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Fabrication of Blister-free van der Waals Heterostructure

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Fabrication of Blister-free van der Waals Heterostructure

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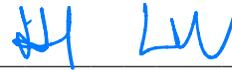
by
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A thesis submitted to Chulalongkorn University,
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To the Faculty of Science, Department of Physics, Chulalongkorn University:

The members of the Committee appointed to examine the dissertation prepared by Kittipat Hiraprayoonpong entitled *Fabrication of Blister-free van der Waals Heterostructure* find satisfactory and recommend that it is accepted.



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ABSTRACT

Van der Waals heterostructure consists of a stack of two or more 2-dimension materials held together by van der Waals force. Such heterostructures allow us to fabricate novel materials by simply stacking various layered materials to create new functionalities as well as observe emergent phenomena which may not exist in the underlying layered materials. In this project, we develop laboratory equipments and recipe for fabrication of blister-free van der Waals heterostructure using pick-up transfer method. Blisters can occur during transferring and stacking 2D material where they could reduce electron mobility. We apply tear-and-stack procedures to create twisted bilayer graphene (TBG) with a controllable twist angle from a single-layer graphene sheet. In particular, we aim at fabricating TBG at a magic twist angle of 1.05° which has been shown to exhibit strongly correlated phases such as superconductivity and Mott insulator. Here we employ two types of polymer, Polypropylene Carbonate (PPC) and Poly(bisphenol A carbonate) (PC), for transfer process. We find that PC polymer improves the yield of blister-free TBG because of a much slower speed during the tear-step, unlike the PPC polymer which requires a sudden tear, causing graphene to damage. In addition, the PC polymer can withstand a temperature up to 180°C , compared to 120°C of PPC, which allows for an effective removal of blisters during stacking process. A complete TBG device is then characterized by optical microscope and atomic force microscope to verify blister-free area on the device. Finally, Raman spectroscopy is employed to confirm the small twist angle of TBG.

Keywords: Van der Waals heterostructure, Twisted bilayer graphene, Raman spectroscopy, Atomic force microscopy

บทคัดย่อ

โครงสร้างหลายชั้นแบบแวนเดอวาลส์ (Van der Waals Heterostructure) สร้างขึ้นจากการซ้อนกันของสารสองมิติจากสารสองชนิดหรือมากกว่าสองชนิด โดยซ้อนกันและยึดติดกันด้วยแรงแวนเดอวาลส์ โครงสร้างดังกล่าวนี้ถูกสร้างขึ้นและเป็นสิ่งที่ให้คุณสมบัติใหม่ ๆ ได้เพียงจากการซ้อนทับกันของสารสองมิติเป็นชั้น เพื่อสร้างคุณสมบัติทางกายภาพใหม่ รวมทั้งสังเกตปรากฏการณ์ที่น่าสนใจที่ไม่มีทางพบในสารสองมิติที่ไม่ได้ซ้อนทับกัน ในโครงการวิจัยฟิสิกส์นี้ เราได้พัฒนาอุปกรณ์การทดลองและวิธีการการสร้างโครงสร้างแวนเดอวาลส์ที่ปราศจากบริสเตอร์ (Blister-free van der Waals Heterostructure) โดยการใช้วิธีการหอบหิ้วและเคลื่อนย้าย (Pick-up Transfer Method) เพราะบริสเตอร์ (Blister) สามารถเกิดขึ้นระหว่างกระบวนการการเคลื่อนย้ายและซ้อนกันของสารสองมิติ ซึ่งจะลดคุณภาพการนำไฟฟ้าได้ โดยเฉพาะอย่างยิ่ง ในโครงการวิจัยฟิสิกส์นี้ ผู้ทำการทดลองมีความตั้งใจที่จะสร้างแกรฟีนสองชั้นที่บิดทำมุมสัมพันธ์กัน (Twisted Bilayer Graphene หรือ TBG) ซึ่งบิดทำมุมสัมพันธ์กันด้วยมุมพิเศษ 1.05 องศา จากวิธีการฉีกและซ้อน (Tear-and-stack procedure) โดยจะทำให้เห็นถึงเฟสที่สัมพันธ์กัน (Correlated Phase) เช่น คุณสมบัติการนำไฟฟ้าแบบยิ่งยวด (Superconductivity) และฉนวนม็อต (Mott Insulator) ในที่นี้ ผู้ทดลองใช้โพลีเมอร์สองชนิด คือ โพลีโพรพิลีนคาร์บอเนต (Polypropylene Carbonate หรือ PPC) และ โพลิบิสฟีนอล เอ คาร์บอเนต (Poly(bisphenol A carbonate) หรือ PC) เพื่อใช้ในกระบวนการเคลื่อนย้ายสารสองมิติ ผู้ทดลองได้พบว่าโพลีเมอร์ PC ได้ผลลัพธ์ในด้านการลดการเกิดบริสเตอร์ของ TBG ได้ เนื่องจากการใช้ความเร็วในการซ้อนสารสองมิติที่ช้ากว่ามากเมื่อเทียบกับของโพลีเมอร์ PPC ที่ต้องฉีกแกรฟีนครั้งหนึ่งอย่างทันทีทันใด ซึ่งนำไปสู่การสร้างความเสียหายให้แกรฟีนได้ อีกทั้งโพลีเมอร์ PC สามารถทนความร้อนได้สูงถึง 180 องศาเซลเซียส ซึ่งสูงกว่าเมื่อเทียบกับโพลีเมอร์ PPC ที่ทนความร้อนได้เพียง 120 องศาเซลเซียส การขึ้นที่อุณหภูมิสูง ทำให้โอกาสการเกิดบริสเตอร์ระหว่างการซ้อนทับสารสองมิติลดลงได้ อย่างมีประสิทธิภาพ หลังจากที TBG สร้างเสร็จสมบูรณ์ TBG นี้จะถูกนำไปตรวจสอบคุณลักษณะเฉพาะโดยใช้กล้องจุลทรรศน์เชิงแสงและกล้องจุลทรรศน์แบบแรงเชิงอะตอม (Atomic Force Microscope) เพื่อใช้ในการยืนยันพื้นที่ที่ไม่มีบริสเตอร์บน TBG และสุดท้าย ผู้ทดลองใช้ผลสเปกโทรสโกปีแบบรามาน (Raman Spectroscopy) เพื่อยืนยันการสร้าง TBG ที่บิดมุมสัมพันธ์กันว่าสำเร็จไปด้วยดีหรือไม่

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Dedication

This senior project is dedicated to everyone who are always besides me
and sharing happiness with each other

Chapter One

Introduction

1.1 Background and Motivation

Nowadays, graphene (denoted as “G”) is one of the most exquisite matter which has excellent conductivity, flexibility and stiffness but only one atom thick. Doing the vdW heterostructure (van der Waals heterostructure) is the making of devices from the individual layers of different 2D material by van der Waals force. In this topic, we are most interested in making vdW heterostructure from graphene and boron nitride (denoted as “BN”.) Making devices from graphene and boron nitride is one of the difficult task due to the size of them and the alignment difficulty. What we have to do is fabricating vdW heterostructure by using transferring process and stack them together as we engineer them. During the transferring process, we will use PC (a.k.a. Poly (Bisphenol A Carbonate)) to pull BN up from substrate before using BN to bring graphene up. The BN flake plays a main role to pull graphene up from the substrate since it has similar crystal structure as hexagon similar to graphene and it is the only one that is able to be used for bringing up and transferring graphene (because we have to exfoliate graphene and put it on the substrate). Finding the suitable procedure to use PC is one of the interesting task to do because normally, people tend to use PPC (Polypropylene Carbonate) because PPC has limitation that cannot be used to fabricate TBG vdW heterostructure properly and reduce the occurred blisters not as well as PC can provide.

Next, everyone mostly focuses on how to make the graphene flakes and BN flake bigger, which they are obtained from exfoliation, because the bigger they are, the easier we can make device for alignment and stacking for fabricating TBG that has to be stacked with two single-layer graphene that are relatively twisted. To find the procedures that increases the yield to obtain the great one and make the devices much easier is an interesting tasks nowadays. Then my motivation is to find the method that makes creating devices easier, including makes BN/G/BN device for laboratory practicing with fundamental procedures and BN/TBG/BN device which is our main aim. Other and most of all, during the transferring process, most of occurred blisters come from hydrocarbon that attached to graphene and BN or even air molecules got trapped. Blisters are often occurred in the bubble-like shape and able to be detect easily by the optical microscope. (Moreover, there is optically unseen blisters which they are able to be detected by using atomic force microscope.) In the scientific industry, we usually want the device that definitively has no blister because we can use the fabricated “device” from the area that is blister-free only, so the occurred blisters are the trouble of us due to increase the difficulty of device fabrication and they reduce mobility of charge carrier, so it is a great task to also find the method reducing the blisters out of the samples to

improve the device quality. If time permits, we will study electrical properties of graphene van der Waals heterostructure later. (Furthermore, one of the interesting phenomena can be found in TBG, which could behaves like superconductor on the very high temperature as 1.05° magic angle of relatively twisted angle is applied for fabrication [1]. This property is very doubtful due to magic-alike stuff, but the device is difficult to be perfectly made which it could be better if we find out the simplest recipe to make one outstanding. Surprisingly, the magical of TBG is its band structure can be changed by relatively twisted them, which implies that their electrical properties can be changed with ease only by twisting them with relative angle.)

1.2 Research Objectives

1. Learn how to make such unique and delicate TBG vdW heterostructure.
2. Find the proper and simplest procedure to make TBG vdW heterostructure by using PC instead of PPC.
3. Try and find the method to reduce the number of blister which occurs during transferring process.
4. Increases the yields of graphene and boron nitride from exfoliation.

1.3 Scope of studies

1. Polymer stacks made from PPC and PC will be employed in order to determine the yield as well as the blister-free area of TBG.
2. Optical microscope, atomic force microscope, and Raman spectroscopy will be used to characterize YBG for both topography and crystal structure.
3. UV ozone, oxygen plasma and thermal annealing will be utilized in order to improve the yield and the size of graphene and boron nitride flakes from exfoliation.

1.4 Expected Outcomes

1. Learn relevant theories during this physics project.
2. Study the logic of the insight of the equipments, experimental methods and scientific process.
3. Obtain reliable recipes for fabricating blister-free TBG vdW heterostructure and exfoliation.

Chapter Two

Related Theories

The theories will be explained further is for the data analysis of this research. They will cover for graphene, Raman spectroscopy and atomic force microscope.

2.1 Graphene

Graphene is a hexagonal lattice made of carbon atom, form as a single layer of atom in two dimensional lattice, which is the basic structural element that mostly found in graphite in the pencil, or even charcoal and carbon-nanotube. It is an allotrope of the carbon in the form of a plane of sp-2 bonded atom with the molecular bond separation distance of 0.142 nanometers. For many layers graphene, such as graphite, they are stacking each other by van der Waals force with the spacing of 0.335 nanometers. It is not only the thinnest ever but also the strongest. As a conductor, it performs greatly as well as copper. A single-layer graphene is almost transparent optically with 97.3% transparent but so dense as no gas atom can pass through it. Yet it is so substantial and such exquisite, it still nowadays is researching and being the prototype that is certain the new technology in the future of humanity, for instance, nigh optically transparent touch screen, light panel and solar cell.



Fig. 1 The person on the left side is Andre Geim and on the right side is Konstantin Novoselov, whom are awarded the 2010 Nobel Prize in Physics for “groundbreaking experiments regarding the two-dimensional material graphene”. Pictures are from www.nobelprize.org.

Historically, Andre Geim and Konstantin Novoselov were awarded the 2010 Nobel Prize in Physics for “groundbreaking experiments regarding the two-dimensional material graphene”. They firstly produced graphene in 2004 by repeatedly peeling the graphite strip with adhesive tape to exfoliate a single-layer graphene, with the analysis of its strength, optical transparency and conductive properties in a paper. Our method we used for the graphene exfoliation in this project based on his experiment and procedures of exfoliation. In 2008, the Manchester team successfully created a 1-nanometer graphene transistor with only one atom thick as 10 atoms across. Novoselov told that it very well could represent the absolute physical limit of Moore’s law, i.e. the perception that the number of transistors on a microchip doubles every two years, and yet the cost of computer is cut in half, which is governing the size reduction and speed growing of computer processor.

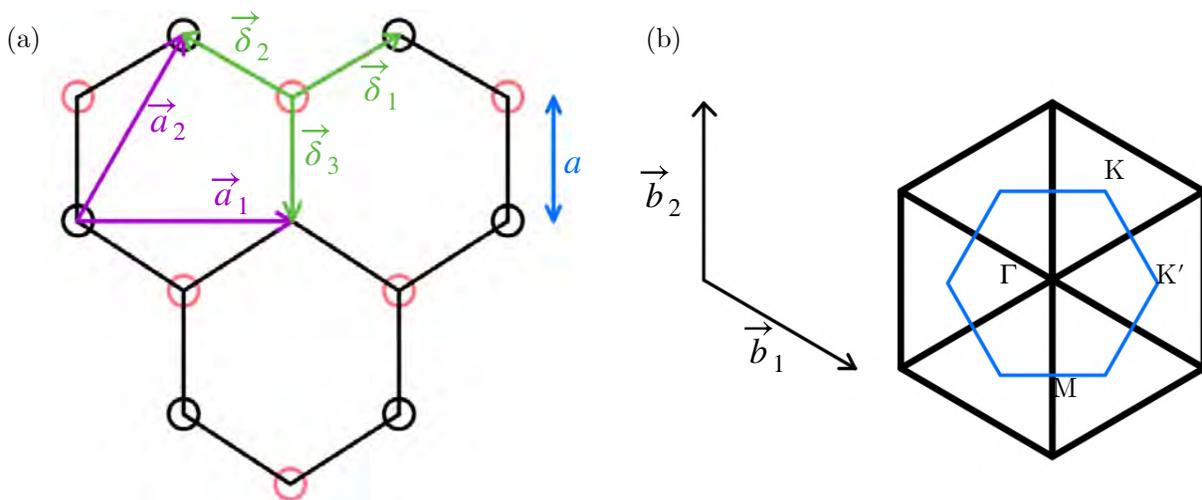


Fig. 2 Graphene structure in real space in (a), and momentum space in (b). In (a), the black circle and red circle represent as A-sublattice carbon atom and B-sublattice carbon atom, respectively. In (b), the first Brillouin zone is represented in the blue hexagon.

In single layer graphene, its one primitive cell contains 2 atoms, A-sublattice and B-sublattice. Each atom has four bonds, one σ -bond with its three nearest neighbor atoms and one π -bond which is oriented out of the plane. To form the unit cell, it can be written by using the lattice vector as below:

$$\vec{a}_1 = \sqrt{3}a\hat{x}, \quad \vec{a}_2 = \frac{\sqrt{3}}{2}a(\hat{x} + \sqrt{3}\hat{y}) \quad (1).$$

Around one chosen carbon atom in graphene, there are three nearest neighbor atoms which has the displacement vector as followings:

$$\vec{\delta}_1 = \frac{a}{2}(\sqrt{3}\hat{x} + \hat{y}), \quad \vec{\delta}_2 = \frac{a}{2}(-\sqrt{3}\hat{x} + \hat{y}), \quad \vec{\delta}_3 = -a\hat{y} \quad (2).$$

Therefore, in the reciprocal lattice, the vectors that used to define with respect to the triangle lattice is spanned as Eq. (3).

$$\vec{b}_1 = \frac{2\pi}{3a} \left(\hat{x} - \frac{1}{\sqrt{3}} \hat{y} \right), \quad \vec{b}_2 = \frac{4\pi}{3a} \hat{y} \quad (3)$$

where a is the molecular bond length (0.142 nm), and \hat{x} and \hat{y} are the unit vector in the real space.

Consider the Hamiltonian with the ability of the electron to hop to the nearest neighbor, the energy for the single layer graphene can be determined and written as Eq. (4):

$$E = \pm t \left| 3 + 2 \cos(\sqrt{3}k_x a) + 4 \cos\left(\frac{\sqrt{3}}{2}k_x a\right) \cos\left(\frac{3}{2}k_y a\right) \right|^{\frac{1}{2}} \quad (4)$$

where t is the hopping parameter which is 3 eV, a is molecular length of 1.42 angstroms and k_x and k_y are the component of the k-space (i.e. momentum space) of the x-axis and y-axis, respectively. Therefore, in the momentum space, we can see from the diagram in the Fig. 3 as the labelled point of K, K', Γ and M point, which we will use to show the band structure of the graphene as Fig. 3.

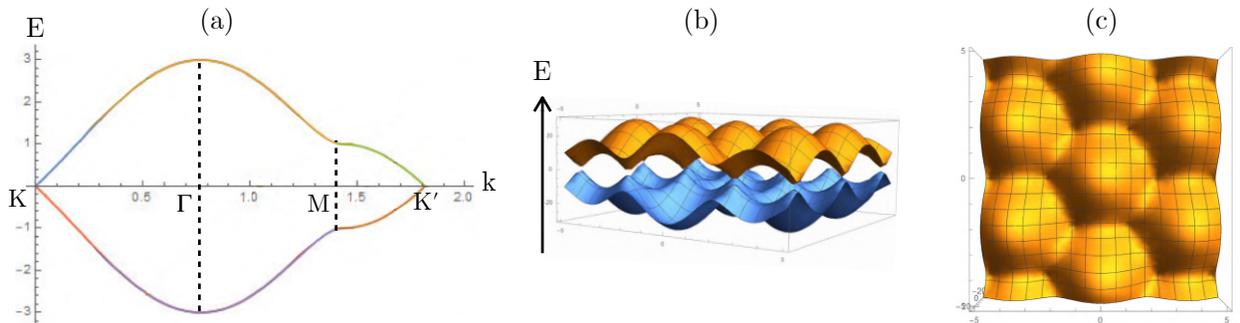


Fig. 3 (a) Graphene band structure of each point in reciprocal space with the wave vector k , where $k = \sqrt{k_x^2 + k_y^2}$. (b) The Dirac cone in the dispersion relation between energy E and the component of wave vector k_x and k_y as Eq. (4). (c) The top view of the 3D graph in (b), showing that it is hexagon, satisfying the reciprocal lattice of the graphene.

