposure dosage is controlled by computer with a filter to modify the intensity of the laser power. Laser beam is focused though the objective lens onto substrate. Stage holding the substrate then moves line by line according to the pattern designed and the desired shapes will be exposed to the laser beam.
After exposure, the sample is developed in MF319 for 1 minute (in sonic bath at the first 10 seconds and the last 10 seconds) and then cleaned in DI water for 2 minutes.

![Figure 4-5](image)

**Figure 4-5** Schematic of laser writer patterning (a) and photograph of laser writer (b).

### 4-5 Electron beam lithography

E-beam lithography provides an accurate and cleaner method to pattern a device. With smaller diffraction limit, the lithography resolution can be improved to around 50 nm (3% 950 kDa PMMA in anisole and using EVO electron lithography microscope). E-beam lithography uses different PMMA molecular weight to create undercut and provides the thickness for better lift off after metal deposition. Therefore, the lift off processes only needs acetone and IPA unlike optical lithography which needs MF319 (MF319 will damage graphene by scrolling flake in 2 minutes) to clean the PMGI resist.

Using scanning electron microscope (SEM) for e-beam lithography, one has to expose position crosses or marks near the 2D heterostructure. The position crosses are required to locate the 2D heterostructure position because the e-beam cannot observe the flake without exposing PMMA resist. Unlike optical lithography, the flakes image can be observed and located by longer wavelength light without exposure. By using position crosses, the total design shift and distortion can be minimized. The closer and smaller position crosses provide high accuracy but are still limited by optical resolution due to usage of an optical image to design devices.
Although the e-beam lithography takes a longer training time and is a more complex procedure, the higher accuracy and better cleanness provided is essential for the experiments. Therefore, in this thesis, all measured devices are made by e-beam lithography.

**Preparation**

Generally, two kinds of PMMA (950 kDa and 495 kDa) will be used for normal purposes. For thicker (>40 nm) metal deposition, bi-layer PMMA (950/495) resist will be used to create undercut to provide better lift off. Under the same e-beam dosage exposure, the PMMA with 495 kDa molecular weight has a large effective dosage than PMMA with 950 kDa. During development the PMMA with 495 kDa has a larger area dissolved, creating an undercut. For thin metal deposition or plasma etch mask, single layer 950 kDa PMMA is enough.

The PMMA resist is spin-coated onto substrate with 3000 rpm. For 3% 950 kDa PMMA in anisole, the thickness is around 100 nm and for 3% 495 kDa PMMA in anisole, the thickness is also around 100 nm. The substrate is baked at 150 °C for 5 minutes to soften and flatten the resist.

For quartz substrate, the extra conductive layer is needed to avoid surface charging. In earlier devices, 5 nm thickness of gold will be deposited on PMMA coated substrates for conduction. Later on, Aqua Save (ingredients: 2−Phosphono−1,2,4−butane tricarboxylic acid, Tolyltriazole and Benzotriazole), a conductive liquid, can be spin coated onto the substrate before baking dry on a hotplate at 110°C.

**Exposure and development**

E-beam lithography uses SEM to observe and pattern on sample. The electron is emitted from a high potential voltage gun (for normal exposure, it is about 10 kV). The electron beam is controlled by electromagnetic lens to manipulate electrons like light. As electron arrives on the sample, it creates secondary electrons which can be detected by sensors and transformed into an image to be observed by the user. The exposure and observation is carried out in a main chamber at a pressure around 10^{-6} mbar to lower atmospheric contamination and improve the signals of the secondary electrons.

To create a pattern on the sample, the pattern generator translates our design into signals to manipulate the projection lens. The electromagnetic projection lens controls the electron beam to form certain patterns and scans the sample surface accordingly. Unlike optical lithography, the xyz piezo-stage holds its position during exposure only electron beam is moving. The idea of
beam scanning indicates the existence of a writing field. The writing field is the area in which one can do lithography because during the exposure the zoom lenses are fixed in one magnification (40x, 200x...etc). The writing field also defines the resolution that can be achieved.

After exposure, Aqua Save is washed off with water or the thin gold film is etched with a potassium indium (gold etcher). The sample is left in the developer (3:1 IPA:MIBK) for 45 second before being transferred to IPA for 1 min to stop the developing process. Finally, N₂ gas is used to dry the sample.

![Figure 4-6 Schematic of e-beam microscope with lithography unit.](image)
4-6 Deposition, flake etching and lift off

In this section, methods of metal deposition and mesa will be discussed in detail. Metal deposition is made by thermal evaporator or e-beam evaporator. For the purpose of electric contacts, metal mask or thin conducting layer, metal deposition should be flat and even. To make electrical contacts, Cr/Au or Ti/Au will be used. Several nanometers thickness of Chromium or Titanium is used to improve the adhesion between the gold and substrate surface. The thickness of metal film, normally from 40 nm to 100 nm depends on the heterostructure.

The metal mask involves Al deposition on BN surface to protect the device from damage during the etching processes. The thin Al layer deposited becomes Aluminum oxide which is very stable with an extremely slow etching rate. However, the hard mask only can be made with e-beam lithography because the developer (MF319) for optical lithography will lift off the Al thin film.

The thin conducting layer is for quartz substrate for electron conduction in lithography processes. A 5 nm gold film is deposited on PMMA coated quartz substrate by thermal evaporator. To avoid unnecessary electron exposes PMMA resist, the e-beam evaporator will not be used for the thin conducting layer on PMMA. After lithography, the thin conducting layer will be removed before development by using a gold etcher. The coated substrate is placed in gold etcher for 1 min and cleaned in DI water for 2 min.

Two types of flake etching can be distinguished in our experiment. Oxygen plasma etching is used to clean flakes which might cause shorting. Hard etching (using CF$_4$/C$_3$F$_8$...etc gases with higher plasma power) is used to shape heterostructure devices which can etch through layers of BN. The oxygen plasma etching uses resists to protect the area that don’t need etch and hard etching uses Al hard mask to avoid damaging the devices.

Thermal evaporator

The thermal evaporator is a vacuum chamber with an electrical powered filament boats to heat up the metal source and deposit metal onto the target substrate. The metal source is placed in the Ta filament boat which is powered by a power supply to control the current through the filament. The metal and filament will be heated up as current is applied. The metal source melts and evaporates into high vacuum (~10$^{-6}$ mbar). The target substrate is placed directly on top of the filament. The metal vapor deposits onto the target substrate with a rate of a few angstroms per second. Once evaporation rate is stable, the shutter is released to allow deposition.
The film thickness is estimated by a quartz crystal sensor which oscillates at a high frequency (6 MHz) which decreases as metal is deposited on it. The parameter has been calibrated by actual film thicknesses measured by a thickness profilometer.

**E-beam evaporator**

The e-beam evaporator uses high voltage electron beams to create metal vapor for metal deposition. The metal sources are stored in a tungsten crucible and bombarded by magnetic-guided electron. The electron is accelerated in an electron gun at 10 kV. The metal source will be heated up as the electron-beam hits and gets vaporized into high vacuum (<2x10^{-6} mbar). The target substrate is also placed directly on top of the boat. The metal vapor deposits on the target substrate at a rate of a few angstrom per second. Once evaporation rate is stable, the shutter is open to start deposition.

Compared to the thermal evaporator, the e-beam evaporator is more convenient and has a cleaner background pressure. With lower background pressure, the metal molecular has less chance to hit or contact with other gas molecules. The gas molecule mean free path in 10^{-6} mbar is around 10^2 m which means a molecule needs on average to travel a 100 meters to encounter another gas particle. The crucible distance to target substrate is about 50 cm. Therefore, the chance of metal vapor contacts with other contamination is low. Most of the metal particles will be directly deposited on the target substrate. To keep background pressure low, the e-beam evaporator has a loading chamber. Sample can be loaded from the loading chamber without opening the main chamber. The loading chamber will be pumped to 10^{-6} mbar before transferring the sample to the main chamber for deposition.

**Metal film lift off**

After metal deposition, the substrate is covered by a layer of metal film. The metal film on top of the resist needs to be lifted off, leaving behind those on the exposed areas. The idea is dissolve the resist to lift the thin metal film off the substrate surface. However in some situations, it is difficult to lift off the metal film due to inadequate thickness of resist or film. Few seconds of ultra-sonic bath in acetone will help lift it off but it involves a certain chance to damage the flakes.
For optical lithography, the coated substrate is placed in acetone for 10 min and then blown with a pipette. The substrate is transferred to MF319 for 1 min to clean the PMGI, followed by DI water cleaning for 3 min. Finally, the substrate is left in IPA for 5 min and then dried it with N₂ gas.

