ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL

INVESTIGATION OF ELECTRONICAL AND MECHANICAL PROPERTIES OF TWISTED BILAYER SYSTEMS OF TWO DIMENSIONAL MATERIALS

M.Sc. THESIS

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Department of Physics Engineering

Physics Engineering Programme

AUGUST 2021

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ISTANBUL TEKNİK ÜNİVERSİTESİ ★ LİSANSÜSTÜ EĞİTİM ENSTİTÜSÜ

İKİ BOYUTLU MATERYALLERİNİN DÖNDÜRÜLMÜŞ ÇİFT KATMANLI SİSTEMLERİNİN ELEKTRONİK VE MEKANİK ÖZELLİKLERİNİN ARAŞTIRILMASI

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To my sister,

FOREWORD

Firstly, I would like to thank to my family for helping me to be who I am and for their endless support. They were always with me and they helped me to overcome difficulties.

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ABBREVIATIONS

AFM : Atomic Force Microscope
FFM : Friction Force Microscope
Fig : Figure
hBN : Hexagonal Boron Nitride
HOPG : Highly Oriented Prylotic Graphite
G : Graphene
nm : nanometer
nA : nanoAmpere
mV : milliVolt
µm : micrometer
PDMS : Polydimetyloxane
PMMA : Poly(methyl methacrylate)
PPC : Polypropylene Carbonate
STM : Scanning Tunneling Microscope
STS : Scanning Tunneling Spectroscopy
CVD : Chemical Vapor Deposition

SYMBOLS

I_t	**:** Tunneling Current
s	**:** Second
sccm	**:** Standart cubic centimeters per minute

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INVESTIGATION OF ELECTRONICAL AND MECHANICAL PROPERTIES OF TWISTED BILAYER SYSTEMS OF TWO DIMENSIONAL MATERIALS
SUMMARY

Twisted systems of two-dimensional materials attract the attention of scientists as these materials exhibit different electronical and mechanical properties than the materials from which they are made. Especially for twisted bilayer graphene, because of the observation of van Hove Singularities on moiré superlattices on highly oriented prylotic graphite (HOPG) surface near the Fermi energy, and following the observation of superconductivity for the magic angle bilayer graphene, this field of research has raised new questions.

Although the wet transfer method of graphene transfer helps for the large area applications of this novel material, for creating twisted bilayer graphene samples, this method gives no degree of freedom for a controlled rotation of the twist angle. Therefore, other approaches were required.

In this study, we built a setup which gives a rotation between the graphene layers with high accuracy. First step was to build a stamping setup, which consists of an imaging part (an optical microscope), a sample stage with two linear and one rotational axis, and a stamp stage with 3 linear axes. Each part of the microscope is collected and mounted for this purpose. This setup allows to prepare twisted bilayer graphene samples with controlled rotation. Also, these samples are prepared by other samples; hexagonal boron nitride (hBN), monolayer graphene, polymers and heaters among other things. Therefore, the preparation methods of these samples, as well as the heating and stamping process was optimized. hBN, the important ingredient for picking up the graphene, arrived late. Thus, our experiments started with picking up the graphene with Bi_2Te_3 van der Waals crystal, just as hBN.

Along with the samples prepared with stamping technique, poly(methyl methacrylate) (PMMA) mediated transfer method of chemical vapor deposition (CVD) grown graphene is used to prepare monolayer and twisted bilayer graphene samples, yet with no rotation control. These samples are investigated with Atomic Force Microscopy (AFM) and Scanning Tunneling Microscopy (STM). Despite the lack of angle control, Scanning Tunneling Spectroscopy (STS) data of an arbitrary angle of twist showed us that it has higher conductivity than monolayer graphene, which was also prepared with this technique.