Talking about bilayer graphene, in nature, the graphene layers are A-B stack or called “Bernal stack”, with there can be two possibilities of stacking which are A'-B stack and B'-A stack, with separation distance between layers of 0.4 nanometer. One unit cell of bilayer graphene contains 4 atoms, labelled as A, B, A' and B' atom. In this project, we will focus on man-made twisted bilayer graphene with the magic angle of twisted bilayer graphene.

One of the optical determination of how we successfully fabricate the twisted bilayer graphene is Moiré pattern by using transmission electron microscope (TEM) as the electron diffraction patterns. Due to the hexagonal crystal structure of single-layer graphene, if both of them are stack together, it could create the periodic

pattern or none that could be partially or obviously recognized, depending on the relatively twisted angle between layers of single-layer graphene, which is being the artful as textiles or unfortunately annoying distractions in digital image.

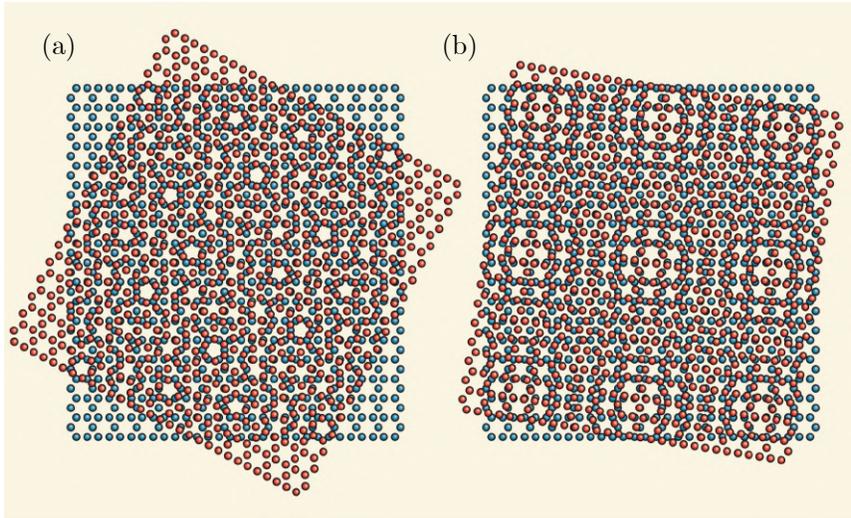


Fig. 4 (a) and (b) are the two layers of graphene are overlapping at an angle of 27.8° and 9.0° , respectively, which in (a) has more number of atoms per period than in (b). Hence, they are not completely repeated, as it is formed “quasi-crystal”. This crystal structure simulation image comes from the paper entitled *Graphene moiré mystery solved?* [11].

In van der Waals heterostructure, specifically in this project of twisted bilayer graphene, a commensurate Moiré superlattice, i.e. a periodic structure of layers of two material which in this case is two layers of graphene, will only form when satisfying the Eq. (5),

$$m\vec{a}_1^{top} + m\vec{a}_2^{top} = m'\vec{a}_1^{bottom} + n'\vec{a}_2^{bottom} \quad (5)$$

where \vec{a}_1^{top} , \vec{a}_2^{top} , \vec{a}_1^{bottom} and \vec{a}_2^{bottom} are primitive lattice vectors for the top layer and bottom layer of 2D material respectively, and m , n , m' and n' are integers. Therefore, we can use the twisted angle θ , or another name of “commensurate angle” as the representation of commensuration when θ satisfies Eq. (6),

$$\cos \theta = \frac{3p^2 + 3pq + q^2/2}{3p^2 + 3pq + q^2} \quad (6)$$

where p and q are two coprime positive integers. We will say that the structure is commensurate when the twisted angle is made some translation symmetries are retained. Hence, commensurate superlattice, i.e. the Moiré pattern with precisely periodic translation symmetry, occurs on only “commensurate angle”. Otherwise, the quasi-crystal is occurred, which is almost like it has periodic pattern but really it is not. Nevertheless, incommensurate superlattice, i.e. the quasi-crystalline pattern, lacks translational symmetry in real space but preserving the rotational symmetry. Restrictedly, we use the twisted angle within the range of $(0, \pi/3)$ radian due to the crystal symmetry of the graphene lattice.

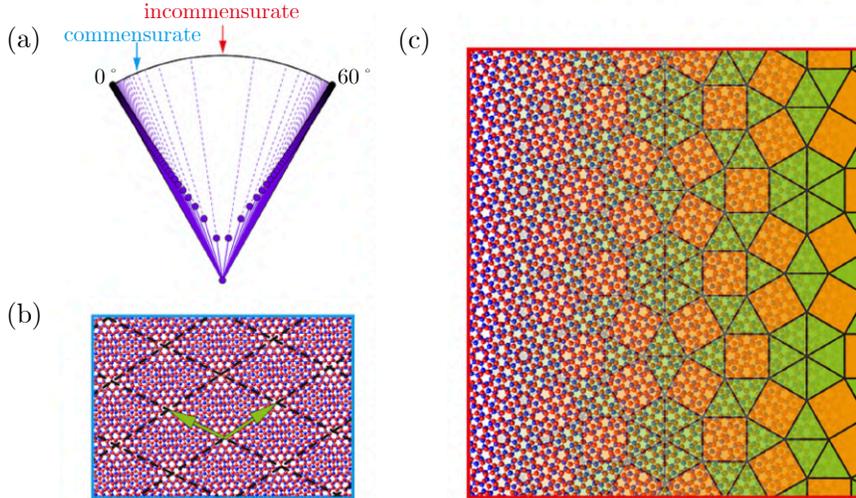


Fig. 5 (a) The distribution of possible commensurate angles which represents as dash line to form commensurate twisted bilayer graphene where assuming $q = 1$ in Eq. (6), while the length of solid line represents as the Moiré period in the logarithmic scale. (b) The commensurate superlattice of twisted bilayer graphene with twisting angle of 7.34° , indicated by the blue arrow in (a), shows the Moiré pattern with precisely periodic translational symmetry all over sample. Green arrows are the Moiré reciprocal lattice vector of the twisted bilayer graphene. These images are from the paper entitled *Quasicrystalline 30° Twisted Bilayer Graphene as an Incommensurate Superlattice with Strong Interlayer Coupling* [17].

At some commensurate angle, it is magic angle which yields the surprisingly magical phenomena for the twisted bilayer graphene as twisted bilayer graphene behaves as superconductor on 1.05° relatively twisted bilayer graphene. Additionally, there are tons of magic angle that physicists have been found out. The reason we choose this 1.05° magic angle twisting is because it is the first magic angle that superconducting state of twisted bilayer graphene occurs.

For this project, we aim to fabricate twisted bilayer graphene specifically with 1.05° twisting due to the fact and researches that TBG vdW heterostructure, i.e., the device, behaves as superconductor. Hence, the theories behind still are the discussion now but various of models are used to explain this such unique phenomena. What is interesting is the band structure (which is the dispersion relation between the energy and the value of k in the momentum space) of the twisted bilayer graphene is changed as the twisting angle is changed. It implies that its electrical properties are changed as what angle we twist and fabricate. Such this substantial phenomena leads to the ability to change its electrical properties just by twisting the two-layer of graphene relatively with specific magic or non-magic angle, whether how we want, and it will be superconductor or else.

2.2 Deterministic Placement Method for Fabrication

From literature review, entitled *Recent progress in the assembly of nanodevices and van der Waals heterostructure by deterministic placement of 2D material*, they explained how to transfer 2D material to fabricate and create the heterostructure as they have been engineered. There are tons of methods for transferring and fabrication but we will use van der Waals pick-up transfer method in this project.

Van der Waals pick-up transfer method is one of the best method that suits the purpose of this project the most, to make the blister-free device, and it gives the highest yields of making the fabricated device or transferring 2D material with the highest cleanliness but trading with easiness and speed. It is the method that takes time most along with other methods. This method is nowadays scientists and researchers use the most because of high-cleanliness. Blister-free devices have the very great electron mobility, which means it is better to conduct the electrons more than devices with blisters. The recipe of van der Waals pick-up transfer method are further explained as below:

1) The polymer stack, i.e. the polymer layer that is at the outer surface that is used to pick up the target 2D material, with hexagonal boron nitride flake on the PPC polymer is mounted with micromanipulator to precisely control the movement of it for excellent alignment.

2) Align them perfectly and polymer stack is lowered until the BN flake contacts the target flake.

3) Slowly lift up the polymer stack to pick up the target flake from the substrate.

4) Align precisely with the target substrate and coordinate as we designate.

5) The stacked flakes are lowered down to the target substrate.

6) Release them gently to make PPC cover the transferred stacked flakes on the new target substrate.

These recipes will be used and adapted to be suitable with this project and fabrication goal of blister-free fabricated devices.

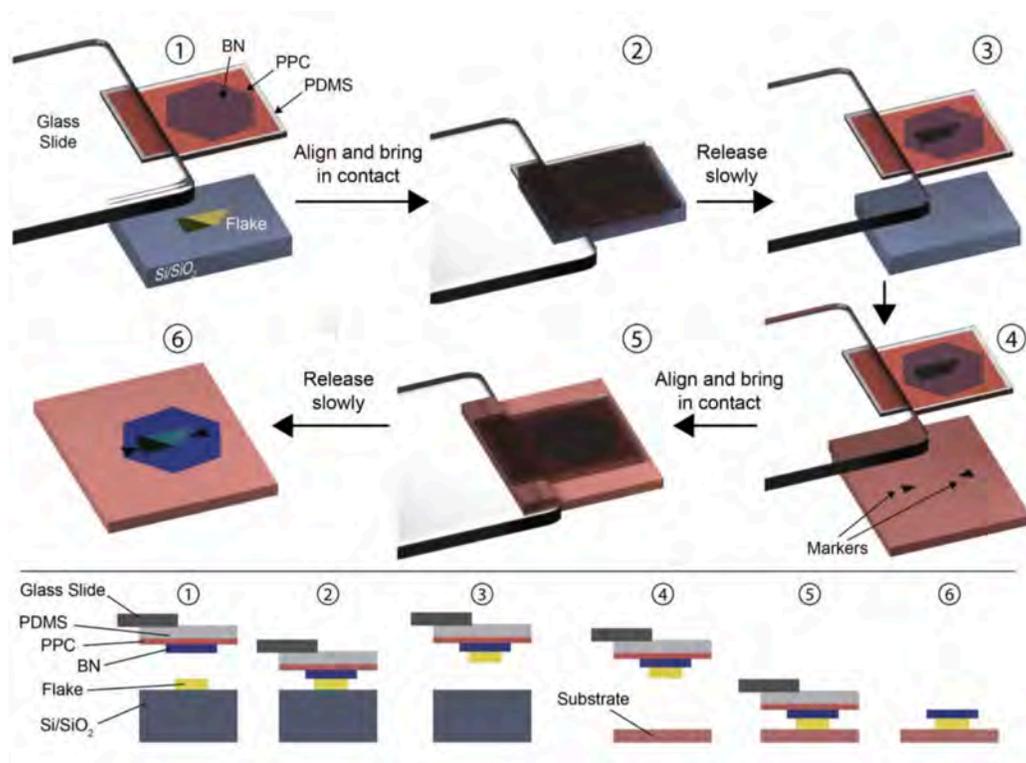


Fig. 6 The van der Waals pick-up transfer method. The step-by-step recipe follows the sequence of further explanation above. This image comes from the paper entitled as *Recent progress in the assembly of nanodevices and van der Waals heterostructures by deterministic placement of 2D materials* [4].

2.3 Reliable Exfoliation of Large-Area Graphene Flake

This section is from the literature review, entitled *Reliable Exfoliation of Large-Area High-Quality Flakes of Graphene and Other Two-Dimensional Materials* [7]. This paper will be used to be referred and the based-on adaptation for the new procedures to increase the yields of exfoliation. Their modified exfoliation is adding the annealing process, heating the substrate with tape at 100°C for 2 minutes and the oxygen plasma cleaning. Their outcomes is surprisingly excellent. Comparing to the standard exfoliation, i.e. no annealing process added, the exfoliated graphene size varies from 10×10 to 20×20 microns, but for modified exfoliation, they obtained the monolayer graphene in size of maximum width and length of 385×510 microns, leading to the conclusion that oxygen plasma cleaning and annealing process play a major role of the reliable and high-quality exfoliation which the yields are increased significantly. These recipes will be added and adapted to this project to make the exfoliation more reliable and being the high-quality exfoliation.

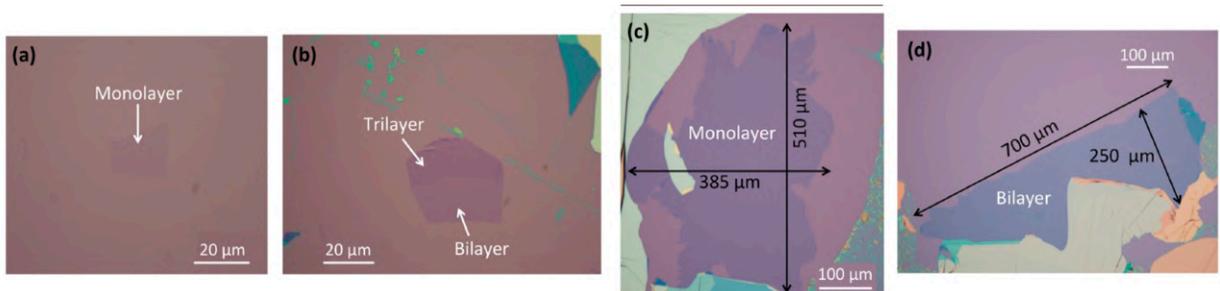


Fig. 7 These are the optical microscopy images from the exfoliation. Here, (a) and (b) are the exfoliated graphene flakes obtained from standard exfoliation, and the substrates are cleaned by oxygen plasma method. (c) and (d) are the exfoliated graphene flakes obtained from the modified exfoliation, adding the annealing process, which are exceptional results as they are significantly bigger. These images are from the paper, *Reliable Exfoliation of Large-Area High-Quality Flakes of Graphene and Other Two-Dimensional Materials* [7].

2.4 Interface Cleaning

We had reviewed this paper, *Cleaning interfaces in layered materials heterostructures* [15], which is talking about how they clean the sample and suspended the blisters between the interface layer. Their recipes are similar to the procedures of this project that is used with PPC polymer stack but they use PC polymer stack. It follows to the pick-up transfer method, doing at 40°C . But when the graphene is encapsulated, i.e. articulate with top and bottom BN flake, they do stack at 180°C with the tilted PC polymer stack to easily control and making the stacking being rolled with more smoothness as the CF in Fig. 8 makes the blister escape and rolled up, leading to the reducing of the blister occurrence probability. At such high temperature, hydrocarbons are escaping out and sticked to the sample less than at low temperature. However, they did not tell about how long they take to fabricate the device. Additionally, they show to roll and push the occurred blister on post-fabrication by using the advantage of the CF as it is able to push and roll the blister

to let it move, implies that even the hydrocarbon is trapped as blister form, it is able to move by pushing as using CF of the PDMS and PC.

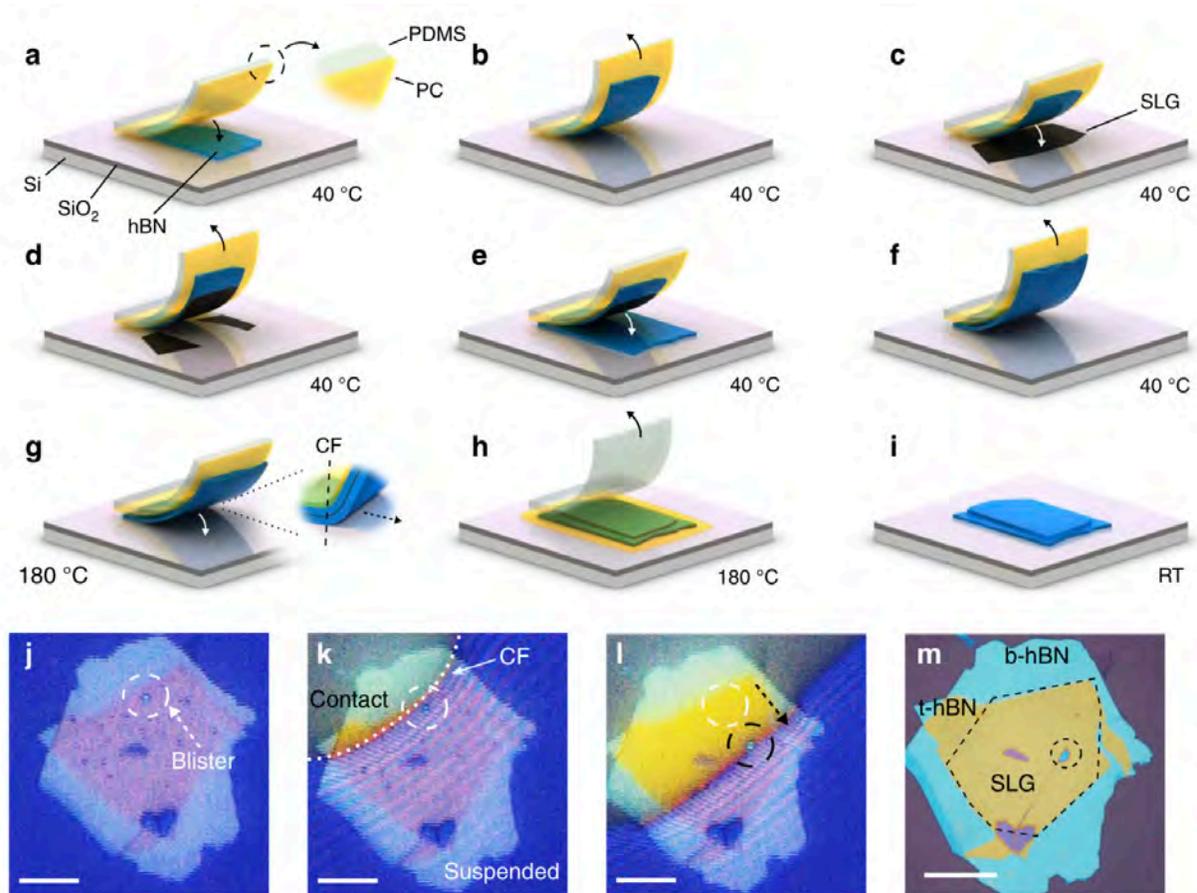


Fig. 8 The schematics and captured images of the sample cleaning process. (a) and (b) are using the PC polymer stack to pick up the BN flake (in this image, it labelled as “hBN”). (c) and (d) are using the picked-up BN flake in (a) and (b) to bring the single layer graphene (SLG) up from the substrate. (e) and (f) are the process to encapsulate graphene as the BN-flake-sandwich-like and pick-up the bottom BN flake. All of the process from (a) to (f) have done in 40 °C. (g) is the process of pushing the blister at 180 °C, as shown in optical images in (j), (k) and (l), as the blister is being pushed by using the advantage of CF rolling it. (h) shows that the PDMS is lifted up at 180 °C to adhere the PC on the substrate. And the device is cleaned to remove the PC by using chloroform in (i). These schematics and optical images are from *Cleaning interfaces in layered materials heterostructures* [15].