The e-beam lithography uses only PMMA so only acetone is needed for lift off. The PMMA coated sample is placed into warm acetone (~70 °C) for 10 min and then blown with a pipette. As the metal film is clean, move the substrate to another clean acetone for another 10 min. The substrate is transferred in to IPA for 5 min to clean the acetone residue before drying it with N₂ gas.

**Oxygen plasma etching**

Oxygen plasma etching uses the same instrument that is used in SiO₂ or quartz substrates cleaning at the beginning of flake fabrication. The oxygen plasma not only can remove organic compounds but also can remove graphene and graphite. With resist’s protection, the recommended etching time for single layer resist is 90 sec, for bi-layer resist is 150 sec. The etching rate for resist is faster than that of graphite, so in 150 sec etching only can remove around 10 layers of graphene. Longer etching time indicates thinner resist thickness and the harden resist will be more difficult to remove.

**Hard etching**

To shape the heterostructure, thicker flakes needs to be fully removed by more powerful plasma etcher and reactive gas. The heterostructure made by flake picking method, is usually encapsulated by layers of graphene and hBN. The shape of device is not suitable for transport measurement so knowing how to shape the stack of flakes into Hall crosses is important. HBN flakes thicker than 3 layers cannot be removed by the oxygen plasma etcher that is commonly used for surface cleaning. Therefore, one has to use a more powerful plasma etcher and reactive gases to decompose flakes. However the resist cannot protect the area which does not need etching. Therefore, the Al hard mask has been used to prevent unnecessary etching. The etching rate for hBN is about 14 nm per minute.
**Harden resist remove and cleaning**

After etching, the resist surface will form a layer of harden resist which cannot dissolve in solvent and will heavily dope graphene as the hardened resist attaches onto devices. To avoid further contamination, the etched sample will be placed in an ultra-sonic bath acetone to break the harden resist for 30 sec. For optical lithography, the substrate is transferred to MF319 for 1 min to clean the PMGI followed by DI water cleaning for 3 min. Finally, leaving the substrate in IPA for 5 min and then dry it with N₂ gas. For e-beam lithography, we leave the substrate in another acetone for 10 min, then in IPA for 3 min and then dry it with N₂ gas.

To remove hard mask, the sample is placed into MF319 for 1 min. It is then cleaned with DI water for 2 min, followed by IPA for 3 min and finally dried with N₂ gas.
Chapter 5

Electronic Properties of Graphene Encapsulated with Different Two-Dimensional Atomic Crystals

Since the discovery of graphene, 2D materials have attracted people’s attention to their electronic properties. By layering different 2D materials, the 2D heterostructures starts a new cutting edge in condense matter. However, as graphene attach with other 2D materials, the electronic properties will be changed by surface properties by those 2D materials. In this chapter, the encapsulated graphene devices have been made on different 2D material surfaces and examined its electronic properties, to investigate how surface properties changes the electronic properties of graphene and also provides a reference for future applications. In this chapter, the fabrication of devices and measurement data are only based on my work. The
contribution of following paper is also on graphene/2D oxide materials and LiNbO₃ devices fabrication.

5-1 Device fabrication

The rise of 2D heterostructures is fully based on transferring flakes on different 2D materials. Aiming higher quality and unique electronic properties, different categories of 2D material have been tested. In this chapter, two 2D TMDs (MoS₂, WS₂), three 2D oxide (BSCCO, mica, V₂O₅) materials and LiNbO₃ published wafer have been examined as a substrate for graphene. Here, in this section, only bismuth strontium calcium copper oxide (BSCCO), mica and LiNbO₃ will be introduced.

Figure 5-1 The image of graphene-based capacitor on LiNbO₃ substrate (a). The Schematic of the hBN/graphene/LiNbO₃ substrate capacitor. The capacitance was measured between graphene and top gold electrode by Andeen-Hagerling AH2550A capacitance bridge.

Start with LiNbO₃ published wafer, the contrast of graphene flake on LiNbO₃ wafer is poor even with the color filters. Therefore, graphene flake is exfoliated on PMMA/PMGI spin-coated Si substrate and dry transferred onto LiNbO₃ wafer. The flake peeling method cannot be applied on LiNbO₃ wafer because poor adhesion between graphene and wafer. Thus, the transferred membrane has been scribed on wafer then cleaned in warm acetone for 10 min. After PMMA
membrane has been clean by acetone, the sample in transferred to IPA for 5 min then dried with N₂ gas.

To clean the PMMA residue from transferring process, anneal sample in H₂/Ar environment at 275 °C for 3 hours. Place a 10 nm thickness hBN flake on graphene by dry transfer method after annealing process is done. The hBN flakes should only partly cover graphene for electric contacts and the cover area is larger than 50 μm². Finally, patterning electrodes by e-beam lithography system on PMMA coated sample then deposited 4/40 nm in thickness of Cr/Au for electrodes. Figure 5-1 revealed the completed graphene/LiNbO₃ capacitor device.

![Diagram](image)

**Figure 5-2** The Schematic of the hBN/graphene/2D oxide substrate capacitor on quartz wafer. The capacitance was measured between graphene and top gold electrode by Andeen-Hagerling AH2550A capacitance bridge. The bias voltage was provided between two electrodes on graphene flake.
BSCCO and mica are a hydrophilic surface which adsorbing water molecule in atmosphere. The graphene transfer must be processing as soon as possible after the 2D oxide material has been exfoliated on quartz wafer. Figure 5-2 shows the schematic of encapsulated graphene capacitor on different 2D oxide materials. In this case, the PMMA membranes with graphene flake were prepared before BSCCO or mica substrate was attached on wafer. Mica and BSCCO will be exfoliated and hunted when PMMA membrane already floats on water or on washer/tape window holder. The searching and transferring time is controlled in 5 minutes to finish entire processes. The flake peeling method is also not suitable for these two substrates due to poor adhesion again. Ideally, mica /BSCCO flakes should be an atomically flat surface like hBN providing good adhesion to graphene. However the few layer of water strongly screens the Van der Waals force between graphene and substrate which causes the poor adhesion. Interestingly, the interface of graphene and these two substrates do not create bubbles in it. In contrast, there is always a bubble formation at the interface while graphene on hBN or graphene on 2D TMD flakes vise versa. Despite no bubble formation between graphene and mica/BSCCO substrates, mica/BSCCO substrates would form bubbles at the interface with SiO₂.
and quartz wafer. This kind of bubble has blue color and increases with time while exposes the sample to atmosphere.

Figure 5-4 The image of graphene graphene-based capacitor on mica substrate. Some bubbles are formed at the interface of graphene and hBN layer. Some blue color bubbles also can be observed at the edge of mica substrate. Those blue color bubbles are located at the interface of mica flake and quartz wafer. To keep the homogeneity of the electric field from top electrode, the top electrodes have shaped according to the position of bubbles.

To avoid further water molecule adsorption on surface, the samples were always covered by PMMA for storage. The PMMA covers were cleaned by warm acetone and processes as soon as possible before anneal or transfer procedure started. The BSCCO sample did not process anneal procedure due to BSCCO may be thermal decomposed or structure reformatted in furnace. The pattern designs have to avoid those bubbles and creaks (inhomogeneity) on devices. Therefore, the top electrodes become irregular shapes. Patterning of electrodes was also done by e-beam lithography then deposit Cr/Au on top. The thickness of Cr/Au film depends on the thickness of flakes have been used, usually around 60 to 90 nm. After the metal is deposited, lifting off the
metal film in warm acetone for 10 min and transfer to flash acetone for another 10 min then IPA for 5 min. Finally dry in N₂ gas and bind on chip carrier for characterization. Figure 5-3 and figure 5-4 revealed the completed hBN/graphene/BSCCO and hBN/graphene/mica capacitor devices.

5-2 Characterization

To characterize the electronic properties and the device quality of graphene capacitor on different substrates, the commercial capacitance bridge has been used to measure the change of capacitance depends on bias voltage. The measurement has been hold in cryostat at 2 K and can vary the magnetic field from zero to 17 T.