İKİ BOYUTLU MATERYALLERİN DÖNDÜRÜLMÜŞ ÇİFT KATMANLI SİSTEMLERİNİN ELEKTRONİK VE MEKANİK ÖZELLİKLERİNİN ARAŞTIRILMASI

ÖZET

İki boyutlu materyallerden oluşturulan van der Waals hetero yapıları ve döndürülmüş çift katmanlı sistemler, oluşturuldukları malzemelerden farklı elektronik ve mekanik özellikler taşıdıkları için dikkatleri üzerlerine çekmişlerdir. Özellikle çift katlı döndürülmüş grafen bunlar arasında en ilgi çekici olanıdır. Öncelikle, çok düzenli katmanlı grafitte (HOPG) taramalı tünelleme mikroskobu (TTM) ile süper periyodik yapılar gözlemlenmiş, bu yapıların HOPG'den farklı elektronik özellikler sergilediği tespit edilmiştir. Teorik olarak da iki grafen tabakası arasındaki katmanların döndürme açısına göre bant yapısında düzleşme olacağı teorik olarak gösterilmiş ve bu yapıların mekanik özellikleri de incelenmiştir. TTM ile yapılan deneylerde taramalı tünelleme spektroskopisi (TTS) van Hove Tekilliklerinin Fermi enerjisi yakınlarında gözlemlenmesi super iletkenlik gözlemlenebileceğini göstermiş ve son olarak süper iletkenlik davranışı 4-uç tekniği ile oluşturulan döndürülmüş çift katmanlı grafen cihazında super iletkenlik görülmesi bu araştırma alanı yeni sorular getirmiştir.

Bu çalışmadaki ilk adım, iki grafen katmanı üst üste konulduğunda aralarındaki açıyı çok hassas bir şekilde ayarlanabileceği bir deney düzeneği tasarlanmasıdır. Bu düzenek iki kısımdan oluşmaktadır: bir optik mikroskop, örneğin yatau düzlemde hareket edebilmesi ve data sonra iki grafen katmanı arasındaki açının oluşturulabilmesi için altında iki lineer ve bir rotasyonel eksenli örnek standı ve damganın hem örneğe yaklaşması, hem de yatay düzlemde hareket edebilmesi için üç lineer eksenli damga kısmı. Optik mikroskop kısmında CCD kamera, demet ayırıcı, tüp lens ve uzun çalışma aralığına sahip objektif lensler kullanılmıştır. Objektif lenslerdeki bu seçim, lensle örneğin arasına damgayı yerleştirme ihtiyacından kaynaklanmaktadır. Tüp lens ise sonsuz düzeltmeli objektif lensler sebebiyle sonsuzda oluşan görüntüyü CCD kameraya odaklamak amacıyla kullanılmıştır. Demet ayırıcı, örneği yukarıdan hem görebilmek, hem de aydınlatabilmek için sisteme entegre edilmiştir. Aydınlatma için ise bir halojen lamba kullanılmıştır. LED lambaların tek katmanlı grafenin mikroskopta görülmesi için uygun olmadığı saptanmıştır. Örnek standında iki adet lineer ve bir adet motorize rotasyonel translasyon standı bulunmaktadır. Bunlar hem örnek alanında gezinmeyi, hem de döndürülmüş çift katmanlı grafen örnekler hassas bir şekilde kontrollü bir açıda oluşturulmayı sağlamaktadır. Damga standı ise iç eksende de hareket etmektedir, bu sayede hem yatay düzlemde damgayı grafenle denk getirilmesi, hem de damganın inip kalkmasına olanak sağlamaktadır. Çift katmanlı grafen örnekler, tek katmanlı mekanik olarak soyulmuş grafen, hekzagonal boron nitrat (hBN), polimerler ve grafen ısıtıcılar gibi diğer örnekler aracılığıyla hazırlanmaktadır.

Grafen ve hBN örnekler, mekanik olarak katmanlarna ayırma yöntemiyle hazırlanmıştır ve öncelikle optik mikroskop ve Atomik Kuvvet Mikroskobu (AKM) ile incelenmiştir. Seçilen grafenin tek katmanlı olup olmadığı ve kullanılan hBN'nin istenilen kalınlıkta olup olmadığı bu yöntemlerle saptanmıştır. Ayrıca, grafen örneklerin hazırlanması sırasında kullanılan, grafenin ve hBN örneklerin üzerine aktarıldığı SiO_2 yüzeyleri öncesinde oksijen ve argon akısı altında plazma ile temizlenmiştir. Bu temizlik sonrası SiO_2 yüzeyinde bazı çukurların oluşması ve yüzeyin aktive edilmesi sonucu grafenin bu yüzeylere daha iyi tutunduğu, bu sebeple

hem daha geniş alanlı, hem de daha fazla sayıda tek katmanlı grafen bölgelerinin oluştuğu da gözlemlenmiştir.