2.5 Raman Spectroscopy

Raman spectroscopy is one of the spectroscopic technique used to determine vibration mode of molecules and based on Raman scattering, which is the process occurs when incident light that we use in the equipment interacts with molecular vibration in the sample that we would like to test. Hence, the Raman scattering is the light that is scattered as the very small portion compared to the Rayleigh scattering, as the elastic process. Then the Raman scattering process is needed to amplify the intensity since it is the very tiny occurrence. One of the method they use is surface-enhanced Raman spectroscopy, a.k.a. SERS. The mechanism how SERS works still is a debate nowadays. By the way, it is a technique that use the

absorption of molecule of the rough metal surface, or by specific nanostructure, which they can be enhanced in the factor of 10^{10} to 10^{11} approximately, which means that just one molecule can be used for spectroscopy. It can be detected from the color change from Raman scattering process and each sample has its own characteristic which does find out from spectroscopic detection. Moreover, wavenumber (in the program, it is labelled as “Raman Shift”) is used to plot the graph with the intensity of Raman scattering, says “count”, because they are linearly dependent to the energy and excitation wavelength.

For graphene, its characteristics that we always see are called G-band and 2D-band. (We will not explain about the D-band because it is not shown due to the crystal symmetries in the pristine graphene. Therefore, 2D-band is the second-order overtone of D-peak.) The 2D-band is always allowed because the second scattering in the process is the inelastic scattering from a second phonon either both on a single electron/hole or on an electron/hole pair. Most of all, it can be seen in the Raman spectroscopy at the wavenumber around $2,690\text{ cm}^{-1}$, based on 532 nm -green light laser. Another mentioned peak is G-band, a primary in-plane vibrational mode, which is seen at the wavenumber around 1580 cm^{-1} , based on the citation that uses 532 nm -green light. By the way, from the sample, we will see the peak from boron nitride (denoted as “BN”) since we fabricate device by using BN at around $1,365\text{ cm}^{-1}$ for 532 nm -green light laser but it is not significant for this research because it doesn’t tell anything further about the fabricated devices.

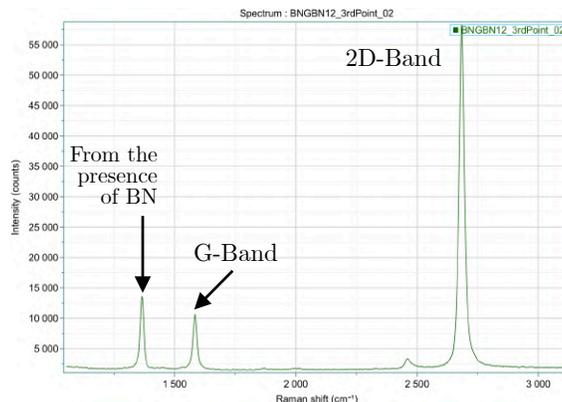


Fig. 9 This graph is the data from BNGBN12, shows the G-band and 2D-band as the relation between the intensity of Raman scattering and the wavenumber in unit of cm^{-1} .

Fortunately, we use Raman spectroscopy for purposes: identification of the number of layer of the exfoliated graphene and the success of fabrication of twisted bilayer graphene that we mainly aim to do. Furthermore, we can truly identify the number of layer of the exfoliated graphene by simply analyze the characteristic of the obtained graph that is significantly difference between the intensity of the Raman scattering and the wavenumber as the Fig. 9. Also, the ratio between G-band and 2D-band can briefly categorize the number of layer of the exfoliated graphene. For the single layer graphene, the 2D-band will have much higher intensity than the G-band. For the natural bilayer graphene and twisted bilayer graphene, the 2D-band and G-band will have similar intensity. And more than 3-layer graphene, the G-band will dominate. Last but not least, we can identify the success of fabrication of twisted

bilayer graphene from the characteristic of the obtained graph. If it is the twisted bilayer graphene, the graph will be different from the natural bilayer as shown in Fig. 11. [8].

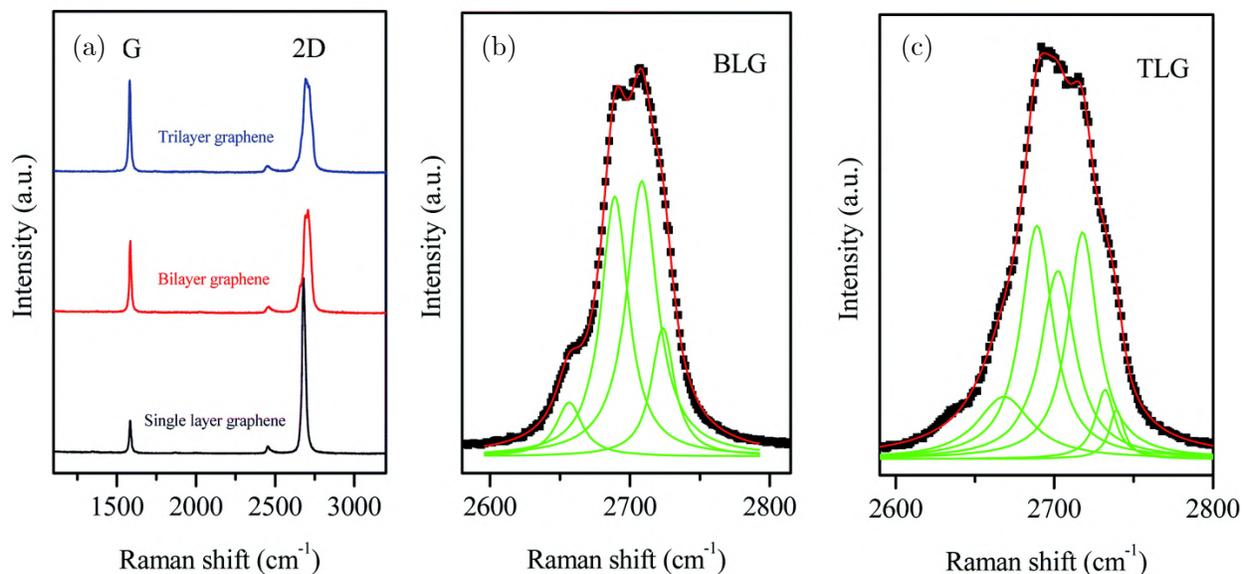


Fig. 10 (a) The ratio between the G-band and 2D-band of single layer graphene, bilayer graphene and trilayer graphene. (b) The characteristics of the 2D-band of the bilayer graphene. (c) The characteristics of the 2D-band of the trilayer graphene. This image is from the article of *Tuning the electrical properties of exfoliated graphene layers using deep ultraviolet irradiation* [8].

From relevant literature review, the natural bilayer graphene and man-made twisted bilayer graphene show the different characteristic of Raman spectroscopy [2]. This will be one of the simple way to verify the success of twisted bilayer graphene fabrication due to we always have to check the number of graphene layer on the overlapping area and non-overlapping area after fabrication.

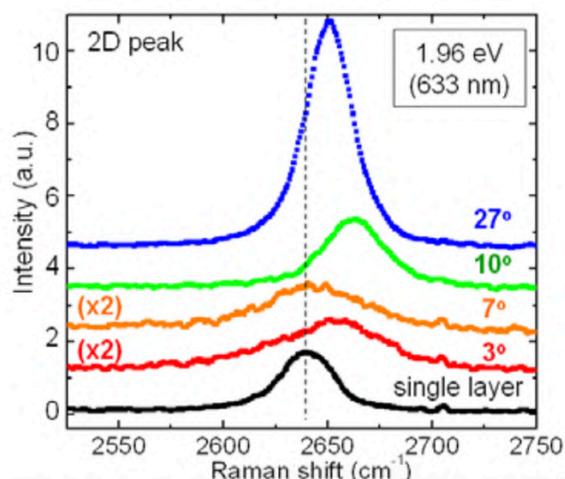


Fig. 11 The characteristic comparison between single layer graphene and twisted bilayer graphene at several twisting angle. This image is cited from the paper entitled *Raman Spectroscopy Study of Rotated Double-Layer Graphene: Misorientation-Angle Dependence of Electronic Structure* [2].

2.6 Atomic Force Microscopy

Atomic force microscopy (AFM) is the technique that scan by using mechanical probe and the optical system to detect the tips's deflection of the surface of the sample, then analyze the obtained data for measurement of the sample's profile, visualizing data of the surface in the atomic resolution as a nanometer scale. It can be used to measure the sample's stiffness, topography and manipulation (i.e. change the properties of the sample as scientists want to). In this research, we may use the AFM to see the roughness of the fabricated device that there are unseen-by-the-naked-eye blister or not.

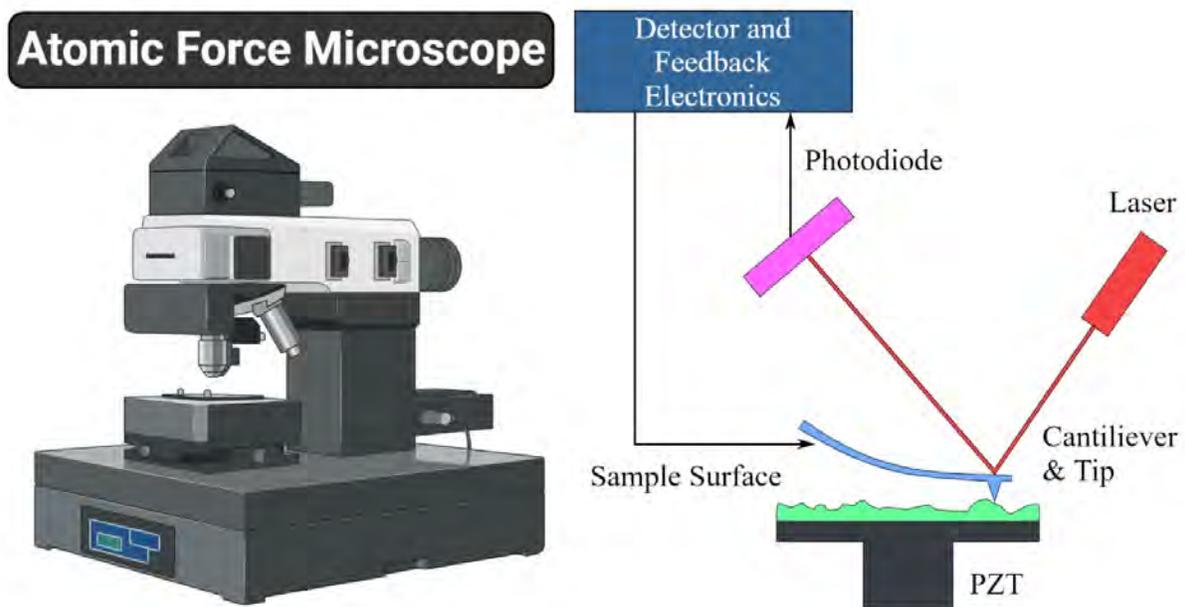


Fig. 12 The atomic force spectroscopy. This picture source is <https://microbenotes.com/atomic-force-microscope-afm/>.

Chapter Three

Experimental Method

3.1 Graphene / Hexagonal Boron Nitride Exfoliation

The procedures of the exfoliation for graphene or hexagonal boron nitride are as followings:

1) The graphite piece is put on the special tape which made for exfoliation purpose, and the tape with the graphite piece is rolled on the edge of the table to make the layers of graphite peeled off from the graphite piece. (In hexagonal boron nitride (hBN or BN) exfoliation, BN big flake is used instead.)

2) Take out the graphite piece from the tape and redo the first step but changing the position around the first spot you did to put down the graphite piece, making the area of the peeled-off graphite around 0.8 cm width and height, respectively. And make it the same but do it oppositely, as Fig. 13. (For BN exfoliation, use the BN big flake instead and making the area of the peeled-off BN flake around 0.3 cm in width and height instead, respectively, following the Fig. 13.

3) Stick the tape of one end to the opposite end as Fig. 13, and align the tape that makes the peeled-off graphene, or peeled-off BN flake, of both side to not overlap themselves. Then peel the tape off from each other sides, and repeat this step 2-4 times to make the number of graphene / BN has area density much enough on the tape to use in the next step.

4) Clean the substrate by oxygen plasma for 10 minutes to use the substrate for exfoliation in the next step. (The chamber of plasma etching must be cleaned before use. Be sure to always take note about how long you clean the substrate and how much oxygen gas pressure you use each time.)

5) Slowly adhere and roll the tape with exfoliated graphite or BN on the substrate, silicon wafer, simultaneously by using the flat-head tweezer. Then press the tape on the substrate hardly by the eraser that is big enough and cover the whole substrate surface. After that, leave it for 5 minutes.

6) The substrate with tape sticked on is heat on hot plate at 100°C for 2 minutes.

7) The tape is slowly peeled off from the substrate, and keep the sample (referred as the exfoliated graphene or exfoliated BN on the silicon wafer) in the tray and put them in the desiccator to control the moisture for not damaging and making the sample unusable.

8) The sample is examined and the graphene flakes are mapped optically by using the microscope. All usable flakes are almost transparent which they will be a little bit more grey tone relative to the substrate observed color and are big enough, as 20 microns width and height or more, respectively. To capture the data, “Rising View” program is being used on the connected personal computer which

connects to the capture camera attaching on the microscope at 5, 10, 20, 50 and 100 times object lens magnification, respectively, and the coordinate of the graphene flakes is recorded to be used later when you need the usable flake with suitable BN flake.

NOTE All of the laboratory detail must be recorded. Note-taking is necessary for the case you want to later check and repeat. In case it fails, you will know the cause of troubles and later settle them. For the old method of exfoliation, we clean the substrate by UV ozone for 5 minutes and the sixth step (annealing) is undone. The difference of results between old and new method will be presented later.

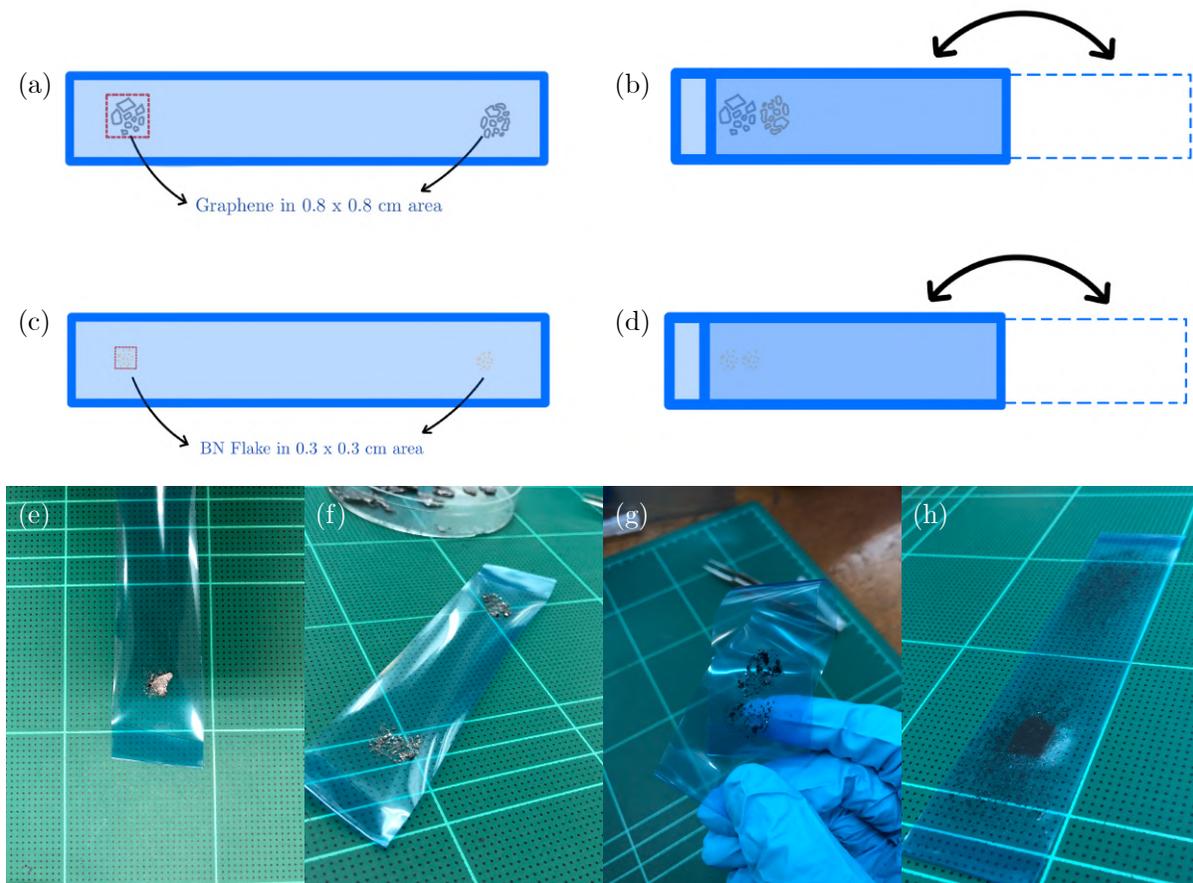


Fig. 13 (a) and (c) The location to put graphite flake / BN big flake on several times on the tape for exfoliation preparation. (b) and (d) The position to stick the tape to exfoliate graphene. Be sure not to overlap them. (e), (f), (g) and (h) show the graphene exfoliation step by step in actual taken photos.