The capacitance includes the geometry capacitance and quantum capacitance. The geometry capacitance is a constant as device has done which would not vary by bias voltage and magnetic field. The quantum capacitance is the intrinsic properties of graphene which correlates to its electron density of state. Landau levels (LLs) start to split while the magnetic field is applied. Figure 5.4 shows the capacitance that start to split at 4.5 T and becoming obvious at higher magnetic field. For a high mobility device, the LLs splitting can be observed at lower magnetic field for example the mobility equals to 100,000 cm²V⁻¹s⁻¹ starts to split at 0.1 T. Therefore the quality of the device can be determined that can be based on the magnetic field starts of LLs splitting.

The mobility of hBN/graphene/LiNbO₃ capacitor is only around 2500 cm²V⁻¹s⁻¹ which is similar with graphene on SiO₂ substrate. The mobility of hBN/graphene/mica and hBN/graphene/BSCCO capacitor is around 1000 cm²V⁻¹s⁻¹ which LLs starts to split at near 8 T. The hBN/graphene/BSCCO capacitor has a strong chemical doping (V_b has to apply to 4 V to reach the Dirac point of graphene). The graphene capacitors on MoS₂ and WS₂, unlike 2D oxide substrates, have good mobility around 60,000 cm²V⁻¹s⁻¹.
5-3 Result and discussion

The disparity of 2D oxide and chalcogenide materials not only can be observed by the capacitance measurement, but also during fabrication processes. The MoS\(_2\) and WS\(_2\) have good adhesion with graphene which can process dry peeling method to transfer flakes. Once the flake transfer is done, bubbles occur between the interfaces. On the other hand, no bubble forms between graphene and mica/BSCCO. Furthermore, the adhesion between graphene and 2D oxide materials are too weak to transfer flakes by dry peeling method. From the AFM data, same behavior also has been observed which confirms our observation during fabrication.
According to the pervious observation from TEM cross section image\textsuperscript{35}, the bubble traps hydrocarbon together and leaves other places fully contacts between graphene and hBN flake. The strong adhesion of two surfaces pushes interlayer contaminations into bubbles and creates atomically flat areas. The contamination self gathering has been also revealed of graphene on MoS\textsubscript{2} and WS\textsubscript{2} here we call self-cleaning process. With self-cleaning process, graphene shows higher carrier mobility on hBN, MoS\textsubscript{2}, and WS\textsubscript{2} substrates. Those substrates are lipophilic and atomically flat which assist or occur the self-cleaning process. In contrast, for hydrophilic materials such as mica, BSCCO, and V\textsubscript{2}O\textsubscript{5} absorb water molecule on surface under atmosphere. The self-cleaning process does not happen due to different surface affinity. Therefore, no contamination can be gathered into bubble to create atomically flat areas. Despite the surface of mica, BSCCO, and V\textsubscript{2}O\textsubscript{5} substrate are atomically flat, graphene on those substrates is not contacted but laid on several layers of water molecule. Thus the charge carrier mobility of graphene on oxides is much lower than hBN, MoS\textsubscript{2}, and WS\textsubscript{2} substrates which are also atomically flat surfaces.

The self-cleaning process is important for assembling 2D heterostructures by Lego method under atmosphere. The contaminations between interfaces can be automatically gathered and leave other areas are atomically flat. As the stack finished, etching those bubble away provides a highly homogeneous 2D heterostructure. Without self-cleaning process, the inhomogeneous surface destroys the great electronic properties of graphene or other 2D materials by the interlayer contaminations. The contaminations are atmospheric from air. Thus, for those 2D oxide materials, is still able to have a homogeneous surface under controlled environment such as a glove-box.
Electronic Properties of Graphene Encapsulated with Different Two-Dimensional Atomic Crystals

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Supporting Information

ABSTRACT: Hexagonal boron nitride is the only substrate that has so far allowed graphene devices exhibiting micrometer-scale ballistic transport. Can other atomically flat crystals be used as substrates for making quality graphene heterostructures? Here we report on our search for alternative substrates. The devices fabricated by encapsulating graphene with molybdenum or tungsten disulfides and hBN are found to exhibit consistently high carrier mobilities of about 60 000 cm² V⁻¹ s⁻¹. In contrast, encapsulation with atomically flat layered oxides such as mica, bismuth strontium calcium copper oxide, and vanadium pentoxide results in exceptionally low quality of graphene devices with mobilities of ~1000 cm² V⁻¹ s⁻¹. We attribute the difference mainly to self-cleaning that takes place at interfaces between graphene, hBN, and transition metal dichalcogenides. Surface contamination assembles into large pockets allowing the rest of the interface to become atomically clean. The cleaning process does not occur for graphene on atomically flat oxide substrates.

KEYWORDS: Graphene, boron nitride, transition metals dichalcogenides, layered oxides, carrier mobility, capacitance spectroscopy

Until recently, the substrate of choice in microfabrication of graphene devices was oxidized Si wafers. This was due to their availability and versatility, excellent dielectric properties of thermally grown SiO₂, and easy visualization and identification of monolayer and bilayer graphene on top of such substrates. However, it has soon become clear that the quality of graphene-on-SiO₂ devices was limited by several factors including surface roughness, adatoms acting as resonant scatterers and charges trapped at or near the graphene–SiO₂ interface. Search for better substrates had started and eventually led to the important finding that cleaved hexagonal boron nitride (hBN) provides an excellent substrate for graphene. Typically, graphene-on-hBN exhibits a 10-fold increase in the carrier mobility, μ, with respect to devices made on SiO₂. This quality of graphene has made it possible to observe the fractional quantum Hall effect and various ballistic transport phenomena. Although hBN is now widely used for making increasingly complex van der Waals heterostructures, it remains unclear whether it is only the atomic flatness of hBN that is essential for electronic quality or other characteristics also play a critical role. Even more important is the question whether hBN is unique or there exist other substrates that may allow graphene of high electronic quality.

In this Letter, we report on our studies of various layered materials as atomically flat substrates for making graphene devices and van der Waals heterostructures. By using transport and capacitance measurements, we assess electronic quality of monolayer graphene encapsulated between transitional metal dichalcogenides (TMD), such as MoS₂ and WS₂, and several layered oxides such as muscovite mica, bismuth strontium calcium copper oxide (BSCCO) and vanadium pentoxide (V₂O₅), on one side and hBN on the other. As a reference for electronic quality, we use graphene-on-SiO₂ and hBN/graphene/hBN heterostructures. In the latter case, we can usually achieve μ ~100 000 cm² V⁻¹ s⁻¹ and with using the "dry-peel" transfer μ can go up to 500 000 cm² V⁻¹ s⁻¹, allowing ballistic devices with scattering occurring mainly at sample boundaries. The MoS₂/graphene/hBN and WS₂/
Chapter 6

Hierarchy of Hofstadter states and replica quantum Hall ferromagnetism in graphene superlattice

The aligned graphene and hBN superlattice devices have two methods to investigate the Hofstadter state and self-reproducing quantum Hall ferromagnetism under high magnetic field. Transport measurement detects the voltage change in parallel and perpendicular current direction of device. The voltage change directly indicates the quantum Hall effect. The DoS of electrons can be translated from quantum Hall effect base on measurements and approximations. On the other hand, the capacitance measurement only observes the static electrons on two electrodes. The DoS of electron in graphene depends on charge carrier concentration. Thus the geometrical capacitance only contributes a small and
even amount in the measurement. In other words, the main capacitance variation is the quantum capacitance of graphene which directly correlated with its electron DoS\textsuperscript{88,113}. Therefore, by directly probing the DoS of electron, aligned graphene and hBN capacitor has been made for further study. In this Chapter and this paper, I personally contributed to the fabrication of the aligned graphene/hBN capacitors. One of them revealed finest detail of Hofstadter state ever observed from graphene/hBN devices.

**6-1 Device fabrication**

For device fabrication, first clean the quartz wafers with acetone and IPA in ultrasonic bath for 10 min to remove resist which is coated to avoid dusts during wafer scribing. The quartz wafers were cleaned with oxygen plasma for 10 min to remove organic compounds. Cleave hBN crystal into thin flakes using water solvable tape and then place on quartz wafer while plasma etching procedure is done. Evenly press the tape for hBN flakes can contacts with quartz wafer. Remove the tape by directly peeling it off from quartz wafer.

![Figure 6-1](image)

**Figure 6-1** Schematic of the aligned hBN/graphene/hBN superlattice capacitor on quartz wafer.
Search suitable thickness of hBN flake for bottom substrate under microscope. The thickness of hBN substrates have to counter the surface roughness from quartz. The thickness should be around 15 to 35 nm (blue to yellow-white color) with straight edges. The straight edges should angle 30 degree or the angle can be fully divided in 30 degree (like 60°, 90°, 120°, 150°) to ensure the edge is armchair or zigzag. Exam the hBN flakes with dark field under optical microscope. The area should be clean and without bubbles, faults and un-even surface as following figure 6-2 shows.