Damgalar, transparan polimerler olan polidimetiloksan (PDMS) ve polipropilen karbonat (PPC) ile hazırlanmıştır. Bu iki malzemenin de transparan olması sayesinde örnekle lens arasına girdiğinde grafen örneklerin yine görülebilmesi sağlanmıştır. PDMS, yumuşak olması sebebiyle damgalamaya uygundur ancak daha yapışkan bir malzemeye ihtiyaç olduğu için PPC ile kaplanmıştır. Burada PPC, PDMS'e banttan bir çerçeve yardımıyla tutturulmuştur.

Damgalama yöntemi birden fazla örnek ve farklı tipte polimerden oluşmaktadır ve prosedür sırasındaki sıcaklık, örneklerin ve polimerlerin kalınlığı gibi parametrelere de bağlıdır. Bu sebeple, damgalama prosedürüyle birlikte bu bileşen örneklerin ve polimerlerin hazırlanması da optimize edilmiştir. hBN kristali, hem grafenin bant yapısını manipüle ederek süper iletkenlik göstermesine yardımcı olduğu gibi, van der Waals kristali olması ve damgalama prosedüründe grafeni koparması amacıyla kullanılmaktadır. Grafenin bölgesel olarak alınıp koparılması amacıyla kullanılan hBN kristali elimize geç ulaştığı için, örnekleri hazırlamak için bir diğer van der Waals kristali olan Bi_2Te_3 ile başladık. Bu örnekleri plazma prosedürü olmadan hazırlanmış grafen ile hizalayıp grafeni koparma prosedürünü ise oda sıcaklığında başarılı bir şekilde gerçekleştirdik. Grafen bölgesinde Bi_2Te_3 bölgelerinin değdiği yerlerde önce ve sonra alınan optik data bunun sağlandığını göstermiştir.

Deneylerimizin sonraki aşamalarında kullanılan grafen örnekler, plazma ile temizlenen SiO_2 yüzeyleri üzerinde hazırlanmıştır. Bu proses daha çok ve daha büyük tek katmanlı grafenler elde etmemizi sağlasa da, grafenin hBN ile oda sıcaklığında koparılmasına engel olduğu denemeler sonucunda görülmüştür. Bu sebeple örneğin ısıtılması gerekmektedir. Ancak bunun için kullanılacak yapışkan polimerin ısıya dayanıklı olması gerekmektedir. Elimizdeki PPC ise ısıya dayanıklı değildir ve sıcak bir yüzeyle temas ettiğinde kolay bir şekilde bozulmaktadır. Bu sebeple başka bir polimerin kullanılması gerekmektedir.

Damgalama yöntemi dışında, kimyasal buhar biriktirme (KBB) ile büyütülen bakır yüzeyinde grafenin poli(-metil-metakrilat) bazlı transfer yöntemiyle de tek katmanlı ve döndürülmüş çift katmanlı grafen örnekler hazırlanmıştır. Bu yöntemde grafen, koruyucu bir tabaka olan PMMA ile kaplanıp, daha sonra bakırın solüsyon üzerinde çözünmesi ile büyütüldüğü yüzeyden ayrılmaktadır. Daha sonra bu solüsyon deiyonize su ile seyreltilip, grafen su yüzeyinde yüzerken aktarılacağı yeni yüzey tarafından avlanır. Ikinci grafen katmanı ise aynı yöntemle bu sefer grafen tarafından avlanır, fakat bu yöntemle dönme açısının ayarlanmasının tamamen el ayarına bağlı olmasından ötürü kontrolsüz bir şekilde gerçekleşmektedir. Bu yöntemle hazırladığımız örnekte açı, grafenin engebeli bir yüzey olan bakır yüzeyinde büyütülüp SiO_2 üzerine aktarılması sonrası engebelere bağlı oluşan izler aracılığıyla saptanmıştır. Bu örnekler, AKM ve TTM ile incelenmiştir. KBB yöntemiyle hazırlanan grafen örneklerde tek katman gözlemlenebileceği gibi, karbon kaynağı olarak kullanılan metan gazının akısı ve işlem süresine bağlı olarak iki, üç ya da çok katmanlı bölgeler de olabilmektedir. Bu sebeple, çift katmanlı olarak aktarılan grafenin de yalnızca çift değil, çok katmanlı yapıda olduğu tespit edilmiş, TTS ile elektronik yapıları gözlemlenmiştir. Açısal kontrol sağlanmıyor olmasına rağmen, bu yöntemle üretilen örnek üzerinde Taramalı Tünelleme Spektroskopisi verileri, döndürülmüş çift katmanlı grafenin, tek katmanlı graphene göre daha iyi iletkenliğe sahip olduğunu göstermiştir.