3.2 Procedures of Making PPC Polymer Stack

The recipes of making PPC polymer stack are as explained below:

1) The glass slide is wiped by delicate task disposable wiper to remove the dusts and make it completely clean.

2) The PDMS (a.k.a. Polydimethylsiloxane), approximately 1.5×1.5 millimeter size, is put on the glass slide on the middle of the width side and away from the width side for approximately 1 centimeter.

3) Stick the tape and roll the tape around the PDMS to make the tape stick to the glass slide. Then cut the tape and the result will be as Fig. 14.

4) Clean the glass slide that got from step 3 by UV ozone for 5 minutes. (Make sure that the chamber of UV ozone is cleaned before use.)

5) Drop the filtered PPC on the PDMS area for a few drops and spin it at 1,500 rpm for 30 seconds.

6) Heat the glass slide which is cleaned and well-prepared with PPC covered on tape and PDMS (referred as “PPC polymer stack”) at 100°C for 5 minutes after finish spinning.

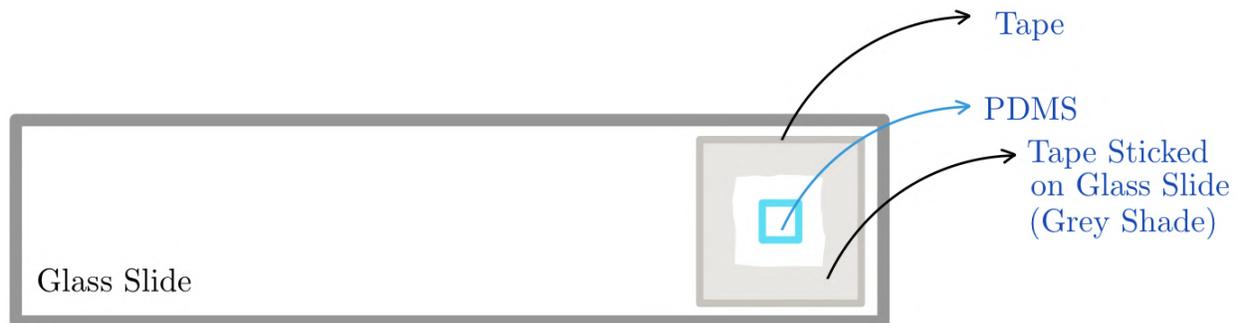


Fig. 14 The schematic of prepared glass slide that has PDMS and secured by the tape on it.

3.3 Procedures of Making PC Polymer Stack

Later on, we will use the PC polymer stack for fabrication because of the limitation of the PPC polymer stack from using the higher temperature that melt the tape. The method of making the PC polymer stack are as followings:

1) The glass slide is wiped by delicate task disposable wiper to remove the dusts and make it completely clean.

2) The PDMS (a.k.a. Polydimethylsiloxane), approximately 1.5×1.5 millimeter size, is put on the glass slide on the middle of the width side and away from the width side for approximately 1 centimeter.

3) A few drop of filtered PC is dropped on a glass slide and immediately scrape off by using the surface of the another glass slide to make the PC spread out widely, flat and as smooth as possible to not be the optical problem as it may make the light from the microscope diffracted and disturb during fabrication process.

4) The scrapped PC is lightly cut as a square to make a streak and pulled it up by using the prepared transparent square sticker which is bigger than the scrapped and prepared PC with the square hole bigger than the size of the PDMS (which should be around 4.0×4.0 millimeter) sticks to the scrapped and prepared PC at the center of it. Then pull them up very slowly or they may broken.

5) Lightly and slowly Put the prepared transparent square sticker with the pulled-up prepared PC on top of the PDMS on the glass slide and press the sticker around by tweezer to seize and hold the PC in place by the sticker's glue. This successful made one is called “PC Polymer Stack”.



Fig. 15 (a) The schematic of prepared PC polymer stack. (b) The prepared PC polymer stack. (c) The perfectly scarp-off PC.



Fig. 16 The schematic of the difference between PPC polymer stack and PC polymer stack.

3.4 Device Fabrication

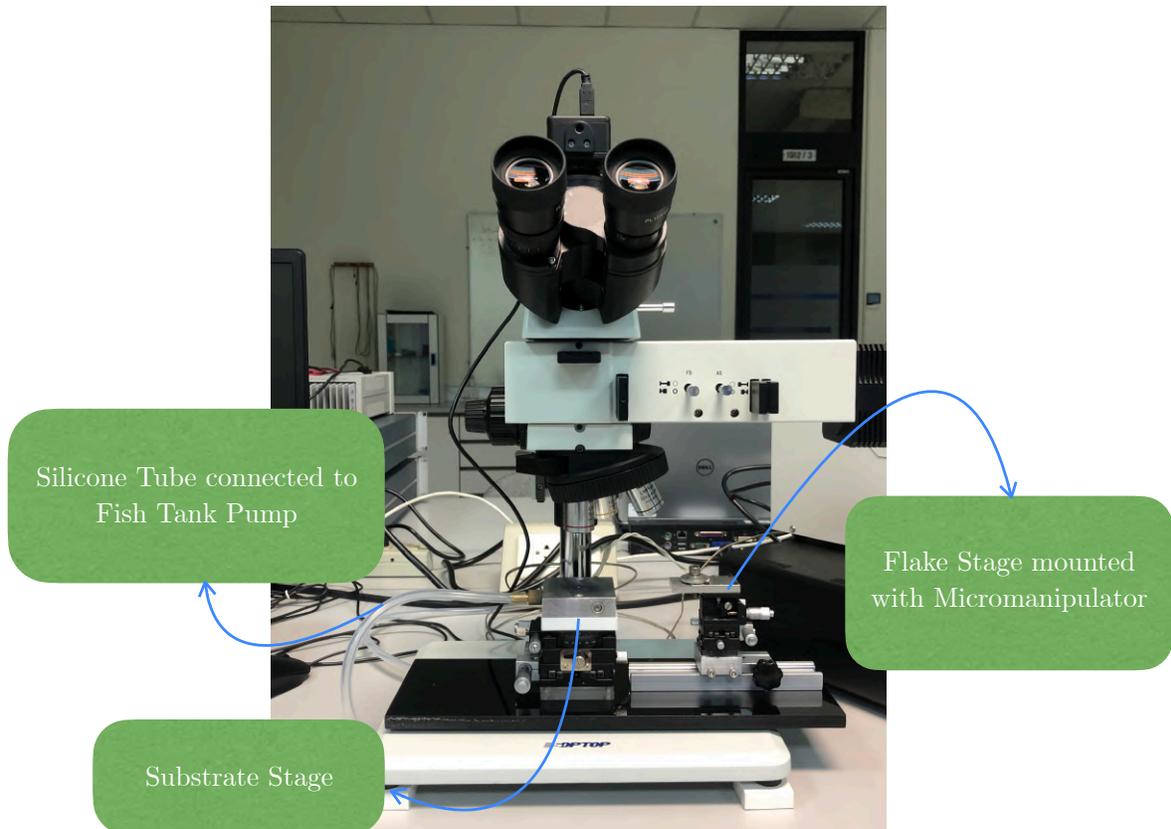


Fig. 17 The transferring stage for van der Waals heterostructure fabrication. The micromanipulator is tilted infinitesimal as the washer is inserted to make the polymer and the substrate start contacting on the left side of the contacting area. The silicone tube is connecting to the modified fish tank pump to make the vacuum suction to the substrate.

3.4.1 Pick Up the Hexagonal Boron Nitride Flake



Fig. 18 The capturing microscope to recheck the result in higher resolution.

From the BN exfoliation, the BN flakes now are on the substrate, which we had recorded the coordinates and captured the image to decide which flakes are usable. It is necessary to recall them and choose one flake that is the most suitable with the proper chosen graphene flake. The procedures of picking up the BN flake are as followings:

- 1) The substrate that has the chosen and usable BN flake is set up on the transferring station, at the center of the hole located on the center of the transferring station. This hole plays a role as the vacuum suction to hold the substrate in place, and computer is used to capture the video of all the process you make devices.

- 2) Mount the PPC/PC polymer stack to the micromanipulator and use the optical microscope to align them perfectly. Then the substrate is baked at 60°C until the BN flake is brought up from the substrate successfully.

- 3) Slowly move the PPC/PC polymer stack down to make BN stick to PPC (if you use the PPC polymer stack) or PC (if you use the PC polymer stack). Alternatively, it is different between PPC polymer stack and PC polymer stack.

- 3.1) If you use the PPC polymer stack, stop moving down when you see the PPC contact area full on the 5 times objective lens magnification microscope sight. Then leave them for 5 minutes.

- 3.2) For PC polymer stack, simply stop when the contact area is passing the target flake for the three-quarter of the display from the camera on the 5 times objective lens magnification sight.

4) The fourth step is slightly different for the PPC polymer stack and PC polymer stack.

4.1) For PPC polymer stack, raise the PPC polymer stack expeditiously to bring the chosen BN flake up from the substrate. (It will be like you snap out of it.) Then turn off the heat.

4.2) For PC polymer stack, right after the third step, raise the PC polymer stack on the suitable speed, not too slow and not too fast. If it is not brought up, repeat the third and fourth step.

5) Check and capture the picture of the BN flake on the PPC/PC after finishing the process by the optical microscope at 5, 10, 20, 50 and 100 times objective lens magnification, respectively. If it is not usable anymore, find the new usable one and redo all of these steps.

3.4.2 Stacking BN with Graphene (and Doing Twisted Bilayer Graphene)

These procedures should be followed exquisitely and precisely. The recipe of fabrication twisted bilayer graphene are started as below:

1) The substrate that has the chosen and usable graphene flake is set up on the transferring station, at the center of the hole located on the center of the transferring station. This hole plays a role as the vacuum suction to hold the substrate in place, and computer is used to capture the video of all the process you make devices.

2) Mount the PPC/PC polymer stack which has the suitable BN flake (The one we obtained from 3.4.1) to the micromanipulator and use the optical microscope to align the graphene flake and the BN flake perfectly in half at the 20 times magnification sight. (It is very important to align it in half at the right orientation of the graphene flake structure.) Then the substrate is baked after this at 60°C.

3) Slowly move the PPC/PC polymer stack down the halfway to recheck the alignment of BN and graphene. (To roughly check that it is halfway, to you can do it by adjust the focus of the microscope and make it focus on the halfway of the distance between graphene and BN. It is measurable roughly by counting the number of round we spin the fine focus.) Repeat the halfway moving down process 4 - 6 times until they are very close to each other. When it appears the Newton's ring on the on-screen monitor (i.e. the diffraction ring), move down the PPC/PC polymer stack more slowly to make the graphene and BN getting closer. When BN is almost stacking on graphene (we can see it on the monitor that when BN almost stacks on graphene, the boundary of the contact area between PPC/PC and substrate is moving toward the sample), stop moving down and leave it for a while, then the polymer will move down by itself a little in the micron scale. After that, rechecking is needed as if it may stop moving down by itself. If it is really stopped, increase the temperature of the heater 1°C or moving it down manually but just a very-little-distance to make it continue stacking. (This process could take time for 20 - 30 minutes to prevent the occurrence of the blister.) After this, the method between PPC polymer stack and PC polymer stack is just slightly different.

3.1) If you use the PPC polymer stack, repeat these until the boundary of the contact area passes the area around the target flake (5-10 microns radius surrounding the target flake and make sure that the temperature is not more than 90 ° C), then the PPC polymer stack is able to be moved down quickly. Stop moving down when you see the PPC contact area full on the 5 times objective lens magnification microscope sight. Then cool down them to 60°C. After the temperature reaches 60°C, leave them for 5 minutes.

3.2) For the PC polymer stack, also repeat the heating-and-making-it-move-down- by-itself process until the boundary of the contact area passes the target flake for 5-10 microns and the temperature reaches 90 ° C. Then immediately follow the fourth step.

4) The fourth step is different for PPC polymer stack and PC polymer stack.

4.1) For PPC polymer stacks, raise the PPC polymer stack expeditiously to bring up the used BN flake and the target graphene flake as they are stacking, from the substrate. (It will be like you snap out of it.) Check the result as if the graphene flake is torn apart in half. If it is failed, repeat all of the steps, starting from picking up the BN flake on 3.4.1)

4.2) For PC polymer stack, raise the PC polymer stack on the suitable speed, not too slow and not too fast. If it is not brought up, repeat the third and fourth step. If it is successful, we will see the graphene flake being torn apart in half. If it is failed, repeat all of the steps, starting from picking up the BN flake on 3.4.1)

5) Rotate the substrate stage on the angle we want to twisted them relatively. (In this research, we mostly aim for 1.05 ° twisted bilayer graphene. But we may change and consider using the other magic angle we twist later) After that, repeat from the second step to the fourth step but using the same PPC polymer stack or PC polymer we use previously which is now having the BN on top of the graphene flake that we obtain from the third and fourth step before.

6) The BN-Twisted Bilayer Graphene on the polymer stack is used to capture the picture by the optical microscope at 5, 10, 20, 50 and 100 times objective lens magnification, respectively. If it is found out that is broken, find the new usable flake of BN and graphene and redo all of these steps from 3.4.1.

3.4.3 Device Stacking

1) The substrate that has the chosen and usable BN flake is set up on the transferring station, at the center of the hole located on the center of the transferring station. This hole plays a role as the vacuum suction to hold the substrate in place, and computer is used to capture the video of all the process you make devices.

2) Mount the PPC/PC polymer stack which has the suitable BN-TBG stacking (The one we obtained from 3.4.2) to the micromanipulator with the flake stage and use the optical microscope to align the BN-TBG stacking and the chosen BN flake perfectly half at the 20 times magnification sight. (It is very important to align it in half at the right orientation of the graphene flake structure for applying tear-and-stack procedure, which.) Then the substrate is baked the whole time after this at 110°C.

3) Slowly move the polymer stack down the halfway to recheck the alignment of BN-TBG stacking and BN flake. (To roughly check that it is halfway, you can do it by adjust the focus of the microscope and make it focus on the halfway of the distance between BN-TBG stacking and BN. It is measurable roughly by counting the number of round we spin the fine focus.) Repeat the halfway moving down process 4 - 6 times until they are very close to each other. When it appears the Newton's ring on the on-screen monitor (i.e. the diffraction ring), move down the PPC/PC polymer stack more slowly to make the BN-TBG stacking and BN getting closer. When BN-TBG stacking almost stacks on BN (you can see it on the monitor that when they almost stack, the boundary of the contact area between PPC/PC and substrate is moving toward the sample), stop moving down and leave it for a while, then the polymer will move down by itself a little in the micron scale. After that, rechecking is needed as if it may stop moving down by itself. If it is really stopped, increase the temperature of the heater 1°C or moving it down manually but just a very-little-distance to make it continue stacking. (This process could take time for 20 - 30 minutes because we don't want any blister on the fabricated devices.) Repeat these until the boundary of the contact area passes the target flake for 5 - 10 microns radius surrounding the target flake) or the temperature reaches 170°C (for PC polymer stack) or 120°C (for PPC polymer stack), then the polymer stack is able to be moved down quickly. Stop moving down when you see the PPC/PC contact area full on the 5 times objective lens magnification microscope sight. Then leave them for 5 minutes. Beware that for PPC polymer stack, the temperature must not reach beyond 130°C or the tape as the part of PPC polymer stack could be melted and ruin the devices which is unable to remove with care by any kind of chemicals. Beware that for the PC polymer stack, at above 140°C , the polymer will contact itself with the substrate and the BN-TBG and bottom BN flake will contact each other significantly faster. It is very important to keep an eye on the fabrication all the time.

4) The fourth step is different for PPC polymer stack and PC polymer stack.

4.1) For PPC polymer stack, raise the PPC polymer stack very gently to make PPC covers the device. Now the device is made as BN-TBG-BN stacking device and it will be left on the substrate with PPC or PC covered on the fabricated device. Then turn off the heat to cool down.

4.2) For PC polymer stack, raise the PC polymer stack rapidly to release the PC, making it covering the device. Now the device is made as BN-TBG-BN stacking device and it will be left on the substrate with PC covered on the fabricated device. Then turn off the heat to cool down.

5) Check and capture the picture of the BN-TBG-BN device on the substrate after finishing the process by using the optical microscope at 5, 10, 20, 50 and 100 times objective lens magnification, respectively. If it is not usable anymore, find the new usable one and redo all of these steps from 3.4.1.

NOTE All of the laboratory detail in the every step of device fabrication must be recorded. Note-taking is necessary for the case you want to later check and repeat if it is successful. In case it fails, you will know the cause of troubles and later settle them.