**Figure 6-2** The image of a suitable hBN flake under white light (a), dark field (b). The scale bar is 50 μm.

Meanwhile, PMMA/PMGI resists are coated on plain Si substrate for dry transfer processes. Cleave natural graphite using water solvable tape and evenly press the tape on the PMMA/PMGI surface. Peel the tape off directly and search graphene flake under microscope with color filters. The graphene flake should be strip shape and isolated from thicker graphite flakes. The suitable flakes also should have a long straight edge and angle with other edge in 30° or an angle is 30° multiplied with an integer number. Scratch the PMMA membrane around the graphene flake at 5x objective lens (about 2.5 mm in diameter) and float the membrane by adding MF319 droplets to dissolve PMGI under layer. Transfer the membrane to water when the membrane is fully floating on MF319. Fish the membrane with washer or tape window.

Align the graphene and hBN flakes’ edge under microscope or monitor with a straight line or a ruler. Gently approach the membrane to the substrate and manipulate the x-y micro-
positioning system to keep aligned position until contact. Scratch the membrane while the membrane is fully attached on surface.

Bake the quartz wafer on a hot plate at 130 °C for 5 min to ensure the PMMA membrane is soft and the flakes are fully contacted with the substrate. The sample was cleaned with warm acetone for 10 min and IPA for 5 min. After cleaning processes, the bubble between graphene and hBN substrate will appear due to good adhesion of two flakes. The adhesion force purges the surface hydrocarbon together and creates bubbles as last chapter shown.

The samples were annealed in H$_2$/Ar gas filled furnace at 275 °C for 3 hours. The annealing process is not only cleaning the PMMA residue on surface, but also gathers the interface bubbles. Some bubbles will migrate during annealing usually small bubbles gather with a big bubble as figure 6-3 shows.

![Figure 6-3](image)

**Figure 6-3** The image of hBN/Gr/hBN structure before (a) and after (b) H$_2$/Ar annealing. The bubbles in green broken circle are vanished after annealing. The bubble pointed by green arrow shifted its position and the bubbles pointed by blue arrow grow large/ more spherical after annealing.

Hexagonal BN flakes were also prepared with normal dry transfer method and selecting hBN spacer under 20 nm in flake thickness. The spacer thickness should be thicker than 3 nm. The actual thickness affects the size of top electrodes for enough capacitance to measurement. The top electrode needs bigger if spacer is thicker. The correlation of spacer thickness and electrode area is linear. After hBN spacer has been transferred, spin coating a layer of 950 kDa PMMA (soft bake at 160 °C for 10 min) and Aqua save (bake at 110 °C for 1 min) on sample for e-beam lithography. Pattern the position crosses (10 um cross in 200 um distance for a 6x6 array)
around the hBN/Gr/hBN structures. Develop the pattern in MIBK/IPA (volume ratio 1/3) solution and then deposit Au/Cr layer in 40/4 nm thickness on the sample. Lift off the metal thin film in warm acetone for 10 min (blow with pipette) and move to another clean acetone for another 10 min and then IPA for 5 min. Samples were dried with N₂ gas.

**Figure 6-4** A series of image of aligned hBN/graphene/hBN capacitor during fabrication (a)-(h). The image of a graphene strip sized nearly 20 x 100 μm with a very straight edge (as red broken line labeled) (a); a hBN substrate with two crystalline edges (red broken lines) (b); the graphene strip was aligned and transferred on hBN substrate (c); after first annealing (d); a hBN spacer transferred which also has a straight line edge as red broken line labeled (e); after second annealing (f); e-beam lithographed with contacts and top electrodes. The corners of electrodes had been rounded to avoid PMMA cracking on hBN and the shape of top electrodes had been designed to avoid covering bubbles (g); the final image after fabrication (h).
Anneal the sample again in H₂/Ar gas filled furnace at 275 °C for 3 hours again to remove PMMA residue and create more space for top electrodes as bubble gather. After annealing processes were finished, photo the images under optical microscope with different objective lenses from 5x to 100x for designing metal contacts and etch mask (if necessary). The contacts and top electrodes were designed based on those images. Graphene should be contacted at two ends by electrodes that provide extra information for graphene quality. The top electrodes were designed with curved corners to avoid electron accumulation at the corners during exposure. The sharp corner electrodes sometime cause unexpected exposure between each exposed area. Furthermore, the top electrodes were not covered on bubbles for higher homogeneity.

Use e-beam lithography to pattern the design and develop the pattern in MIBK/IPA solution. Deposit Cr/Au for 4 nm and 70 nm in thickness with e-beam evaporator. Lift off the metal thin film in warm acetone for 10 min (using pipette to blow the unwanted metal film away) and transfer the samples to another clean acetone for another 10 min and then IPA for 5 min. Samples were dried with N₂ gas.

Make one more e-beam lithography process for etch mask if necessary. Develop the PMMA etch mask pattern in MIBK/IPA solution and etch the electric shorting area by plasma etcher for 1 to 2 min. Clean the PMMA in acetone with ultrasonic bath for 30 sec and fresh acetone for 10 min then IPA 3 min. Finally samples were dried with N₂ gas.

### 6-2 Characterization

To characterize capacitance variation at different magnetic fields, the Andeen-Hagerling AH2550A capacitance bridge and a superconductor magnet cryostat have been used. The samples were bounded on chip carrier with silver paint and gold wires. The bounded sample placed in the cryostat insert then dipped into the cryostat for low temperature measurement (2K). The capacitance measurements for higher magnetic field (B > 17 T) were made at High Magnetic Field Laboratory in Grenoble.

The capacitance of graphene capacitor can be described in three terms, the geometry capacitance \(C_G\), the quantum capacitance \(C_Q\) and the parasitic (parallel) capacitance \(C_p\).

\[
\frac{1}{C} = \frac{1}{C_G} + \frac{1}{C_Q} + \frac{1}{C_p}
\]
The geometry capacitance $C_G$ can be determined by the thickness $d$ of hBN spacer and the electrode area $A$ both are contents in a capacitor. The geometry capacitance can be measured independently by the periodicity of the magnetocapacitance oscillations. The quantum capacitance $C_Q$ is the intrinsic property of graphene which corresponds to its electron density of states (DoS). The relation of quantum capacitance and DoS can be wrote $C_Q = A e^2 \times \text{DoS}$, where $A$ is the electrode area and $e$ is the electron charge. In this research, $C_Q$ is the most important quantity to be determined for investigating the electron DoS variation at different bias voltage and magnetic fields in graphene-hBN aligned capacitor. The parasitic capacitance $C_p$ is the only the fitting parameter in this experiment. The $C_p$ is around 1 fF which only contributes near 1% of total capacitance in our capacitor devices. Therefore, in most of cases no fitting is needed for following results.

The electron in graphene starts to circle while the magnetic field applied. The electron circle only allows integral quantum number, or filling factor, orbits to exist (depends on electron energy). In other words, the electron DoS will be split due to electron energy disparity under magnetic field. The split DoS (LLs) can be observed on the magnetocapacitance spectrum as a fan diagram. The spin and valley degeneracy begins to lift up (filling factor $\nu = 0, \pm 1, \pm 3, \pm 4, \pm 5, \pm 7...$) due to many-body interaction at higher magnetic field ($B > 3\, \text{T}$, but still depends on the mobility of devices). The many-body interaction indicates the existence of quantum Hall ferromagnetism (QHFM)\textsuperscript{114-116}.

For graphene-hBN aligned capacitors, a larger periodic potential is formed by matching graphene-hBN lattice. The new periodic potential is just like the moiré pattern, which varying with the alignment angle. With the new periodic potential, the electron of superlattice structure still follows a hexagonal shape in a few ten nanometers size due to the moiré pattern of hBN and graphene hexagonal lattices\textsuperscript{117}. The theory suggests\textsuperscript{118,119} the extra neutralities are Hofstadter minibands from the hBN-graphene superlattice structure. In figure 6-5, total three neutrality points have been revealed, the main Dirac point at zero gate voltage and another two neutrality points at near ±4.5 V of both electron- and hole- side of the spectrum at zero magnetic field.