Çalışmalarımızda çok katmanlı grafenin katman sayısına ve çift katmanlı grafenin dönme açısına bağlı olarak elektronik özelliklerinin ve sürtünme özelliklerinin incelenmesi amaçlanmıştır. Pandemi sebebiyle bu çalışma hayli yavaş ilerlemiştir.

1. INTRODUCTION

1.1 Purpose of Thesis

In this thesis; we aimed to create twisted bilayer systems of two-dimensional materials with controlled angle and study their electronical and tribological properties with respect to their twist angles. For this purpose, a stamping set-up with the ability of preparing the twisted bilayer graphene samples with controlled angle is built. After many iterations of changing and optimizing the structure of the microscope, we were able to tear and pick up a graphene flake with a Bi_2Te_3 flake while we were waiting for the hBN samples. hBN is a van der Waals crystal and is crucial in preparing the twisted bilayer samples and for graphene to show unconventional superonductivity. Because of the pandemics, it was not possible to present in the laboratory for almost a year and as a result, the process of preparing the samples was quite slower than it should have been. Furthermore, electronical properties of twisted bilayer system which is prepared by conventional PMMA mediated wet transfer method of CVD grown graphene was studied. It was observed that these samples show better conductive properties than monolayer graphene. The same result, and especially unconventional superconductivity, was expected for the twisted bilayer graphene, which is prepared with stamping set-up. Another aspect of the thesis was studying the tribological properties of twisted bilayer graphene with respect to their twist angles.

1.2 HOPG

Highly oriented pyrolytic graphite (HOPG) is basically a stack of two dimensional carbon layers, and commonly used in surface science, as a source of graphene and as a calibration sample for scanning probe microscopy techniques due to it flat and inert surface. In each layer, carbon atoms have the hexagonal (honeycomb) structure and they are sp^2 hybridised. Layers of carbon atoms are held together by van der Waals interaction with interlayer distance of 0.335 nm, which is bigger than its lattice constant, 0.142 nm [1]. Also, the layers are stacked in a special way, which is called

AB, or Bernal, stacking. In this configuration, two consecutive layers are shifted with respect to each other. The schematical representation of Bernal stacking and STM measurement of an HOPG are shown in Figure 1. In the scheme, we see two layers of a crystal and each layer, there are red and blue carbon atoms. Red atoms are called α atom and these atoms sit on top of the carbon atoms of the bottom layer. Blue atoms are called β atoms, which sit on the center of the hexagon of the bottom layer. Since p_z orbitals of α atoms interact each other, they happen to show a lower density of states with respect to β atoms [2]. As a result, STM images mostly shows triangular pattern because of the higher density of states of β atoms and as α atoms seem darker.

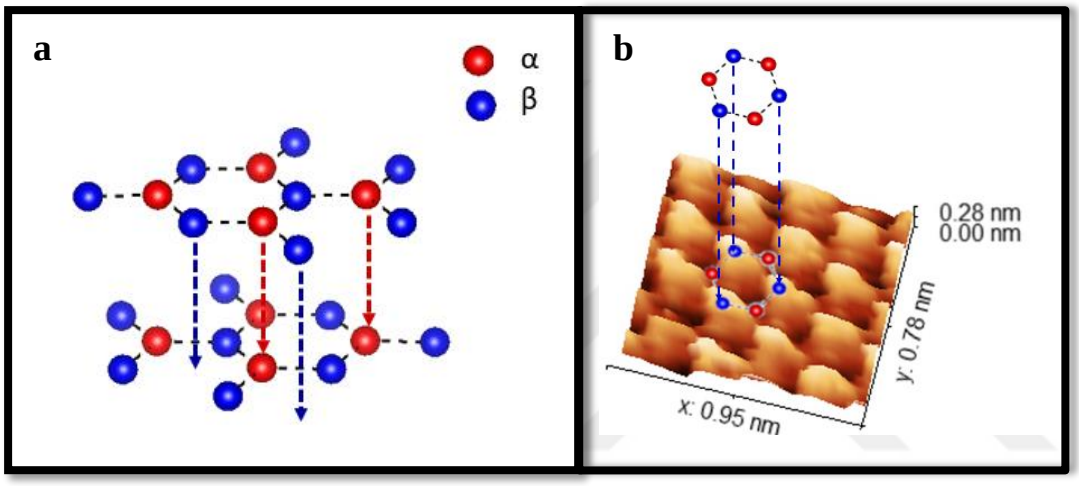

Figure 1.1 : a) Scheme of HOPG and b) STM data of HOPG with 0,6 nA and 100mVtunnelling parameters.