3.4.4 Covering Polymer Removal

It is important to check before you start polymer removal. Make sure that you have use all of the usable BN flakes because this cleaning process may damage or make the usable one becomes unusable. If it is all used, you can start the covering polymer removal as these steps:

1) There is slight difference between PPC removal and PC removal

1.1) Soak the substrate that has the sample you want to clean in the anisole for 30 - 60 minutes to remove PPC. (Time duration depends on how difficult PPC can get removed.) Then wrap the beaker with aluminum foil and write the time you started soaking the substrate and the experimenter's name to let other experimenters know when they see it.

1.2) Soak the substrate that has the sample you want to clean in the chloroform for 30 - 60 minutes to remove PC. (Time duration depends on how difficult PC can get removed.) Then wrap the beaker with aluminum foil and write the time you started soaking the substrate and the experimenter's name to let other experimenters know when they see it.

2) Put the substrate which has wet surface immediately from the first step in the acetone for 15 - 20 seconds. During soaking, lightly waggle the substrate by gripping the substrate using the tweezer.

3) Put the substrate which has wet surface immediately from the acetone in the IPA (a.k.a. isopropanol) for 15 - 20 seconds. During soaking, lightly waggle the substrate by gripping the substrate using the tweezer.

4) Put the substrate on the aluminum foil and hold it with tweezer tightly. Then blow the substrate with nitrogen gun until it is completely dry. (Don't forget to clean the beakers after use in the first, second and third step, and blow them with nitrogen gun until they are dry.)

5) Check and capture the picture of the BN-TBG-BN device on the substrate after finishing the process by the optical microscope at 5, 10, 20, 50 and 100 times objective lens magnification, respectively. If it is not usable anymore, find the new usable one and redo all of these steps from 3.4.1.

3.5 Data Analysis

We use three analysis methods of the data but only two is mainly used: optical analysis and Raman spectroscopic analysis and additional analysis: atomic force microscope which the result is shown in Appendix C.

Firstly, the optical analysis is the brief verification to the presence of the blisters which the outcome will be analyze from the captured images obtained from optical microscope. Adjusting contrast and exposure of the images are done to detect the blisters simpler.

Secondly, the Raman spectroscopic analysis is further explained. The analysis was previously mentioned in the related theories entitled *Raman spectroscopy* in section 2.5. The procedures for analysis are as followings:

1) Put the sample on the glass slide on the stage and secure them tightly with clip locks. Then adjust focal depth appropriately while firstly using 10 times magnification objective lens. The reference point is set on the bottom left of the substrate as zero calibration in the “Labspec 6” program.

2) Optically find the sample by entering the coordinate of the fabricated device that was recorded before. Then adjust the objective lens magnification to 100 times and fine focus is used to adjust to make the visualization crisper and sharper.

3) Move the target point that green laser will be incident to the sample on the overlapping area of the graphene where it is twisted bilayer graphene and optically capture the picture of the sample to keep the record about what point or area of the sample we did the Raman spectroscopy. Beware that the objective lens will be very close to the sample. Carefulness and delicacy are necessarily needed.

4) Change the mode from visualizing mode to Raman mode, then using the 532-nm green laser with the maximum intensity. Enter the appropriate values of accumulation times and repeating count to not make the obtained data reach too high intensity (or count) of green laser to the sample.

5) Repeat the third step to fourth step but changing the target point to the other coordinate of the same twisted bilayer graphene overlapping area. The data that obtained from various point should not be different because it is the same physical twisted bilayer graphene, or else implies something wrong. If the problem occurs, it is necessary to find out what causes the problem. And it is very important to always record the data and condition we used each time we collect the data.

6) Export the collected data as PDF file to save it visually and be able to open later on various devices, and as text file to later use for plotting in Igor Pro program, which is unlocking the potential to mathematically analyze the obtained data in detail more than just using the naked eye. But in this project, visualizing analysis is just enough to compare the data because it is obvious to differentiate between the natural bilayer graphene and man-made fabricated twisted bilayer graphene where it is the indication of successful fabrication.

Chapter Four

Results and Discussion

4.1 Graphene Exfoliation

Graphene exfoliation can be divided into two sections: example of usable exfoliated graphene flake and result comparison between non-annealing and annealing graphene exfoliation.

4.1.1 Example of Usable Exfoliated Graphene Flake

There are almost one hundred flakes of exfoliated graphene that we did exfoliate in this project. Fig. 19 shows one example of the exfoliated graphene flake on the silicon wafer with silicon oxide on the surface which the photos are captured in 5 times and 100 times magnification of the objective lens. Here, the usable graphene flake is especially considered when it satisfies the conditions as followings:

1. It must be single-layer graphene, otherwise is not usable “for this project”.
2. The usable flake must not be contaminated from dusts or tiny particles.
3. It should be uniform. If it’s not, it is compromised for large area of single layer graphene.

4. It would be good if around the usable flake does not have the few-layer graphene or it could be the disturbance of the pick-up transfer method. Anyway it is considerable to be used if we are running out of usable flake.

5. It should be big, in the size of 20×20 microns is excellent. Too small flake is considerably remained unused due to tear and stack method is applied or it will be too small when it is torn in half and giving us the hard time to fabricate devices. On the other hand, too big flake is either unused unless there is a suitable size BN flake.

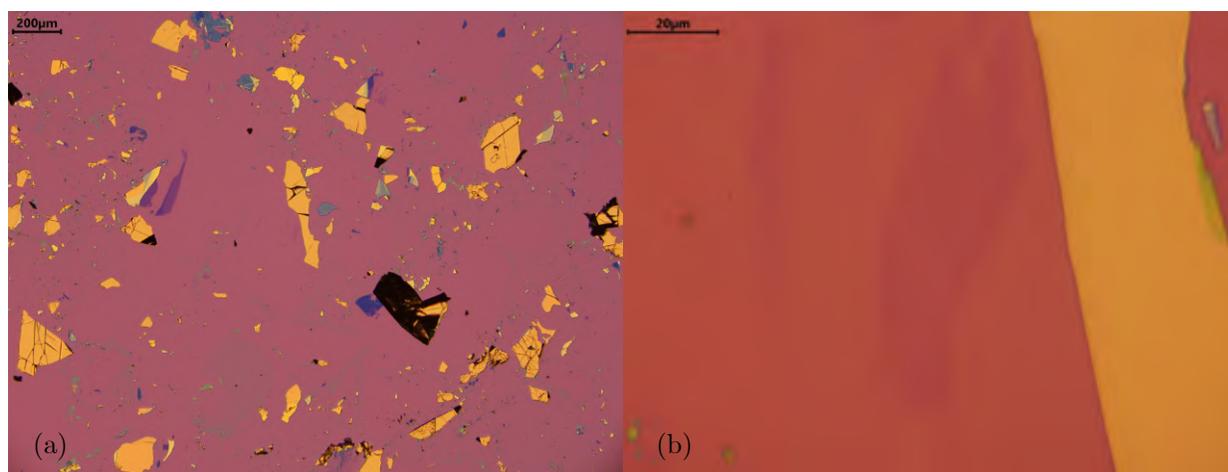
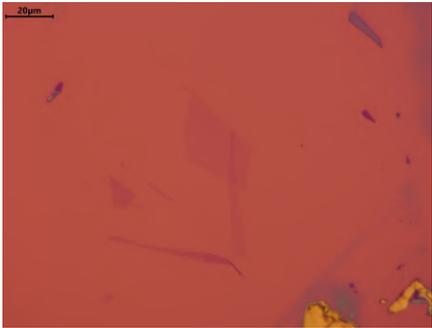
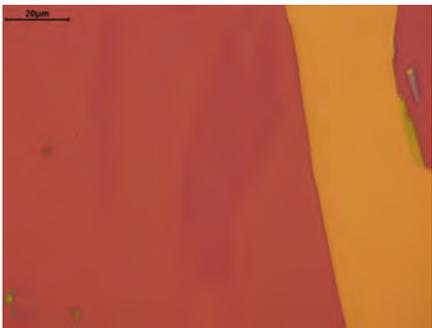
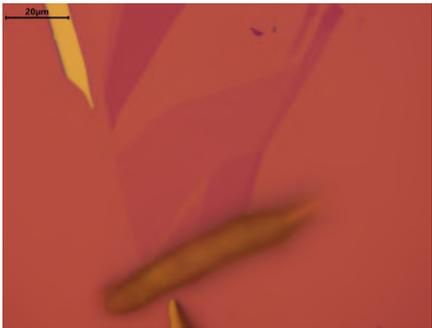
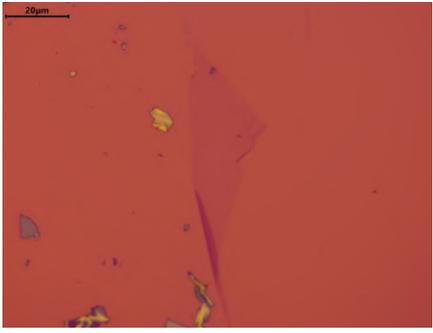


Fig. 19 The capturing photo of exfoliated graphene on substrate of silicon wafer with silicon oxide on the surface in the 5 times and 100 times objective lens magnification in (a) and (b) respectively.

In this report, we will choose some captured photo of the exfoliated graphene flakes at 100 times magnification of the objective lens as an example of the three usable graphene flakes and three unusable graphene flakes in Table 1.

Table 1: The Example of Usable and Unusable Graphene Flakes

No.	Flake label	Captured Photo	Detail
1	G08_17 (8th Attempt, Flake No.17)		<ul style="list-style-type: none"> • This graphene flake is usable. • From its color shade relatively to the contrast and substrate background color, it can be identify as a single-layer graphene. • Its size is acceptable and we interest in non-overlapping area to make twisted bilayer graphene.
2	G08_20 (8th Attempt, Flake No.20)		<ul style="list-style-type: none"> • This graphene flake is usable. • From its color shade relatively to the contrast and substrate background color, it can be identify as a single-layer graphene. • This kind of flake is used to fabricate twisted bilayer graphene due to its size is big, lead to easier to tear and stack the twisted bilayer graphene.
3	G11_02 (11th Attempt, Flake No.2)		<ul style="list-style-type: none"> • This flake is identified as single layer graphene and being usable for fabrication. • The big grain of something is a dust that is nearby the usable area. It can be blown by using nitrogen gun to scatter it and do no damage to the graphene flake.

4	G07_03 (7th Attempt, Flake No.3)		<ul style="list-style-type: none"> • This flake is obviously not the single-layer graphene, which can be seen from its shade where it has more gray shade than other flakes, relatively more contrast to the background substrate color.
5	G07_02 (7th Attempt, Flake No.2)		<ul style="list-style-type: none"> • This flake is kind of usable but we consider it as unusable since it would be torn in half more difficult because of the presence of bilayer graphene in the same flake. • It is contaminated from other tiny flake.
6	G10_01 (10th Attempt, Flake No.1)		<ul style="list-style-type: none"> • This flake is unusable. • Even though it is thin that might be single layer graphene, but it is dirty and contaminated.

4.1.2 Result Comparison between Non-annealing and Annealing Graphene Exfoliation

There are two major differences between non-annealing and annealing substrate that affects the yields of graphene exfoliation: the increasing number of usable flake per exfoliation and the significantly bigger size of usable flake which means we use the same resources but obtaining more usable flake and taking much less time. For non-annealing exfoliation, there is no annealing step and using UV ozone for 5 minutes to clean substrates as the hydrocarbons are gone out. For annealing exfoliation, the exfoliating tape contacted with substrate is heat on the hot plate at 100 °C for 2 minutes and before that, the substrate is cleaned by using oxygen plasma for 10 minutes to reduce the hydrocarbons on the surface of the substrate, letting the more flakes much easily stick to the substrate.

Firstly, the number of usable flake per exfoliation is dramatically increased. The results as the number of usable flakes per attempt of the non-annealing exfoliation varies for 2 - 4 usable graphene flakes. But for the annealing exfoliation,

the obtained usable flakes are increased to 10 - 20 flakes. This is the big step of increasing yields of the graphene exfoliation which is easily done by just cleaning the substrate by oxygen plasma and adding the annealing step to the recipe. Additionally, although we do the annealing, if we don't do the cleaning step by using oxygen plasma, the number of usable flake is dramatically dropped to 1 - 3 flakes. This really shows how cleaning the substrate plays a big role for exfoliation.

Lastly, the size of the usable flakes obtained from annealing exfoliation are much bigger than the flakes from non-annealing exfoliation, with the bigger size of more than 20×20 microns compare to mostly-smaller than 20×20 microns. Using the annealing exfoliation, we had obtained the biggest usable graphene flakes of 40×200 microns. We prefer the bigger one because it is easier to fabricate twisted bilayer graphene since we have to tear the graphene apart to do "tear and stack" method. But too big is going to be the problem because there would not be the suitable-size of boron nitride flake (BN flake) to do pick-up transfer method. Furthermore, although it is too big, we can verify that annealing exfoliation truly affect the size of graphene exfoliation.

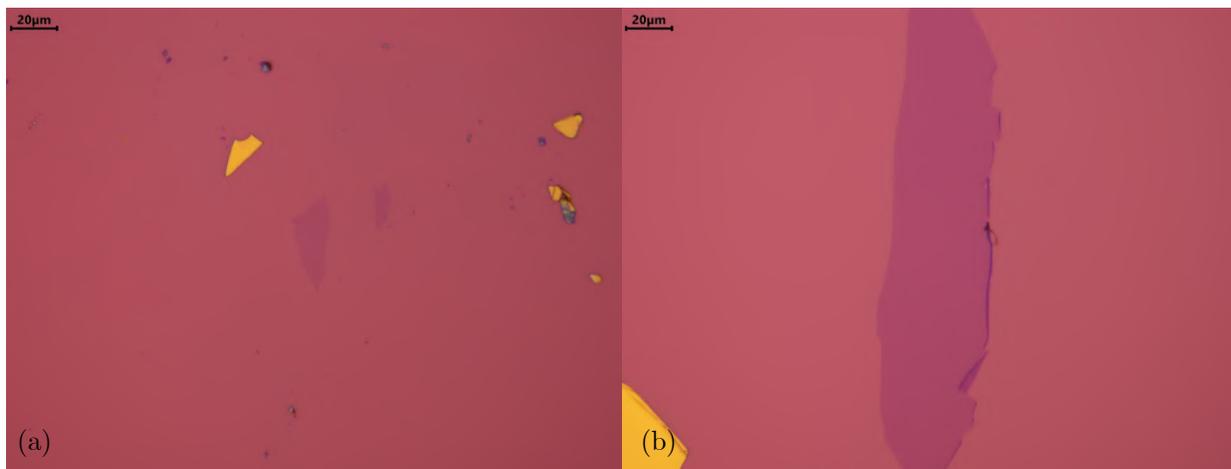


Fig. 20 The capturing photo of exfoliated graphene flake. In (a), the flake is obtained using the non-annealing exfoliation. And in (b), the flake is obtained using annealing exfoliation. This shows the significant increase in size of the graphene flake from different exfoliation.

4.2 Hexagonal Boron Nitride Exfoliation

Hexagonal boron nitride exfoliation can be divided into two sections: example of usable exfoliated hexagonal boron nitride flake and result comparison between non-annealing and annealing hexagonal boron nitride exfoliation.

4.2.1 Example of Usable Exfoliated Hexagonal Boron Nitride Flake

In this project, we have obtained almost two hundred exfoliated BN flakes so far. Therefore, not all flakes are usable. There are conditions that must be satisfied to be the usable BN flake that is allowed to be used in pick-up transfer method and

fabrication of twisted bilayer graphene. In this project, we use 2 BN flakes per one-time fabrication, the top and the bottom BN flake. The top flake is used to pick-up the graphene flake as pick-up transfer method. The bottom BN flake is used to be the shield and preventing the potential fluctuation from the silicon oxide. Then the fabricated device will look like the sandwich as twisted bilayer graphene on the middle of BN flake. Furthermore, their conditions are as below:

1) It must not be too thick. Although we don't have the method to exactly identify the number of BN flake layer, but we can approximate optically by its color. The usable flake should be greenish. Yellowish flakes are too thick to be used. If the flakes are greenish with a little blue tone that seems like they are kind of transparent, says it is too thin "to be used for the top BN flake" but still be usable for the bottom BN flake in the fabrication. The considerable used flake for the top BN flake has to be greenish with no transparency. (The top BN flake should be thick enough because the thick one is pick up the graphene flake stickier than the thin one does.)

2. The usable flakes must not be contaminated from dusts or tiny particles or it could ruin the fabrication and be the nightmare. Blister doesn't matter.

3. It should be uniform. If it's not, it is compromised for very large area of BN flake to be used as bottom BN flake. If it is uniform and thick enough, it is priorly considered and used for top BN flake.

4. It would be good if around the usable flake does not have the other BN flake, says it is standalone, or it could be the disturbance when we pick up the BN flake by PPC polymer stack or PC polymer stack. Anyway it is considerable to be used if we are running out of usable flake, giving an attempt to see if it is usable and the nearby flake may not disturb the picking up step and fabrication.

5. Its size should be more than 20×20 microns, or quite bigger than the graphene flake because we have to tear graphene flake in half and the contactless area is for the preparation of the misalignment between BN flake and graphene flake. Size of the BN flake significantly matters or the fabrication could come undone.

6. Additionally, the shape of the BN flake should be relevant and match to the graphene flake to fabricate easier. It could prevent the nightmare from the misalignment but if it does not satisfy this condition, it is acceptable since delicacy and skill matter more than luck.