At near 10 T, the magnetic flux $\Phi$ is about $\frac{3}{2} \phi_0$ flux per area of superlattice unit cell. The QHFM gap at $\nu = 3, \pm 4, \pm 5$ has been suppressed and reappeared after magnetic flux increase ($\nu = 3, 4, 5$). Moreover, the similar phenomenon also can be observed at higher magnetic field as the magnetic flux equal to the flux per area of superlattice unit cell ($\Phi = \phi_0$). This behavior is different with non-aligned graphene-hBN capacitor had been shown\textsuperscript{88,109}. In this paper, we attribute the suppressing QHFM to reverse Stoner transition (spontaneous spin polarization breaking due to kinetic energy increase of many-body interaction)\textsuperscript{119} at all rational flux values $\Phi = \phi_0(p/q)$, where $p$ and $q$ are integers. At the magnetic flux equal to the flux per unit area of
superlattice unit cell ($\Phi = \phi_0$), the QHFM gap at $v = \pm 1$ are narrower than in lower magnetic field which normally is exponentially broadened into a certain width for non-aligned devices. The shrinking of spin-valley ferromagnetism’s gap results the trend of system is back to normal metal state$^{119}$.

![Magnetocapacitance spectrum of graphene-hBN aligned capacitor.](image)

**Figure 6- 5** The magnetocapacitance spectrum of graphene-hBN aligned capacitor.

With a high magnetic field ($B > 24$ T), more minigaps have been revealed. The minigaps follows the main QHFM ($v = 0, \pm 1, \pm 2$) and creates a hierarchy states such as $(v, v_L) = (0, -1)$ and $(0, 1)$. Intuitively, the minigap will be considered as the third generation Dirac fermions. However, even the gap of filling factor $v = \pm 2$ owns its minigaps $(2, -1), (-2, 1)$ and $(-2, 2)$. The $v = \pm 2$ quantum Hall state has no spin- nor valley- polarization. Therefore, the third generation Dirac fermions explanation cannot fit these odd-integer gaps $(\pm 1, 0)$ by ideal superlattice effects without involving the spontaneous lifting of the degeneracies. In the supporting information of this paper, we qualitatively analyze the entire hierarchy gaps. The states $(\pm 2, v_L), (0, v_L)$ and $(\pm 1,$
±1) are determined by weaker exchange interaction of the third-generation Dirac fermions at 0-th LLs state and the (±1, 0) gaps collapse due to reverse Stoner transition when Φ > φ₀.

6-3 Result and discussion

Start from the device fabrication, the atomically flat hBN flakes not only provide a great surface for graphene based devices but also reveal the interesting superlattice effect for physics. The interface self-cleaning effect helps graphene to have a good contact with hBN surface and gathers contaminations into large bubbles. The H₂/Ar annealing processes also help self-cleaning effect and removes PMMA residue on surface. The graphene-hBN flake alignment only processes by naked eye with 1 to 2 degree in alignment error. However with this method still enough to observe Hofstadter states in limited bias voltage which can be applied to graphene-hBN capacitor with negligible loss. The electrode has to be designed in round shape to avoid PMMA creaking which may induce electric shorting. The non-regular shape also has to avoid bubbles for further homogeneity of the surface.

The magnetocapacitance measurement indicates significant difference on graphene-hBN aligned samples. Like the non-aligned devices, the superlattice affects LLs splitting by opening the spin-valley degeneracy with integral quantum number so call filling factor ν. These many-body interaction gaps are respect to QHFM. With aligned graphene-hBN capacitor, the second generation neutralities also split in magnetic field although cannot be observed of all LLs in experimental data. The second generation neutralities are Hofstadter minibands due to same hexagonal shape in Brillouin zones from the hBN-graphene superlattice structure. Beside the capacitance minima from the neutrality, many gaps have been revealed around Φ = φ₀. We attribute these gaps to LLs originating from replica Dirac spectra. This is because weak modulation compares to the main LLs and QHFM, that individual LLs split into superlattice minibands without intermixing. On the other hand, these minigaps suppressed at Φ = 1/2 φ₀ and Φ = φ₀ even for QHFM at ν = ±1. We suppose that the reverse Stoner transition causes the minigaps suppression which is supported by qualitative analyzes in supporting information of this paper.

Finally, the capacitance measurement is a powerful tool to investigate complex graphene system. Probing the electron DoS by simply detecting capacitance provides more information than transport measurement. In this paper, we utilized capacitance spectroscopy to reveal different many body interactions in graphene-hBN aligned superlattice. With better device
fabrication and characterization method, we expect more new physics and the replica of fractional quantum Hall effect states might be presented in near future.
Hierarchy of Hofstadter states and replica quantum Hall ferromagnetism in graphene superlattices

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Self-similarity and fractals have fascinated researchers across various disciplines. In graphene placed on boron nitride and subjected to a magnetic field, self-similarity appears in the form of numerous replicas of the original Dirac spectrum, and their quantization gives rise to a fractal pattern of Landau levels, referred to as the Hofstadter butterfly. Here we employ capacitance spectroscopy to probe directly the density of states (DoS) and energy gaps in this spectrum. Without a magnetic field, replica spectra are seen as pronounced DoS minima surrounded by van Hove singularities. The Hofstadter butterfly shows up as recurring Landau fan diagrams in high fields. Electron-electron interactions add another twist to the self-similar behaviour. We observe suppression of quantum Hall ferromagnetism, a reverse Stoner transition at commensurable fluxes and additional ferromagnetism within replica spectra. The strength and variety of the interaction effects indicate a large playground to study many-body physics in fractal Dirac systems.

When graphene is placed on top of atomically flat hexagonal boron nitride (hBN) and their crystallographic axes are carefully aligned, the electron transport properties of graphene become strongly modified by a hexagonal periodic potential induced by the hBN substrate⁴–⁶. Replicas of the main Dirac spectrum appear⁶–¹² at the edges of superlattice Brillouin zones (SBZs) and, for the lowest SBZ, the second-generation Dirac cones can be reached using electric field doping⁶–⁶. Because the superlattice period, \( \Lambda \), for aligned graphene-hBN structures is relatively large (~15 nm), magnetic fields \( B \sim 10^5 \) T are sufficient to provide a magnetic flux \( \Phi \) of about one flux quantum per area \( \Phi = \sqrt{3} \Lambda^2 / 2 \) of the superlattice unit cell. The commensurability between \( \Lambda \) and the magnetic length \( l_B \) gives rise to a fractal energy spectrum, the Hofstadter butterfly⁶–¹⁰,¹³–¹⁴. An informative way to understand its structure is to consider the butterfly as a collection of Landau levels (LLs) that originate from numerous mini-replicas of the original spectrum, which appear at all rational flux values \( \Phi = \phi_0 (p / q) \), where \( p \) and \( q \) are integers⁶–¹². At these fluxes, the electronic spectrum can be described⁶–¹⁴ in terms of Zak’s minibands⁶–¹⁴ for an extended superlattice with a unit cell \( q \) times larger than the original one. In graphene, Zak’s minibands are expected to be gapped cones (third-generation Dirac fermions)¹⁵. Away from the rational flux values, these Dirac replicas experience Landau quantization in an effective field \( B_{\text{eff}} = B - B_{\text{LL}} \) where \( B_{\text{LL}} = \Phi_0 (p / q) / \Lambda \).

In this work, we have employed capacitance measurements to examine the electronic spectrum of graphene superlattices and its evolution into the Hofstadter butterfly. In zero \( B \), pronounced minima in the electronic density of states (DoS) are observed not only for graphene’s neutral state but also at high electron and hole doping. The latter minima signify Dirac replicas near the edges of the first SBZ. The replicas occupy a spectral width of \( \sim 50 \) meV, indicating strong superlattice modulation. The temperature \( T \) dependence of the DoS suggests that the second-generation Dirac cones are singly and triply degenerate for the valence and conduction bands of graphene, respectively. In quantizing \( B \), in addition to the classic fan diagram for graphene, we observe many new cyclotron gaps forming from out of finite values of \( B \). They are attributed to the formation of high-field replica Dirac cones¹ and their Landau quantization in \( B_{\text{LL}} \). The local fans are particularly well developed near \( \Phi = \phi_0 \), \( n = 0, \pm 1, \pm 2 \), where \( n = n \phi_0 / \Phi \) is the filling factor and \( n \) is the carrier density. The Hofstadter minibands in this regime cannot be explained by orbital quantization alone. They do not follow the expected dependence on the LL index and are described by the Coulomb energy scale \( E_C = e^2 / l_B^2 \), where \( l_B^2 \) is the magnetic length in \( B_{\text{eff}} = \pm |B - B_{\text{LL}}| \) and \( e \) is the effective dielectric constant⁶–¹¹. We also observe that the SU(4) quantum Hall ferromagnetism (QHF), characteristic of non-aligned devices⁶–¹³, experiences strong suppression at commensurable fluxes. The \( n = \pm 1 \) gaps disappear near \( \Phi = \phi_0 \), whereas the ferromagnetic states at \( |n| = 3, 4 \) and 5 exhibit a re-entrant transition at \( \Phi = \phi_0 / 2 \).