1.3 Graphene

After the theoretical prediction of two-dimensional graphite [2], graphene had waited nearly six decades to be explored experimentally [3]. With this exploration, Geim and Novoselov won the Nobel prize in Physics in 2010 [4]. This noble material is basically graphite in two-dimensions where carbon atoms are sp2 hybridised and aligned in hexagonal (honeycomb) lattice. The carbon atoms are separated 0.142 nm from each other, yet the lattice constant is 0.246m. Lattice vectors of graphene is shown in Figure 1.2. Also, electronic properties of graphene became a centre of attention since its

charge carriers behave like “massless Dirac fermions” due to the linear dispersion in the band structure at the Fermi level [5].

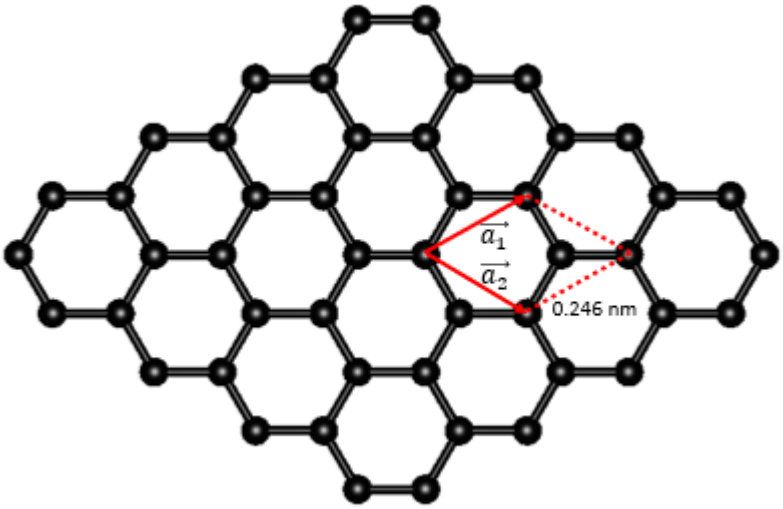

Figure 1.2 : Scheme of graphene.

Apart from the first production with mechanical exfoliation, graphene is produced in different ways, but the most promising method which allows to produce large area graphene sheets is Chemical Vapor Deposition (CVD) growth of graphene on transition metals [6].

1.4 Twisted Bilayer Graphene and Moiré Patterns

Due to their weak van der Waals interaction between the layers, mechanical exfoliation and isolation of a single layer of a layered crystal, such as graphite, led to the research on two-dimensional materials [7]. Graphene, or two-dimensional graphite, has been taking the attentions because of its peculiar electronic structure [8]. Moiré pattern was known as an optical illusion when two periodic structures are misaligned with respect to each other. However, due to a rotation of the topmost layer of HOPG, these super-periodic “moiré” structures are observed with Scanning Tunneling Microscope (STM). Also, Scanning Tunnelling Spectroscopy (STS) measurements showed van Hove singularities and this result considered to be associated with the superconductivity of graphene [9]. In Figure 1.3, moiré pattern for 5^0 rotation and STM data of HOPG with a moiré pattern is shown.