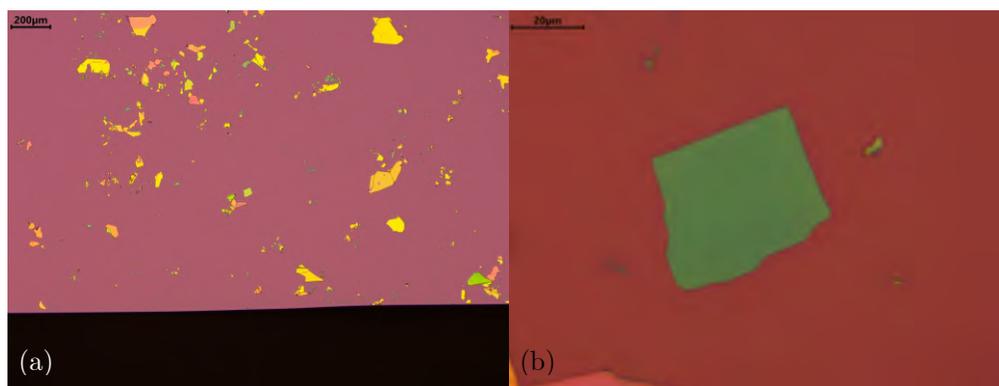
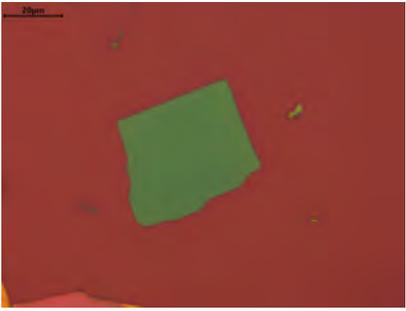
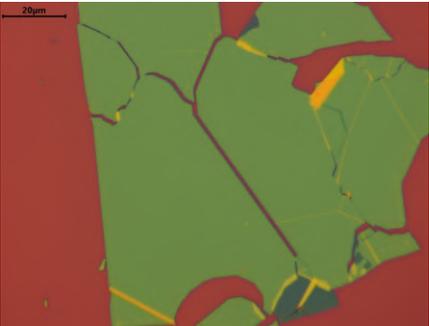


Fig. 21 The capturing photo of exfoliated hexagonal boron nitride on substrate of silicon wafer with silicon oxide on the surface in the 5 times and 100 times objective lens magnification in (a) and (b) respectively.

In this report, we choose some BN flake to be the examples of the usable BN flakes and unusable BN flakes for the fabrication and represent that they satisfy the condition for the usable BN flake that makes the fabrication easier as the captured photo, flake label and their details following the one in Table 2.

Table 2: The Example of the Usable and Unusable BN flakes

No.	Flake label	Captured Photo	Detail
1	BN09_02 (9th Attempt, Flake No.2)		<ul style="list-style-type: none"> • This flake is usable for the top BN flake because it is thick, uniformly smooth and big enough where it will be used as the top BN flake. • It is noticeably greenish color and not kind of transparent.
2	BN07_08 (7th Attempt, Flake No.8)		<ul style="list-style-type: none"> • This flake is usable for the bottom BN flake and it could be suitable with some twisted bilayer graphene device, depends on the size of the device. • Hence, the flake is uniform. Although it is thin but it is usable for the bottom flake.
3	BN10_09 (10th Attempt, Flake No.9)		<ul style="list-style-type: none"> • Although its size seems usable (the right greenish flake), this flake is unusable due to it lacks uniform thickness.
4	BN14_02 (14th Attempt, Flake No.2)		<ul style="list-style-type: none"> • This flake is unusable, even though it has the right thickness as it is perfectly greenish and it is gigantic, but it is not standalone because it is not completely separated from the non-uniform or the other part of BN flake.

4.2.2 Result Comparison between Non-annealing and Annealing Hexagonal Boron Nitride Exfoliation and Substrate Cleaning.

For non-annealing exfoliation, there is no annealing step and using UV ozone for 5 minutes to clean substrates as the hydrocarbons are gone out. For annealing exfoliation, the exfoliating tape contacted with substrate is heat on the hot plate at 100 °C for 2 minutes and before that, the substrate is cleaned by using oxygen plasma for 10 minutes to reduce the hydrocarbons on the surface of the substrate, letting the more flakes much easily stick to the substrate.

From the experiment, we have not found the major significant difference between annealing and non-annealing exfoliation. There is no increasing number of usable BN flake and no increasing BN flake size relatively. So there is no need to do annealing since it is not further giving the greater yields.

Hence, cleaning by using oxygen plasma is more effective than UV ozone which is seen the results as the number of usable BN flake are different with the oxygen plasma cleaning lightly gives the higher number of usable BN flake than UV ozone cleaning. Obviously, cleaning substrate with oxygen plasma gives the significantly greater number of usable BN flake than no cleaning with the number of usable BN flake of 20 - 35 flakes and 6 - 12 flakes respectively.

4.3 Fabrication Results of Twisted Bilayer Graphene

4.3.1 Photo and Raman Spectroscopic Result of the Device

We have obtained the fabricated devices using PPC polymer stack and PC polymer stack which they will be shown in this section in detailed with photos.

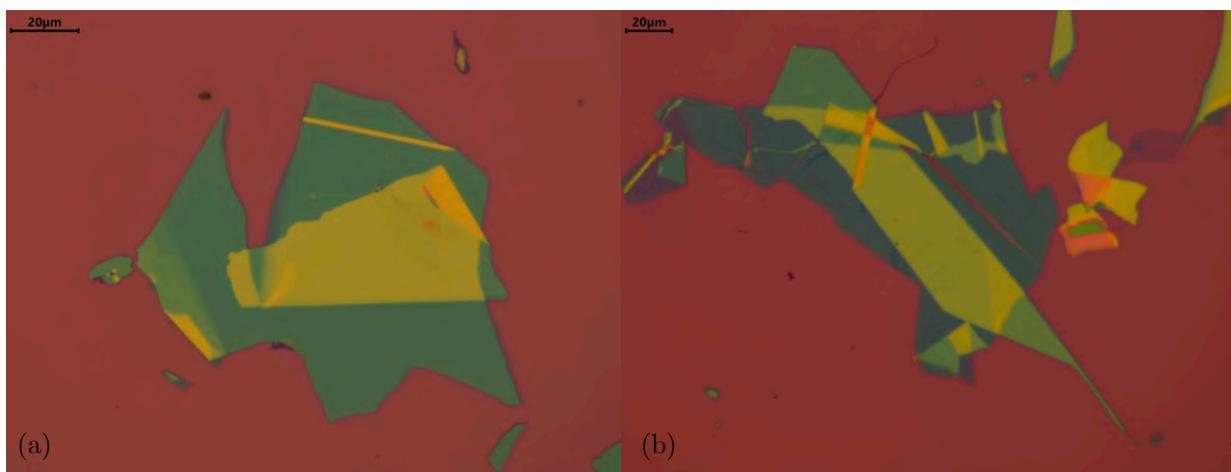


Fig. 22 The capturing photo of successfully fabricated device of twisted bilayer graphene (TBG) made from PPC polymer stack in (a), and from PC polymer stack in (b), on substrate of silicon wafer with silicon oxide on the surface in the 100 times objective lens magnification.

Firstly, the successfully fabricated device and unsuccessfully fabricated device by using PPC polymer stack are shown as lists below this paragraph. They will

further be explained of which graphene flake and BN flakes are used for fabrication. Note that the captured photo of the fabricated device will be shown in 2 photos as the 100 times magnification objective lens in the first photo on the left, and zoom in from the first photo and represent the presence of the twisted bilayer graphene (TBG) as closed loop white line in the second photo on the right. The results are as followings:

(1) This fabricated device named as BNBGN05. This is successfully fabricated in terms of blister-free device. The results of fabrication are shown in Fig. 23. There are details of this fabricated device, which are addressed below:

- This device consists of BN04_30 as the top BN flake, G06_03 as used to make TBG and BN04_18 as the bottom BN flake.
- It takes time for 18 minutes to pick up the graphene, 28 minutes to fabricate the TBG and 19 minutes to stack with bottom BN flake.
- Failed to align to fabricate TBG twice. Succeeded on the third attempt and no flaws on the TBG.
- Annealed them at up to 120°C for 5 minutes to make PPC cover.
- It is blister-free on the TBG area, the size of TBG is around 5×5 microns which is big enough to be used, count it as successfully fabricated device.

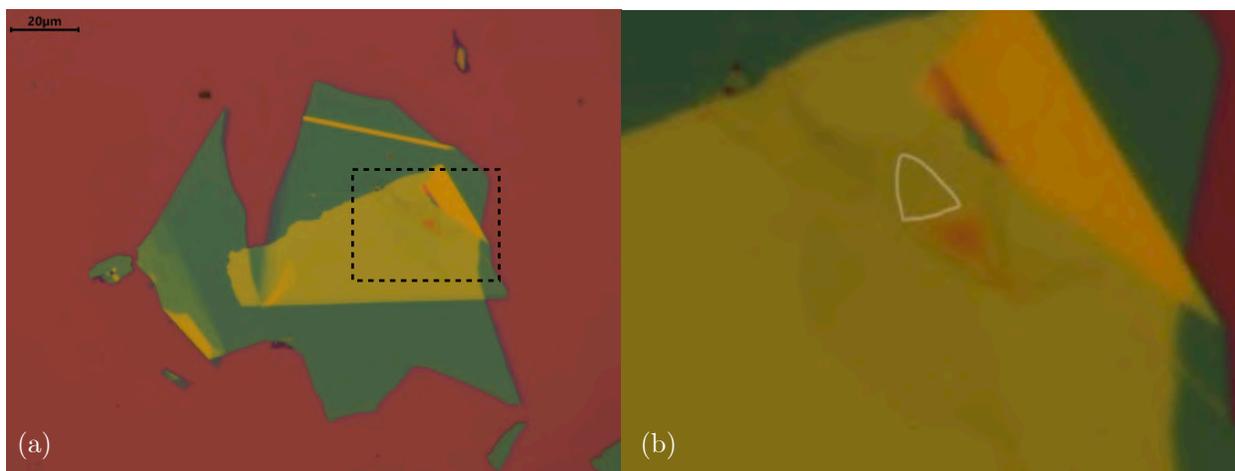


Fig. 23 The capturing photo of successfully fabricated device (BNGBN05) of twisted bilayer graphene (TBG) made from PPC polymer stack. In (a), it was captured by using 100 times objective lens magnification. In (b), the photo zooms in the dot area in (a) and represents the TBG area as a closed white line shape.



Fig. 24 The top BN flake, graphene flake and bottom BN flake that are used for fabrication of BNBGN05. (a) BN04_30. (b) G06_03. (c) BN04_18. These were captured by old microscope with 80 times magnification of objective lens.

Hence, its Raman spectroscopic result is as shown in the graph of Fig. 25. It is noticeably from the ratio between G-band and 2D-band and the characteristic graph of the 2D-band that it is obviously bilayer graphene on the overlapping part, imply that each layer before stacking is single layer graphene. The 2D-band clearly shows the shoulder part of it, the hill-like on the left which is popping out, leads to the conclusion of the verification that is not twisted due to it is similar to the non-twisted bilayer graphene.

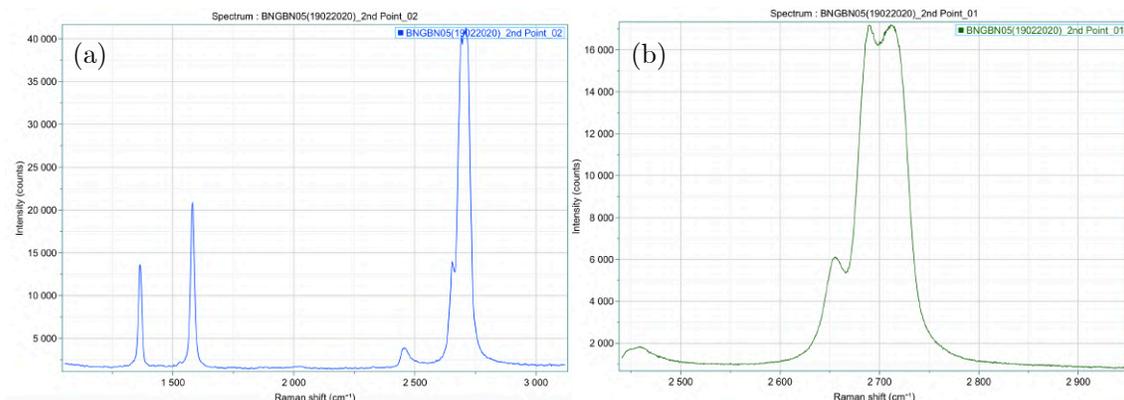


Fig. 25 Raman spectroscopic result of BNGBN05. (a) The ratio between G-band and 2D-band. (b) The characteristic curve of the 2D-band.

(2) This fabricated device named as BNBGN06. This device is unsuccessfully fabricated. The results of fabrication are shown in Fig. 26. There are details of this fabricated device, which are addressed below:

- This device consists of BN03_13 as the top BN flake, G05_03 as used to make TBG and BN03_10 as the bottom BN flake.
- It takes time for 19 minutes to pick up the graphene, 19 minutes to fabricate the TBG and 7 minutes to stack with bottom BN flake.
- Annealed them at 110 ° C and up to 118 ° C for 5 minutes.
- It is not blister-free device, and most of all it was misaligned, count it as unsuccessfully fabricated device.

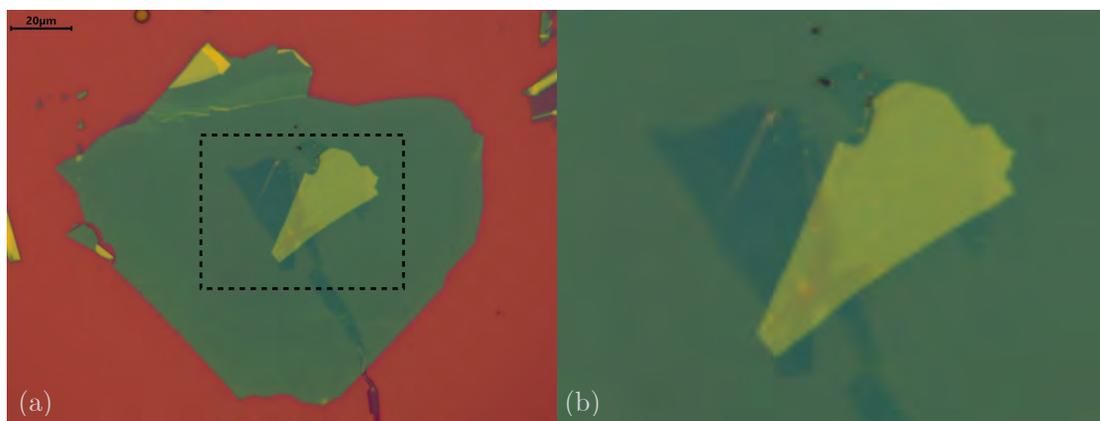


Fig. 26 The capturing photo of unsuccessfully fabricated device, BNGBN06, made from PPC polymer stack. In (a), it was captured by using 100 times objective lens magnification. In (b), the photo zooms in the supposed-to-be TBG area in dot closed line in (a) and shows the failure of alignment to make TBG.

However, it is not successfully fabricated then it is no need to do Raman spectroscopic analysis.

Secondly, the successfully fabricated device and unsuccessfully fabricated device by using PC polymer stack are shown below this paragraph. They will further be explained of which graphene flake and BN flakes are used for fabrication. Similarly, note that the captured photo of the fabricated device will be shown in 2 photos as the 100 times magnification objective lens in the first photo on the left, and zoom in from the first photo and represent the presence of the twisted bilayer graphene (TBG) as closed loop white line in the second photo on the right. The results are addressed in details as followings:

- (1) The fabricated device named as “BNGBN10”. Its details of made are listed:
 - This device consists of BN10_26 as the top BN flake, G08_17 as used to make TBG and BN08_03 as the bottom BN flake.
 - It takes time for 20 minutes to pick up the graphene, 25 minutes to fabricate the TBG and 13 minutes to stack with bottom BN flake.
 - Annealed them up to 170 ° C for 5 minutes.
 - It is good and acceptable to be called as “blister-free device” due to there is area that is blister-free of approximately 5×10 microns.

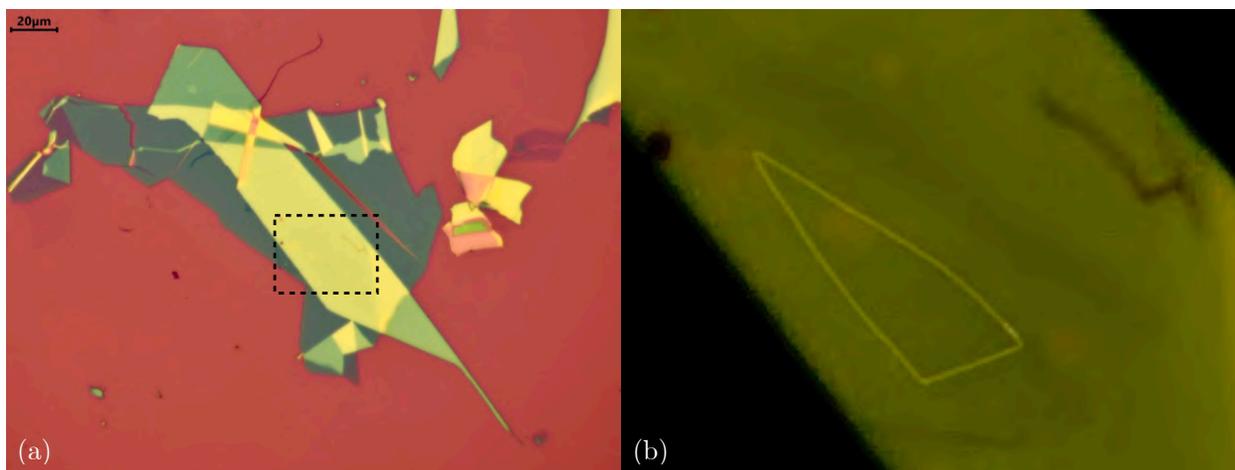


Fig. 27 The capturing photo of successfully fabricated device (BNGBN10) of twisted bilayer graphene (TBG) made from PC polymer stack. In (a), it was captured by using 100 times objective lens magnification. In (b), the photo zooms in the dot area in (a) and represents the TBG area as a closed white line shape.