DoS for second-generation Dirac fermions

Figure 1a shows our capacitor devices. Graphene is placed on top of hBN (50–100 nm thick) and encapsulated with a second hBN.
The twist controlled resonant tunneling transistor is aligning bottom and top graphene to investigate the resonant tunneling between two layers of graphene. Figure 7-1 reveals the structure of the resonant tunneling graphene transistor device. Tunneling current happens while bias voltage applied on two graphene flakes through few layers of hBN. The resonant tunneling is occurred not only by short-range scattering and charge in-homogeneity in the graphene layers but also follow the electron momentum conservation. As the graphene–graphene is aligned, the resonance is dominated by momentum conservation which only
weakly depends on temperature. Therefore, the room temperature graphene tunneling transistor becomes possible.

**Figure 7-1** Schematic of the graphene based tunneling transistor. Two layers of graphene are separated by a few layer (3-5 atomic layer) hBN spacer. These graphene flakes has to crystalline aligned to each other. The tunneling area also locates on thicker hBN flake (about 20-40 nm thickness) to smear surface roughness of SiO$_2$/Si substrate. The gate voltage ($V_g$) is applied between bottom layer of graphene and Si substrate. The bias voltage ($V_b$) is applied on two graphene flakes.

In this chapter and paper, I have contributed the fabrication of resonant tunneling graphene transistors. One of my devices provides highest quality to reveal physics picture of resonant tunneling in two layers of graphene. The differential conductance mappings in this paper are all based on my devices.
7-1 Device fabrication

The aligned graphene-graphene tunnelling transistor starts on SiO$_2$/Si wafer. The SiO$_2$/Si wafer is cleaned in acetone, IPA with ultrasonic bath to remove resist, which protects surface during wafer scribing. The dried wafer placed in O$_2$ plasma etcher to remove organic compounds. Hexagonal BN flakes were cleaved by using water solvable tape while SiO$_2$/Si substrate has been cleaned. Attach the tape with hBN flakes on SiO$_2$/Si wafer. Choose hBN flakes around 20-40 nm in thickness and without bubbles and uneven surface to be bottom substrate of devices. Additionally, although at the beginning the hBN alignment does not be controlled, the edge of hBN should be straight like the condition of aligned graphene-hBN capacitor. The straight edge helps graphene-graphene alignment because the contrast after graphene transferred on hBN is very low. The low contrast will increase the difficulty to align another graphene flake on top. Therefore, the later version of aligned graphene-graphene tunnelling transistor has, at least, a straight edge for bottom fundament.

![Figure 7-2](image)

**Figure 7-2** The series of optical images during the fabrication of resonate tunneling graphene transistor. The scale bars of all figures are 25 µm. The image of a hBN substrate (a); a strip shape graphene flake transferred on BN substrate which marked with green broken line (b); a 4 layers BN flake transferred on graphene flake which marked with blue broken line (c); a twin graphene strip transferred on BN spacer perpendicular with bottom graphene which marked with green broken line (d); e-beam lithographed with contacts for top and bottom graphene (e); final image after fabrication (f).
The strip shape of graphene flakes have been selected on PMMA/PMGI coated Si surface. The graphene strip has one straight edge for alignment (better to have two parallel edges) with 1-5 μm in width. The graphene flake has to be misaligned between hBN and graphene strip in several degrees normally 15° but in some devices the angle difference only around 2°-5°.

With normal dry transfer method, scratch the edge of the membrane as the PMMA and graphene is fully contacted with the substrate. Bake the wafer on a hot plate at 130 °C for 3 min to soft the PMMA membrane. The baking will force flakes attach to each other if the membrane was not fully contacted with the substrate. Clean the membrane with warm acetone (~70 °C) for 10 min and IPA for 10 min and then dry the sample with N₂ gas.

To ensure the interface is clean, the H₂/Ar thermal anneal has been applied on every steps after transfer and lithography. The samples were annealed at 275 °C in H₂/Ar environment for 3 hours to clean PMMA residue. Once the processes of anneal were done, another flake will be transferred as soon as possible to keep the interface clean. Then repeat the cleaning, annealing and transferring processes until the heterostructure has done.

The figure 7-2 shows the optical images at the different stages during the device fabrication. The color difference in background is due to DIC mode or PMMA coating. In the beginning, a hBN flake has been selected as a base substrate although part of the edges are not flat which can be seen under microscope in white light. Then one graphene strip has been transferred on the flat area of hBN substrate. The transferred graphene is misaligned around 2 to 5 degrees to the substrate. After first annealing, a 4 layers hBN flake has been transferred on it which partly covered graphene strip. When the PMMA has been baked and removed, the thin hBN flake surface can observe bubble with white color which is due to self-cleaning of graphene-hBN and hBN-hBN interface as chapter 5 revealed. Once more annealed, another graphene strip has been transferred on it. The place of transfer should be a flat area and the orientation is angled in 90° with bottom graphene strip. The edges of top and bottom graphene are different, one of it is armchair and another one is zigzag. A bi-layer PMMA has been coated on surface for e-beam lithography processes while the heterostructure completed. The designed pattern needs to avoid shorting and covering contacts on the flakes thicker than 60 nm. The contacts on hBN substrate also need to avoid any sharp corner, which may induce cracks in PMMA and shorting other contacts. After the pattern has been exposure and developed, the Cr/Au has been deposited on it. The thickness of metal contacts depends on the thickness of whole heterostructure. For this particular device, the total thickness is around 30 nm. Thus, a 60 nm metal film has been deposited to avoid no connection at the edge of the heterostructure. Finally, lift off the metal film in warm acetone for 10 min and in fresh acetone for another 10 min and then in IPA for 3 min. The device was dried with the blow of N₂ gas.
7-2 Characterization

To characterize the electronic properties of twist graphene tunnelling transistor, totally 6 aligned samples have been made and measured. The characterization is done in cryostat at 2 K and measured by lock-in-amplifier in AC mode. The bias voltage has been applied and scanned at constant gate voltage. To gather the information of differential conductance mapping from the device with higher homogeneity, two lock-in-amplifier have been used together to gather \( \frac{dI}{dt} \) and \( \frac{dV}{dt} \) in AC mode at the same time then combine both information into differential conductance mapping.

![Diagram](image)

**Figure 7-3** Schematic of the relative energy level for a graphene-based tunneling transistor between each layers. Y axis represent the relative energy level and x axis represent the spatial position of each layer. As gate voltage \( V_g \) is applied, the chemical potential of graphene \( \mu_b \) shifts above Si with amount \( eV_g \). For insulators (hBN and SiO2), its potential change linear depends on distance of Si substrate. Meanwhile, bias voltage applied the chemical potential \( eV_b \) and Dirac cone \( \Delta \phi \) of top graphene \( \mu_T \) shifts with amount \( eV_b \) and \( \Delta \phi \). In this case, electron tunnels through hBN spacer from bottom to top graphene.
The energy diagram of graphene tunneling device has been shown in Figure 7-3. The gate voltage controls the chemical potential of two graphene flakes to nearly the same level due to the low electron DoS of graphene. Therefore, the bottom graphene only minimally screens the electric field from Si back gate. The bias voltage manipulates the Fermi levels and the energy of two Dirac points. As the bias voltage is applied, electrons tunnel through the energy barrier which is provided by few layers of hBN flake.

In 2012, Britnell et al has made field effect graphene tunnelling transistors\(^9\), and found resonance tunnelling on some of tunnelling devices in 2013\(^1\). The resonance tunnelling was contributed to electron in plane momentum relaxation which is caused by electron-hole puddling, short range disorder, moire pattern and/or phonon scattering. However, in this thesis, another model of resonance tunnelling mechanism has been discovered. Thus, based on that, controlling the graphene resonance tunnelling at certain voltage becomes possible.