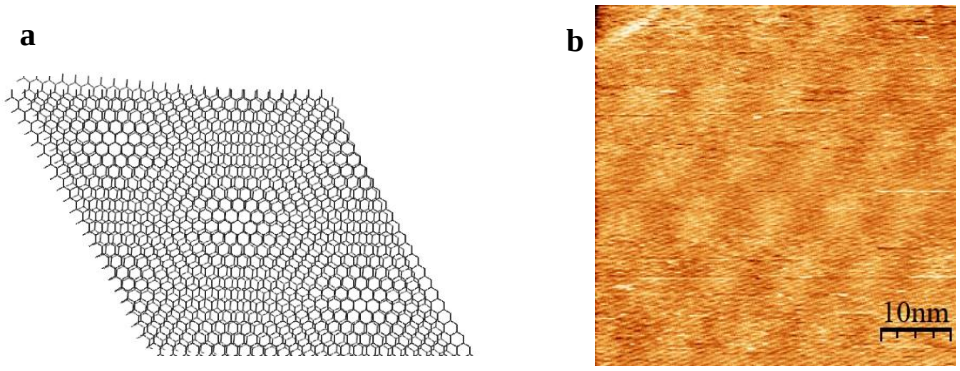

Figure 1.3 : a) Moiré structure for two layers of graphene rotated at 5^0, b) STM data of a moiré zone on HOPG with 0.6 nA and 110 mV tunnelling parameters.

After the research on graphene has reached to a certain point, other two-dimensional materials have been begun to be studied, such as hexagonal-boron nitride (hBN)and molybdenum disulfide (MoS_2), as well as their combinations, i.e. van der Waals heterostructures. Among the heterostructures, graphene-hBN combination became the centre of the attentions: hBN is used as a dielectric protecting layer for graphene, and also, it altered the electronical structure of the graphene [10]. Afterwards, the observation of super-periodic structures on twisted bilayer graphene on hBN with STM is achieved, and van Hove singularities for different twist angles were measured with STS. It was also reported that these observations were the result of graphene-graphene and graphene-hBN interactions [11].

For the super conductivity of twisted bilayer graphene, a “magic angle” was predicted to be 1.1^0 [12]. Finally, along with the band flattening and correlated insulating behaviour [13], a slight change in the carrier density led to the obervation of the superconductivity for magic-angle twisted bilayer graphene, using a 4-terminal TBG device with a quantum Hall effect setup. The measured 4-probe resistance was 0 up to 1.7 K [14].

2. EXPERIMENTAL

2.1 Setups and Techniques

2.1.1 Optical microscopy

In search of seeing smaller objects which cannot be seen with naked eye, optical microscopy is a very useful tool. In the most basic configuration, optical microscope is a combination of two lenses, which magnifies the image of an object. We are limited with the wavelength of the light; however, optical microscopy still has a solid role in scientific research.

As the objective lens, infinity corrected lenses are mostly used. However, since the image is focused to the infinity plane, the image should be recollected and focused to a plane. This is achieved by a tube lens system. The focused image can go to another lens system, which is the eyepiece to see directly or the image can go to a CCD camera. The distance between eyepiece and tube lens should be the total focal length of the two but in case CCD camera, the distance should be the focal length of the tube lens. In our setup, we used a CCD camera and a tube lens with 20 mm focal length.

2.1.2 Scanning tunneling microscopy

Scanning tunneling microscopy is based on the quantum mechanical tunneling phenomena that occurs between the tip and the sample (metal-vacuum-metal tunneling junction). The energy diagram of tunneling junction is shown in Fig. 2.1. φ is the work function of the metal and the work functions of the tip and the sample are considered as equal to make the discussion simpler. When the sample and the tip are put very close to each other, and there is a potential barrier between them, there is tunnelling but there is no net current between the tip and the sample. By applying a bias voltage to the tip, or the sample, a net current flow occurs between the two. Here, the tunnelling current depend on the density of states of the sample at the fermi level, which can be written as in the equation (1.1):

$$\boldsymbol{I \propto V\rho_s(0,E_F)e^{-2\kappa W} \approx V\rho_s(0,E_F)e^{-1.025\sqrt{\varphi}W}} \qquad (1.1)$$

In the equation above, V is the bias voltage, $\boldsymbol{\kappa}$ is the decay constant, which comes from the solution of the Schrödinger equation inside the potential barrier, $\boldsymbol{\rho_s}$ is the local

density of states and $\boldsymbol{\varphi}$ is the work function of the of the sample, and W is the tip-sample distance. The $\boldsymbol{\varphi}$ is about 4 eV and $\boldsymbol{\kappa}$ is about 1/Å.[15]

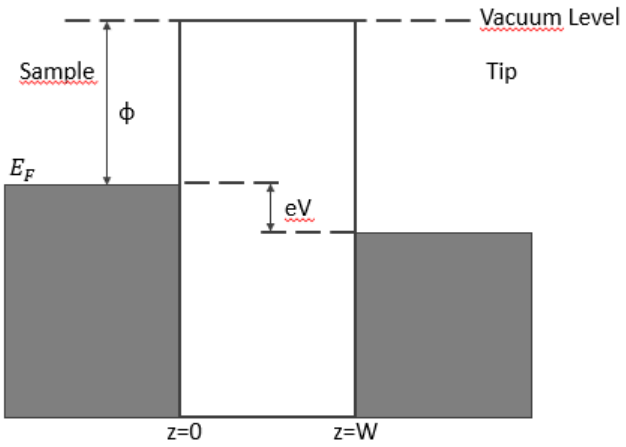

Figure 2.1 : Metal-vacuum-metal tunneling junction.