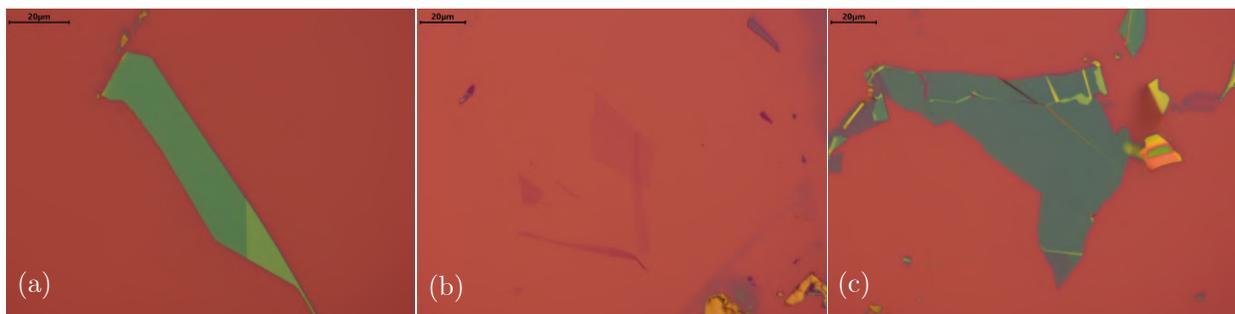


Fig. 28 The top BN flake, graphene flake and bottom BN flake that are used for fabrication of BNGBN10. (a) BN10_26. (b) G08_17. (c) BN08_03. They are on 100 times magnification of objective lens.

Hence, its Raman spectroscopic results is as shown in the graph of Fig. 29. It is noticeably from the ratio that is nearly one between G-band and 2D-band and the characteristic graph of the 2D-band that it is obviously bilayer graphene on the overlapping part, imply that each layer before stacking is single layer graphene. The 2D-band shows the shoulder part of it a little, the hill-like on the left which is popping out a little bit, leads to the conclusion of the verification of twisted bilayer graphene also is successfully made. This device is successfully made in terms of both blister-free and twisted bilayer graphene.

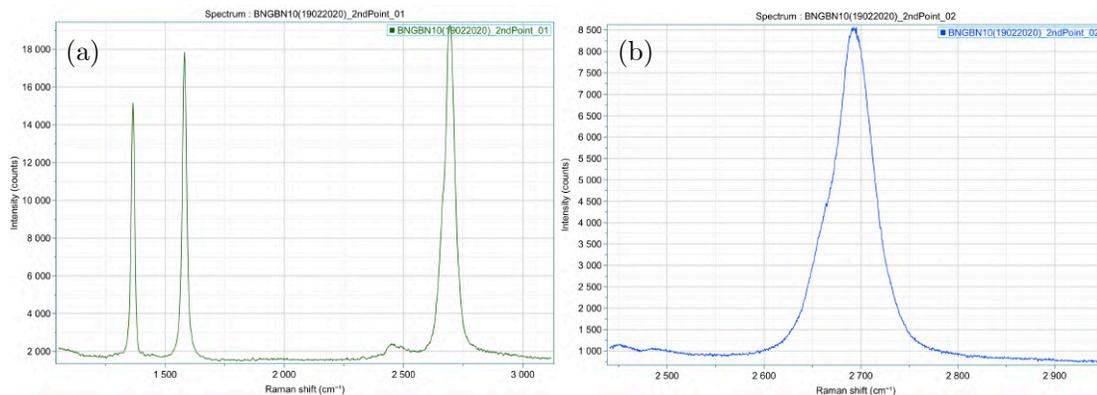


Fig. 29 Raman spectroscopic result of BNGBN10. (a) The ratio between G-band and 2D-band. (b) The characteristic curve of the 2D-band of the TBG.

(2) The second device labelled as “BNGBN11”. Although it is blister-free, it is unsuccessful due to it is not twisted bilayer graphene. Its details are clarified:

- This device consists of BN11_09 as the top BN flake, G08_20 as used to make TBG and BN09_13 as the bottom BN flake.
- It takes time for 15 minutes to pick up the graphene, 30 minutes to fabricate the TBG and 38 minutes to stack with bottom BN flake.
- Annealed them up to 170 ° C for 5 minutes.
- It is good and acceptable to be called as “blister-free device” due to there is area that is blister-free of approximately 5×10 microns.

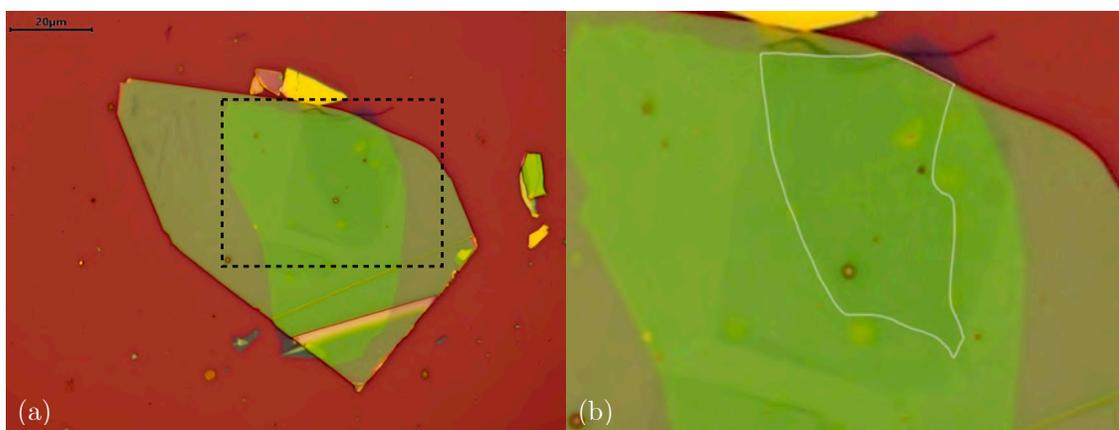


Fig. 30 The capturing photo of successfully fabricated device (BNGBN11) of twisted bilayer graphene (TBG) made from PC polymer stack. In (a), it was captured by using 100 times objective lens magnification. In (b), the photo zooms in the dot area in (a) and represents the TBG area as a closed white line shape.

Hence, its Raman spectroscopic results of BNGBN11 is as shown in the graph of Fig. 31. It is noticeably from the ratio that is nearly one between G-band and 2D-band and the characteristic graph of the 2D-band that it is obviously bilayer graphene on the overlapping part, imply that each layer before stacking is single layer graphene. The 2D-band shows the shoulder part of it a little, the hill-like on the left which is popping out a little bit, leads to the conclusion of the verification of twisted bilayer graphene also is successfully made. This device is successfully made in terms of both blister-free and twisted bilayer graphene. Hence, there is addition in Appendix C.

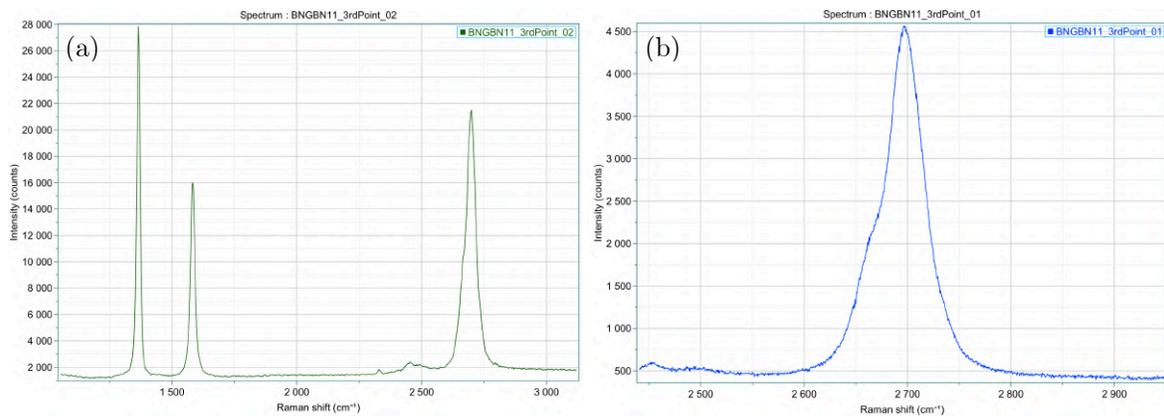


Fig. 31 Raman spectroscopic result of BNGBN11. (a) The ratio between G-band and 2D-band. (b) The characteristic curve of the 2D-band of the TBG.

4.3.2 Fabrication Result Comparison between Using PPC Polymer Stack and PC Polymer Stack

There is a major different outcome between using PPC polymer stack and PC polymer stack, which is the occurrence probability reducing of the blisters. During fabrication process, there are noticeable points that are differentiated as Table 3.

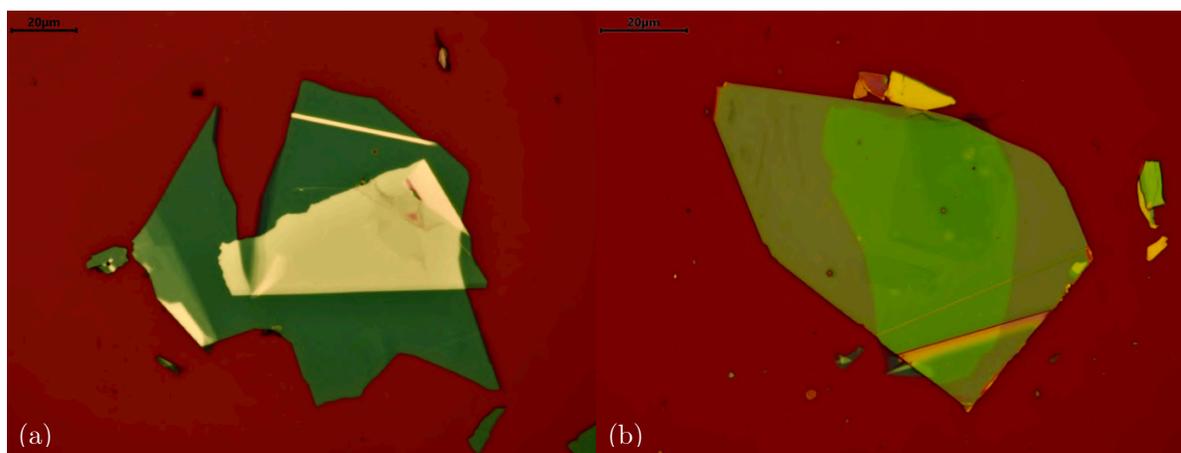


Fig. 32 The capturing photo of fabricated devices, BNGBN05 which is made from PPC polymer stack in (a), and BNGBN11 which is made from PC polymer stack in (b), on substrate of silicon wafer with silicon oxide on the surface in the 100 times objective lens magnification. They are edited the contrast and exposure to make the blister more noticeable.

Table 3: The Differences between Using PPC Polymer Stack and PC Polymer Stack

No.	Detail	Using PPC Polymer Stack	Using PC Polymer Stack
1	Temperature	<ul style="list-style-type: none"> ● Be able to reach up to 120 ° C or the tape on the PPC polymer stack will be melted. 	<ul style="list-style-type: none"> ● Be able to reach up to 180 ° C but we tend to use only 170 ° C to maintain the quality of the heater.
2	Substrate Adhesion	<ul style="list-style-type: none"> ● Using the special tape to hold the substrate securely. ● To reach at such high temperature, at 170 ° C to 180 ° C to reduce the blister occurrence probability, the special holding tape will be less stickier and it will be less securely held. 	<ul style="list-style-type: none"> ● Using the vacuum pump to hold it tightly. ● The substrate will not be bend since the hole for suction is very small relatively to the substrate.
3	Blister Occurrence Probability	<ul style="list-style-type: none"> ● Not significantly be reduced since the temperature only reach up to 120 ° C. 	<ul style="list-style-type: none"> ● Dramatically be reduced due to the ability to reach at such high temperature of 180 ° C.
4	Real-Time Monitoring	<ul style="list-style-type: none"> ● For tearing the graphene or bringing up any flakes, it should be expeditiously lifted up, leading to monitor the result after snapped-lifting was done. 	<ul style="list-style-type: none"> ● There is no need to snapped-lifted up when using PC polymer stack. ● It is lifted up gradually with right speed, leading to able to monitor the result in real time.
5	Fabricator's Skills	<ul style="list-style-type: none"> ● The PPC and substrate are contacting continuously, so it is easily controllable. ● It is necessary to be able to fabricate with high skill as very slow and gently stacking the flakes. 	<ul style="list-style-type: none"> ● The PC and substrate are contacting discreetly at low temperature, i.e. below than 140 ° C, but continuous contacting at above 140 ° C, leading to the summary that it is not easy as using PPC polymer stack. ● It is essential to be able to fabricate with high skill of precisely control, care and delicacy as very slow and gently stacking the flakes.

From the table 3, the only limitation of using PC polymer stack is higher fabrication skill is more essential than using PPC polymer stack, since PC and substrate are not contacting each other continuously at below 140°C . Moreover, it is not quite that disadvantage since fabrication is always the high-skilled task. Using PPC polymer stack or PPC polymer stack needs the professional and obsession. The occurrence of blisters is surely not because the researchers are out of luck, but lacks of professional fabrication skills.

Additionally, there is limitations of the laboratory equipments due to we have to reach at such high temperature of 170°C to 180°C , then the laboratory equipments are essentially required to be improved, which they are further explained in the Appendix A of how we had improved them.

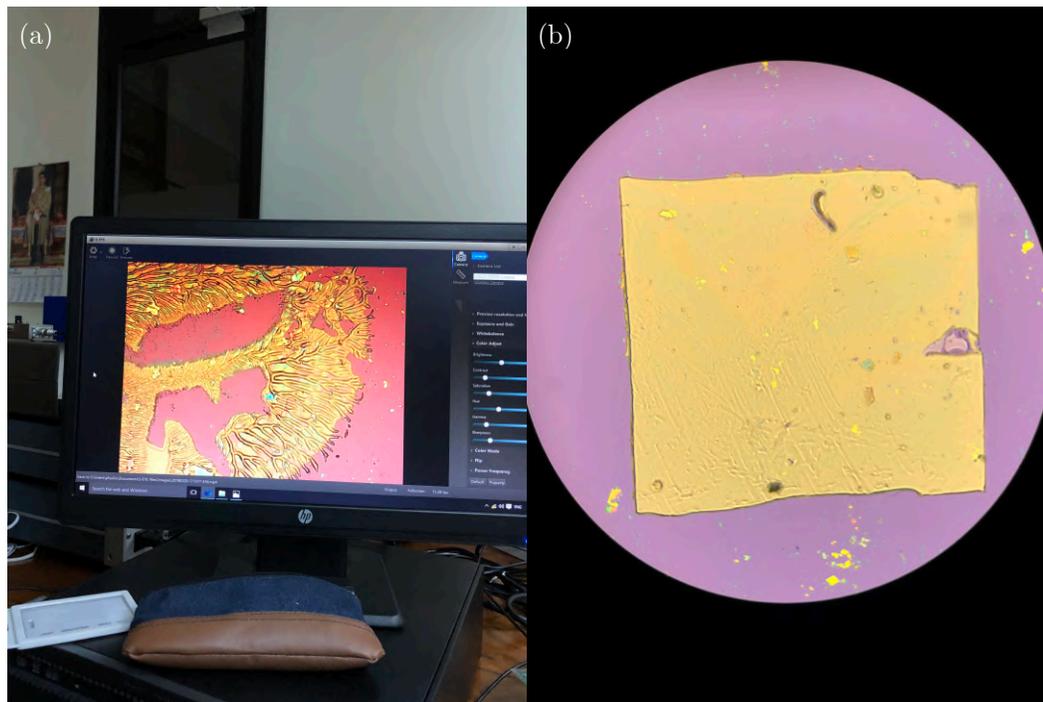


Fig. 33 (a) The failure of making PPC cover the fabricated device. This happened often as it may not cover the area that fabricated device located. (b) The PC covering, which they are always like this, as covering the whole part that PC made contact with the substrate.

Chapter Five

Conclusions

To summarize all of the experiment we have done so far, there are three sections we would like to talk about: the yields increasing of graphene and BN exfoliation, the recipe of fabrication using PC polymer stack and the reducing blister.

First of all, we successfully increase the yields of graphene exfoliation as using the same resources but making the exfoliation more effective to provide us more usable flakes and bigger flakes. The annealing process plays a main role and the cause of making the yields of graphene exfoliation more powerful, not only increasing the number of usable flakes, but tending to make them bigger either. However, the annealing process does not play a main role for increasing the yield of the BN exfoliation since there is no major difference compared with no-annealing process added. It can be said that there is no need to do annealing process for BN exfoliation since usual procedures provide us great size of BN flake and good quality of BN flake but graphene exfoliation.

Secondly, we can verify the suitable and effective recipe of using PC polymer stack for fabrication of blister-free van der Waals heterostructure which is following the procedures in the experimental method in detail. Hence, the fabrication outcomes are shown in the chapter three are used to verify the effectiveness of the recipe as concluded, leading to the limitation of using PPC polymer stack and persuasion of why we should use PC polymer stack instead of PPC polymer stack: higher temperature reachability, reducing the blister occurrence probability and ability of real-time monitoring the fabrication outcome. Anyway, due to COVID-19 outbreak, we could have had time to verify more and been able to address what should be added or discarded to make the recipe more efficient and reliable. Fortunately, the results are much enough to be used for confirmation as it really reduces the occurrence probability of the blister along with delicacy and professional skills to precisely fabricate it with success.