![Figure 7-4 Schematic of two graphene lattices are mismatch at \(\theta\) degree (left), and the momentum difference of two graphene flakes misalign at \(\theta\) degree (right).](image)

For a twist controlled graphene tunnelling device, the mis-orientation of two graphene lattices is only a few degrees off. Thus, the electron momentum of two graphene flakes is also proportional to the mis-align angle of two graphene lattices. The momentum difference is \(\hbar \Delta K_1^\pm = l_z \times \theta K_1^\pm\). The \(l_z\) is the inverse of lattice constant and multiply with \((2)^{0.5}/3\). The \(K_1^\pm\) is the wavevector of electron at + valley and i equivalent corners (i=1,2,3). In theory, if the momentum difference is exactly same as the bias voltage provided will occur the resonance tunnelling.

In the differential conductance mapping, several lines can be observed which indicates different situations while Fermi levels and Dirac points vary. The first peak in the I-V curve, as
figure 7-5 (left) shown, is the chemical potential reach Dirac point at low bias and gate voltage (blue and red line). At Dirac points, the low electron DoS limits the tunnelling current (blue and red line in figure7-5 right). The line in differential conductance mapping crosses with other line (such as green and blue lines crossing in figure 7-5 right) which affects other line to follow the square root relation. The relation is also because the low electron DoS at Dirac points. The largest peak in I-V curve is from resonance tunnelling as figure 7-5 (right) revealed. The resonance tunnelling happened as the overlapping of two Dirac cones becomes linear. The conservation of electron momentum between two Dirac cones is maximizing the possibility of electron tunnelling.

A shoulder next to the resonance peak implies another situation as figure 7-5 (right) shown. In the differential conductance mapping, this conductance change has been marked green line in figure 7-5 (left). The two green lines convert at zero gate voltage and split at non-zero gating. At this bias voltage for graphene resonance tunnelling device call first resonance. The first resonance occurs by one Fermi level, which is overlapping with other Dirac cone. It split of green line in figure 7-5 (left), while the gate voltage applied, due to the gate voltage rises or drops two Fermi levels together. The overlapping for each Fermi level is different which causes the split of first resonance peak when the gate voltage applied.

![Figure 7-5](image)

**Figure 7-5** The I-V curve of resonance tunnelling transistor at zero gate voltage (green), 40 V back gate (red), -40 V back gate (green) [left] and the differential conductance mapping from ±1.5 V bias voltage to ±40 V gate voltage [right]121, both adapted from reference 121.
The angle of the graphene flakes misorientation can be estimated at first resonance in zero gate voltage. The figure 7-6 reveals the diagram of the Fermi level in two momentum-near Dirac cones. The energy of Fermi level drops at top layer of graphene is $\hbar \Delta K v_f/2$ also equal to $eV_b/2$ where $v_f$ is the Fermi velocity. Thus, the momentum variation for tunnelling electrons is $\hbar \Delta K = eV_b/v_f$. On the other hand, the relation between momentum change and lattice misalignment angle is $\hbar \Delta K^2 = l_z \times \theta K^2$. Therefore, the lattice angle difference of two graphene flakes can be estimated as combined those two equations. In case of the device in figure 7-3 which graphene mismatch angle is $1.8^\circ$.

![Diagram of Fermi level and Dirac cones](image)

**Figure 7-6** Schematic of one Fermi level starts to overlap with other Dirac cone at zero gate voltage. In this case, the moment difference of two Dirac cone is $\hbar \Delta K$ and the energy difference between two Fermi levels are $eV_b$. Therefore, $\hbar \Delta K = eV_b/v_f$ where $v_f$ is Fermi velocity. According to the momentum difference is also related to lattice angle difference $\theta$ of two graphene flakes $\hbar \Delta K = l_z \times \theta K$ where $l_z$ is unit vector in z direction. With these equation and measurement data of first resonate happened, we can estimate the misalignment angle $\theta$ of our device and compare with Raman and AFM measurement data.

To confirm our interpretation, an in-plane magnetic field has been applied on resonance tunnelling devices. The in-plane magnetic field is parallel to graphene layers, which provides a momentum shift for tunnelling electrons due to Lorenz’s force. The Lorenz’s force $edB_{||}$ is equal to the wave vector shift $\Delta 0 K$. Therefore, at 15 Tesla, the equivalent lattice difference $\Delta \theta$ is around $0.6^\circ$. Thus, the peak of resonance current is also shifted due to the equivalent lattice difference. The figure 7-6 (a) shows the variation of I-V curves in different magnetic field. The resonance peaks are slightly shifted when magnetic field applied as our expectation. Here we
subtract the differential conductance mapping in two different magnetic fields (0 T and 15 T),
then we reveal a difference mapping. With the difference mapping reveals the basic tunneling
properties has no change at in-plane magnetic field. All the line in differential conductance
mapping only slightly shifted at in-plane magnetic field.

The principle of the graphene resonance tunneling device is subjected to electron
momentum conservation. Therefore, the resonance tunneling is less dependent on
temperature compared to Hofstadter’s butterfly. The resonance tunneling property of aligned
graphene-based transistors does not change at room temperature. The mapping image
becomes slightly fuzzier while electron has more energy at 300 K which increases the tunnelling
probability all the time.
7-3 Result and discussion

Based on the property of graphene resonance tunneling device, a radio frequency (RF) oscillator has been made with this graphene resonance tunneling transistor. In an inductor and a capacitor circuit, the current is oscillating in between when energy was applied and off. The oscillation declines due to resistance in the circuit. The resonance tunnelling transistor plays an important role to enhance the oscillation by negative differential resistance which provides an in-phase current in the circuit. In our experiment, the oscillation frequency can reach MHz in RF region.

The graphene-based tunneling transistor with higher oscillation frequency is possible for future applications. The major factor limiting our prototype high frequency transistors is the capacitance from SiO$_2$/Si back gate. The area of graphene-graphene overlapping is less than few hundred µm square, but the total capacitance is also including the capacitance from SiO$_2$/Si wafer. Thus, the actual capacitance is much less if the back gate is only covered on the graphene-graphene overlapped area. In this case, the oscillation frequency can be further improved to GHz range by making graphene resonance tunneling transistor on quartz with a gold top gate.

To summarize, in this experiment, at least six graphene-graphene aligned tunnelling transistors have been made and characterized. The resonance tunnelling is due to the tunnelling electron momentum conservation. As the intersection of two Dirac cones become linear, the resonance tunneling happened. The electrons have a higher probability to tunneling through the hBN barrier. The examination of momentum conservation by applying in-plane magnetic field is consistent with theoretical expectation and simulation. For future application, the graphene resonance tunneling transistors can fully function at room temperature and first prototype graphene tunneling transistor based LC oscillator has been made and tested. The further improvement can be done by making graphene resonance tunnelling transistors on quartz wafer to reduce unnecessary capacitance.
Twist-controlled resonant tunnelling in graphene/boron nitride/graphene heterostructures

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Recent developments in the technology of van der Waals heterostructures have already led to the observation of new physical phenomena, such as the metal-insulator transition and Coulomb drag, and to the realization of functional devices, such as tunnel diodes, tunnel transistors, and photovoltaic sensors. An unprecedented degree of control of the electronic properties is available not only by means of the selection of materials in the stack, but also through the additional fine-tuning achievable by adjusting the built-in strain and relative orientation of the component layers. Here we demonstrate how careful alignment of the crystallographic orientation of two graphene electrodes separated by a layer of hexagonal boron nitride in a transistor device can achieve resonant tunnelling with conservation of electron energy, momentum and, potentially, chirality. We show how the resonance peak and negative differential conductance in the device characteristics induce a tunable radiofrequency oscillatory current that has potential for future high-frequency technology.

The growing catalogue of two-dimensional (2D) crystals allows us to construct increasingly complex van der Waals heterostructures. The combination of a hexagonal boron nitride (hBN) barrier layer sandwiched between two graphene electrodes is particularly attractive because of the exceptional crystalline quality and the small lattice mismatch of these two materials. For example, by utilizing a third (gate) electrode, recently it was proved possible to make a novel type of field-effect transistor in which tunnelling between the two graphene electrodes is controlled by the gate voltage. In the prototype versions of these devices, the crystalline lattices of the component layers were not intentionally aligned, which meant that tunnelling between the two graphene electrodes required a defect-assisted momentum transfer, so the tunnelling was not strictly resonant.

Here we report a new series of tunnel transistors in which the crystal lattices of the two graphene layers are intentionally aligned to a high degree of precision (within 2°) during the fabrication procedure. Our measurements and theoretical modelling of the device characteristics reveal that the current flow is dominated by tunnel transitions in which both energy and in-plane momentum are conserved. The resonant conditions exist in a narrow range of bias voltages, and result in a resonant peak in the current–voltage characteristics, which leads to a strong negative differential conductance (NDC). In the NDC region, our devices generate radiofrequency oscillations when connected to a simple inductor.

Figure 1 | Schematic representation of our device and its band structure. a, Device schematics with an exaggerated angle θ between two graphene layers (separated by a hBN tunnel barrier shown in light blue). The heterostructure is placed on a SiO2/Si substrate (magenta/light grey), which serves as an electrostatic gate. Both graphene layers are independently contacted by Cr/Au metallization (yellow). b, A rotation by θ of the two graphene layers in real space corresponds to the momentum shift ΔK between two Dirac points. c–e, Relative alignment between the top (left cones) and bottom (right cones) graphene Dirac points; the boundary between magenta (empty states) and blue (filled states) marks the Fermi level.

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In this thesis, several Van der Waals heterostructure devices have been discussed. We began with the basic properties of graphene and other 2D materials such as hBN, MoS₂, mica, etc to introduce 2D materials library and the idea of layering different 2D crystals to construct a Van der Waals heterostructure. Following with the processes of flake hunting and transferring techniques, these knowledge and skills are cornerstones for laying Van der Waals heterostructures. The flake selection, thermal annealing, lithography, and metal deposition are presented in chapter 4. These fabrication details decide the quality of graphene-based devices. Especially, the interface cleanness directly affects the charge carrier mobility of encapsulated
Graphene. The graphene devices with poor charge carrier mobility are usually difficult to be characterized. The continuously progressing of the fabrication processes leads to Van der Waals heterostructures becoming a reality. For example, the transfer methods and instruments enable us to place one flake on top of each other with micrometer accuracy and then releasing the flake as we expected. Because of these critical modern technologies in fabrication which allows us to construct Van der Waals heterostructures like Lego in atomic procession and builds a new artificial material from bottom side up.

Graphene hunting on different substrates serves different purposes. For flake transferring processes, it used to be on SiO$_2$ surface while only wet transfer method was developed. Searching graphene on 300 nm SiO$_2$/Si wafer is relative easy due to its contrast. However, the contamination of KOH and water residue decreases the quality of graphene flakes. Thus the transferred flakes usually are made on PMMA/PMGI coated Si wafer after the dry transfer has been invented. The contrast of graphene flakes varies with the thickness of the resist layer as an exchange for better cleanliness. Therefore, flake hunting has to be based on the contrast with a proper color filter which gives a higher contrast. The contrast of different 2D materials is also varying, for example monolayer hBN has a lower contrast than graphene. In this case, the flake hunting of different 2D materials relies on the experience of hunter. The reason of better cleanliness by using dry transfer is because this method avoids the interface contact with solvent. To have a clean interface, the bottom layer resist (PMGI) is dissolved by MF 319 and the transfer flake with PMMA floats on the solvent. Thus, the heterostructure interface is still clean without touching any solvent. The peeling method and stamp processes provide an even more clean procedure. Despite the peeling and stamp method are still limited by the size of top and bottom flakes and the intrinsic adhesion force between the transferring flake and target flakes. Those methods reduce the numbers of time of the entire stack contacts with solvent such as acetone and IPA.

Before devices being fabricated, the selection of flakes is also important. For fabricating a graphene-based capacitor, the bottom hBN substrate should be large and flat. Graphene should be larger than 15 x 50 μm$^2$ to provide enough capacitance for measurement. The hBN spacer should also be flat with a thickness between 10 to 30 nm. The selection is fully depends on the geometry and composition of devices. During stack assembling, thermal annealing in H$_2$/Ar environment at 300 °C removes PMMA residue on top of surface and improves surface self-cleansing affect. To characterize the heterostructures, lithography is required to pattern electric contacts on it. Electron beam lithography offers higher resolution while same resist (PMMA) as we use in transfer to avoid contamination from other resist. Therefore, the graphene-based devices after electron beam lithography which usually has less contact resistance and chemical doping than optical lithography. Etching the electrical shorting area of the devices with plasma or depositing metal contacts on samples after lithography. For metal deposition, electron beam
and thermal evaporator have been introduced. Although the principle of vaporizing metal is different, it exist slightly differences in the result of metal deposition. The e-beam evaporator is still a better choice to deposit metal due to higher vacuum and stable depositing rate except some special requirements.

Three published journal papers have been included and elucidated into last three chapters, respectively. In chapter 5, the electronic properties of encapsulated graphene-based devices on different 2D crystals substrate have been revealed. The disulfides materials (here MoS$_2$ and WS$_2$ have been used) have higher carrier mobility than oxides (mica, BSCCO, V$_2$O$_5$ and LiNbO$_3$) which characterized by magnetocapacitance spectra. Although the charge carrier mobility is lower than hBN/graphene/hBN structure, the disulfide crystals substrate is still comparable with early non-encapsulated graphene/hBN devices. The thermal annealing cannot improve graphene/MoS$_2$ or grpahene/WS$_2$ structure quality but instead destroys the atomically flat interface. On the other hand, the charge carrier mobility of oxide materials limits by different surface affinities with graphene. The self-cleaning phenomenon relies on the well adhesion of two flakes. However, the surface affinity is different between graphene and oxides. Oxides are hydrophilic surface and absorb water on its surface. The layer of water stops the self-cleaning processes because graphene is lipophilic. Therefore, graphene-based capacitor on 2D oxide materials is heavily doped and poor in mobility. This suggests the dichalcogenides can serve as a high quality of substrate, but not oxides unless oxide materials are prepared and transferred in water free environment.

In chapter 6, the magnetocapacitance spectra of graphene-hBN aligned capacitor have been studied to understand the fine details of many-body interactions in this electronic system. The superlattice effects can be observed in a reasonable range (bias voltage ±10 V and magnetic field <30 T) while the orientation of graphene-hBN lattice is mismatched within 2 degrees. In this paper, capacitance measurement provides more details than transport measurements in other reports. The QHFM states interact with original LLs and create a self-replica spectrum which is called Hofstadter’s butterfly. The mini-gap suppression at integral fraction of magnetic flex also has been discovered. We contribute the suppression to reverse Stoner transition which causes the ferromagnetism breaking. In higher magnetic field, more mini-gaps have been revealed which creates a hierarchy Hofstadter state. The states (±2, v$_L$), (0, v$_L$) and (±1, ±1) are determined by weaker exchange interaction of the third- generation Dirac fermions at 0-th LLs state. The (±1, 0) gaps collapse which is also due to reverse Stoner transition when Φ > φ$_0$.

Finally, in chapter 7, we demonstrate the graphene-graphene aligned resonance tunneling transistor which is possible for future application. Two graphene stripes are orientated within less 2 degree in lattice alignment and separated by a thin hBN spacer which thickness is about 3 to 5 layers. The electrons on the graphene stripe can tunnel through the thin hBN spacer to
another graphene flake as bias voltage is applied. The electrons have a high possibility to tunnel through energy barrier while the momentum is conserved. In this paper, the differential tunneling current mapping is fully characterized with gate voltage dependency. The resonance tunneling happens at the bias voltage in which the intersection of two Dirac cones becomes linear. Theory simulation is highly consisting with our experiment data. For further confirmation, an in-plane magnetic field has been applied on same devices. The Lorentz force shifts the tunneling electron momentum and causes the shift of the resonance. The experimental results also consist with theory simulation. Based on the experimental data and theory simulation, it suggests the resonance tunneling from double layer graphene transistor which is due to the momentum conservation. Therefore, the twist-controlled graphene resonance tunneling transistors are able to work in room temperature. A RF oscillator for concept-proofing has been made by graphene resonance tunnelling transistor at room temperature. Despite the frequency of the oscillation is at MHz region. The graphene-based oscillator can be further improved for higher frequency if altering substrate to quartz and reducing inductance from the electrical contacts.

In conclusion, the rise of Van der Waals heterostructures indicates another avenue (building structure bottom side up) to explore the fundamental physics by creating new artificial materials and employ 2D materials to future applications. The 2D crystals works like Lego blocks which can be assembled in any sequence with atomic layer precision is realized by modern technology. In this thesis, we reveal how the technologies make this idea possible and demonstrate the potential of utilizing Van der Waals heterostructures. Moreover, this is just a beginning of the future.
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