Lastly, we now are able to reduce the blister with effective experimental procedures. Using PC polymer stack breaks the limitation of using PPC polymer stack and able to reduce the blister as we reach the high temperature of 170 - 180 °C due to the hydrocarbon tend to escape from the interlayer between the top BN flake and graphene, graphene and graphene, and BN-TBG and the bottom BN flake, rather than the hydrocarbons that are being stucked to the sample more at low temperature of 120 - 130 °C as we used this range in PPC polymer stack. Also, it is significantly essential to take time much enough for 20 - 30 minutes per one stacking between BN and graphene, graphene and graphene, and BN-TBG and bottom BN flake, to let the hydrocarbon escape in time. Less time-taking is not as effective as more time-taking as the hydrocarbons have more time to go out from the sample. Taking too long time, i.e. more than 30 minutes, may not be great to the device due to the stacking of twisted bilayer

graphene and BN flake are shifted, which may be the problem for twisted bilayer graphene to snap back in place and being non-relatively twisted angle graphene. To verify the success of twisted bilayer graphene fabrication, we can use Raman spectroscopy to analyze by the ratio between G-band and 2D-band and the characteristic of the 2D-band. Hence, its Raman peak only appears of the graphene flake's and BN flake's, which implies the purity of the device and it is not contaminated from other. And confirmation of the fabricated devices that is really blister-free can be told briefly by the edit the captured photo with the suitable contrast to see the blister on the fabricated device which more than 5×5 microns is acceptable to be used for further experiments in the future for determination of its electrical properties or else. To deeply verify the existence of the blister on the fabricated devices, atomic force microscope is required to check the unseen blisters where they are not detected with the naked eyes from the captured photos, which the result is shown in Appendix C.

Appendix

Appendix A: Equipments Modification and Improving

Due to the fact that before modification, the equipment and the recipe is not suitable to deal with the high temperature of 170 - 180 °C as the tape used for holding substrate in place is clearly not able to hold it securely, says its stickiness is less, then it is inevitable to modify the stage to seize the substrate securely even on the high temperature. The modification of its was changing to the vacuum suction. What we had done was modifying the substrate stage by adding the tube system, drilling it with a machine done by mechanics. The finished product is shown in the experimental method part in Fig. 34 as it is connected to the silicone tube to the fish tank pump that has enough power to make the vacuum suction, with 12 Volts maximum.

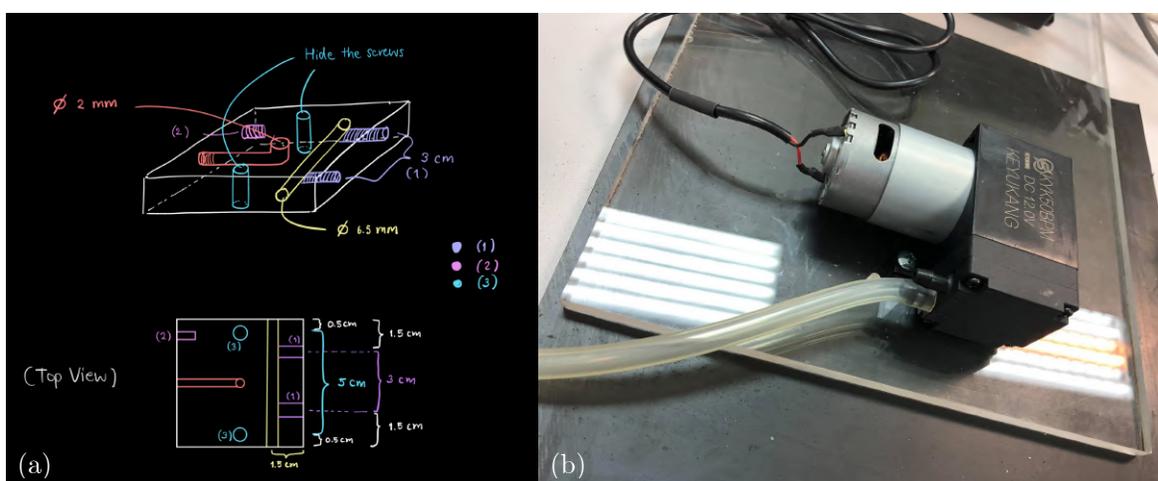


Fig. 34 (a) The blueprint of the modified aluminum alloy substrate stage. The red line represents the tube system to drain the air as making inside of it vacuum suction to the substrate. (b) The fish tank oxygen pump is modified to be used as a vacuum suction by draining the air inside of the tube system in the substrate stage to securely hold the substrate in place.

Next, the micromanipulator rail is modified and added later. We aimed to unlock the ability to move the micromanipulator with ease. Previously, we have to secure the micromanipulator to the base of the microscope by tool clamp and we had to adjust and secure it again every time. The most irritating thing is during fabrication, we could not observe the flake on substrate clearly that the graphene flake is lifted up or torn yet because the PPC or PC polymer stack are obstructed, even they are transparent but they are curved, then they are not optically eye-friendly to us. Adding the rail makes the fabrication easier than before because we can constrainedly move along the rail by moving it out of obstruction with no error rotation of the twisted bilayer graphene and also is easy to mount the PPC or PC polymer stack and move them in the work area without clamping it with tool clamp every single time as before, task is done fluidly with no worries. Then the engineering task was done as we designed the blueprint and talked and discussed with mechanic to see the possibility and prevent the problems that may occur during modification. The new acrylic base is required to be able to add the rail and secure the substrate stage and the rail. Finally, they were modified and be able to use with ease.

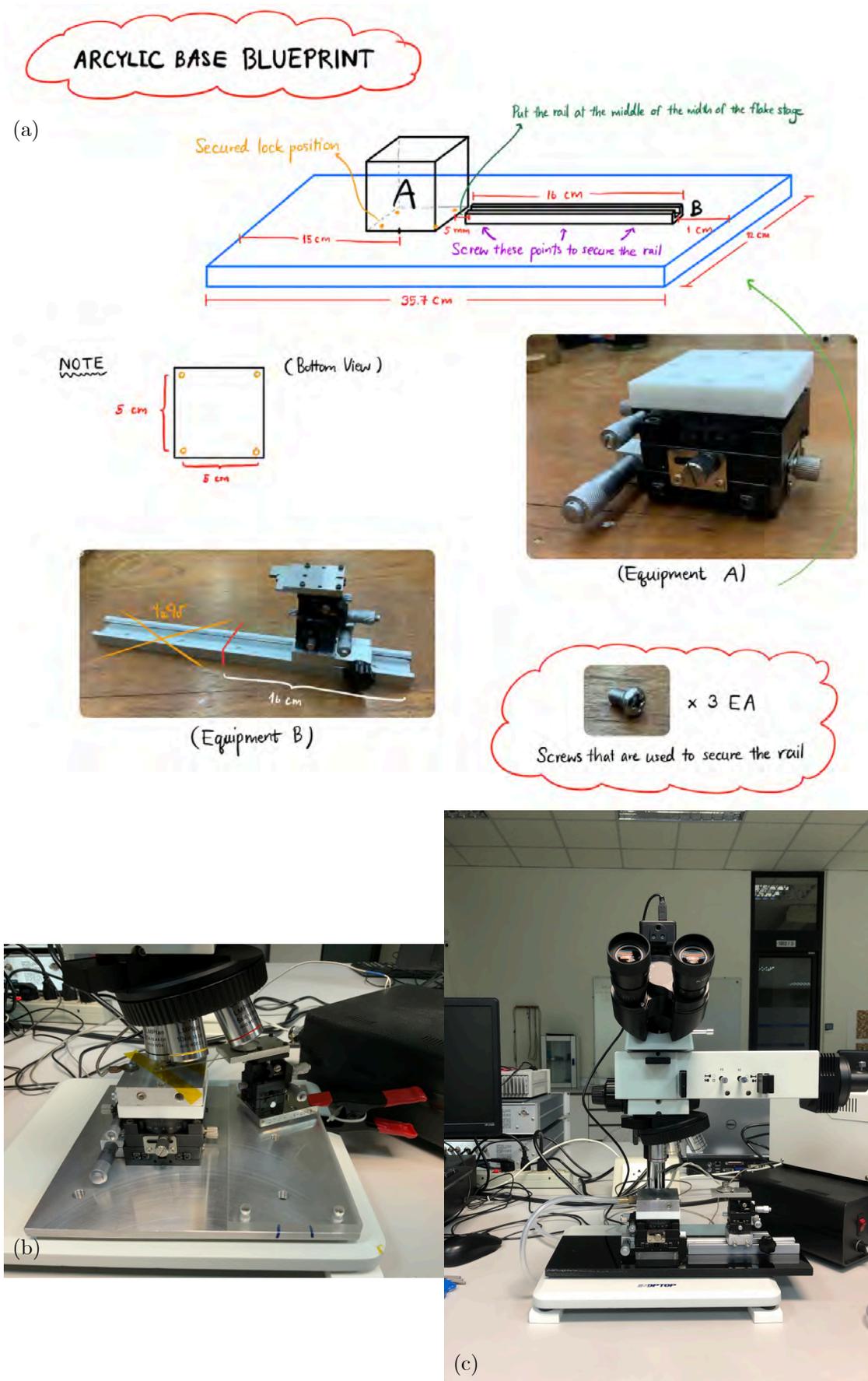


Fig. 35 (a) The blueprint of the modified acrylic base used to add the new rail system. (b) The before modification equipment. (c) Final product of the modified and improved base and added rail on the new acrylic base.

Appendix B: Atomic Force Microscopic Analysis

I was once doing the atomic force microscopic analysis on the BNGBN05 sample, the one that fabricated by using PPC polymer stack and is successful in terms of blister-free device. Optically analyze the captured photo, it can tell that it is clean and almost no blister between interlayer of the BN and graphene flake or between graphene and graphene flake. Therefore, this atomic force microscope is used to detect the unseen-by-the-naked-eyes blisters, which are seen in Fig. 37c.

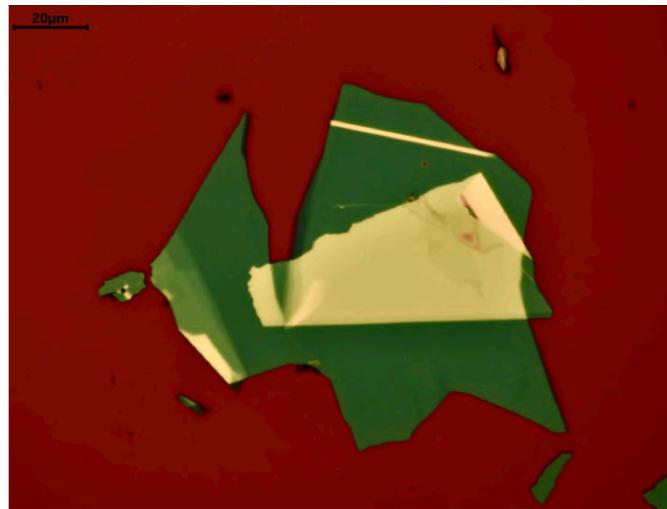


Fig. 36 The captured photo, edited the contrast and exposure to detect blister and overlapping region of the graphene layers easier.

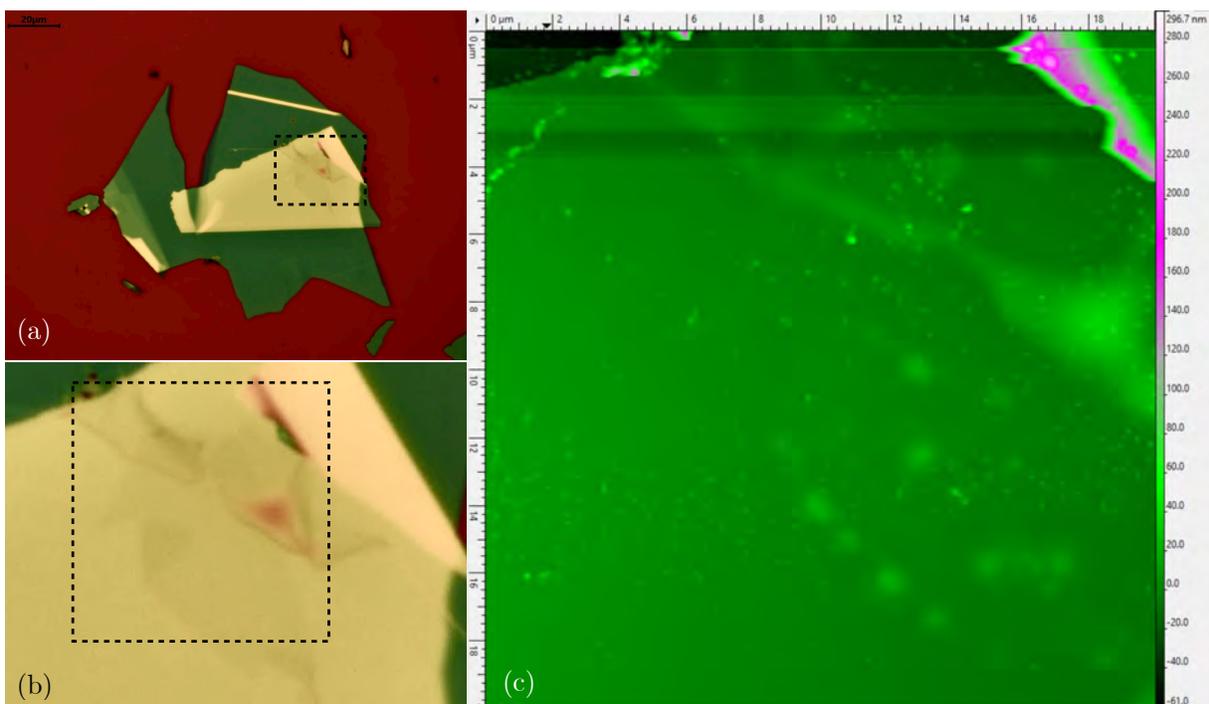


Fig. 37 (a) The captured photo of BNGBN05 with the dot line represent the zoom-in zone of the twisted bilayer graphene. (b) The zoom-in area that is used to analyze by atomic force microscope. (c) The atomic force microscopic result is shown as visualization. The scale bar are along with this visualization.

Appendix C: Raman Spectroscopic Results of Fabricated Devices

In this project, we had finished doing Raman spectroscopy to all suitable fabricated twisted bilayer graphene devices. Therefore, as mentioned, we did show illustration results of them separately. This section tends to show the comparison of the fabricated device results, as shown in Fig. 38.

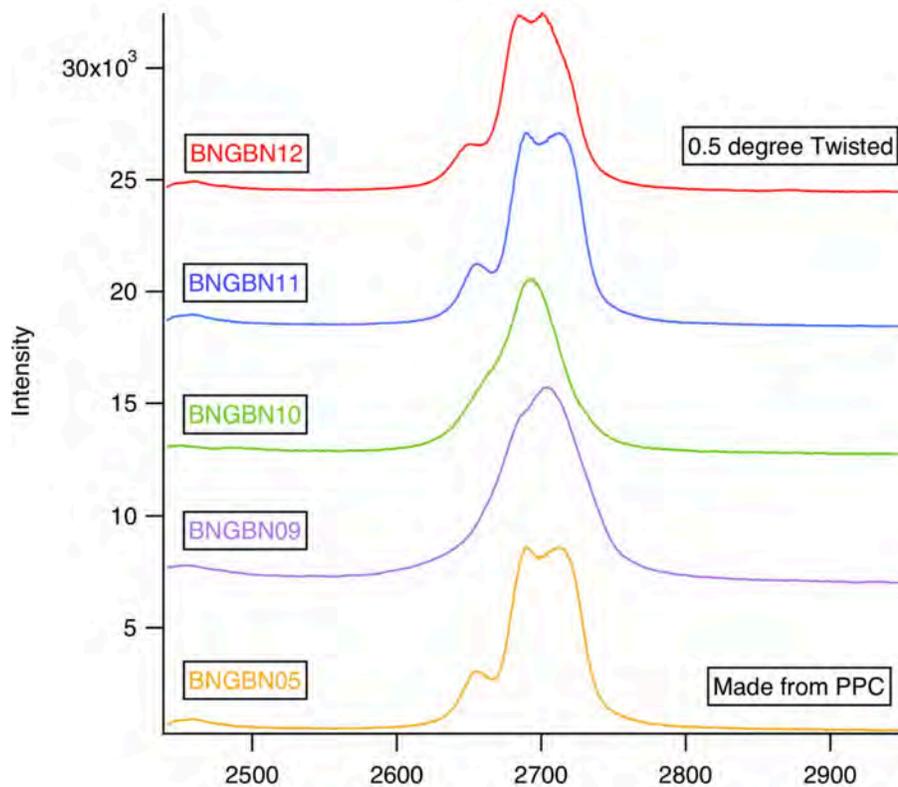


Fig. 38 Raman spectroscopic results of all fabricated devices for comparison.

From the results, they are obviously noticeable on BNGBN05, BNGBN11 and BNGBN12 fabricated devices that are non-twisted bilayer graphene, since we did twist them before stacking but they may snap back to be non-twisted device or could be failed after the stacking process. We can verify that they are non-twisted bilayer graphene from their characteristics of 2D-band as the shoulder part on the left that is hill-like is evidently seen on BNGBN05, BNGBN11 and BNGBN12 devices and the top of the graph is noticeably separated heads. On BNGBN09 and BNGBN10, they are not similar to the natural bilayer graphene, imply that they are twisted bilayer graphene which were successfully well-made. Unfortunately, these Raman spectroscopic results had obtained after a while we did Raman spectroscopy on BNGBN11 and this showed that the twisted bilayer graphene in BNGBN11 had snapped back to non-twisted bilayer graphene somehow, which is unexpected and due to the uncontrollable factor that could happened. Twisted bilayer graphene is not definitively easy to be fabricated since delicacy, professional skill and precision are required.

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