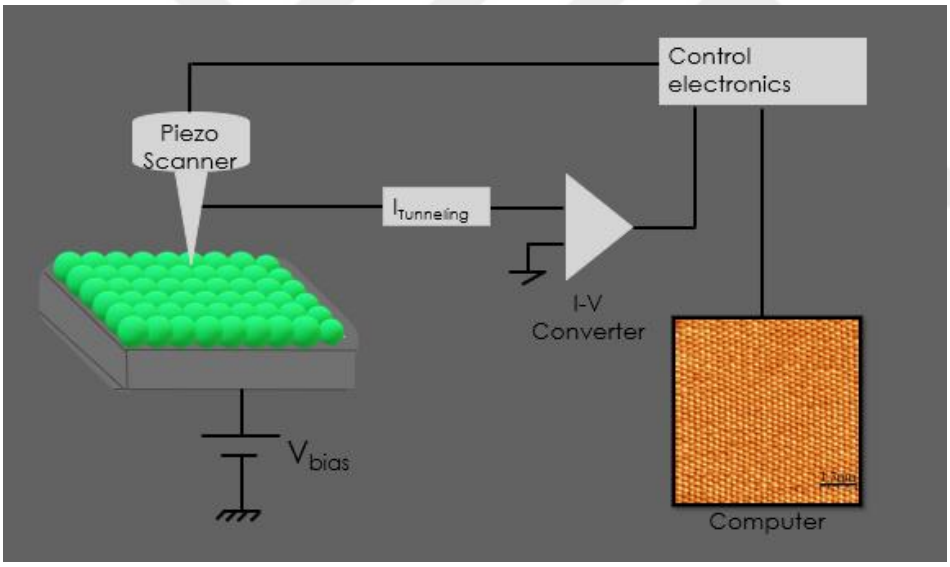

Figure 2.2 : Schematical representation of an STM.

The scheme of a Scanning Tunneling Microscope (STM) is shown in Figure 2.2. The operation principle relies on a feedback loop, which keeps the tunnelling current constant at a given setpoint when raster scanning goes on. Given the bias voltage to the tip, or sample, tunnelling current is measured at each data point and goes to the I-V converter. Behind the tip, there are piezo ceramics which are responsible for the motion in x, y and z directions, and depend on the error signal, the deviations from the setpoint of tunneling current, tip moves towards to or retracts from the sample to keep the current constant.

The idea of an STM explained above was invented by Binning and Rohrer in 1981 at IBM Zurich [16] and their work led them to the Nobel Prize in Physics in 1986[17].

2.1.3 Scanning tunneling spectroscopy

Scanning Tunneling Spectroscopy (STS) is performed to understand how the tunneling current changes with respect to the change of tip-sample distance (I-Z spectroscopy) or applied bias voltage (I-V spectroscopy). This change is a spectroscopic signature for the materials, also the changes in the materials such as the crystallographic orientation, moire structure etc. During I-V spectroscopy, feedback loop is closed to prevent the tip approaches or retracts due to the change of the current. For I-Z spectroscopy, a safe span of motion in z direction is set for a selected data point on the surface during the scanning. While the distance changes, tunneling current data is collected for preset number of points and this data is given in a I-Z graph. For I_V spectroscopy, a safe voltage range is set to prevent the surface gets distorted. In this range, the tip bias varies and for each data point which are set by choice, tunneling current is recorded.

2.1.4 Atomic force microscopy

The STM is a great device to investigate the surface of materials; however, there are some drawbacks. To achieve the tunneling, one need to have a conducting tip and conducting or semiconducting material to investigate. To investigate the whole spectrum of materials, conductor or insulator, other solutions are needed. This need led to invention of another device, the Atomic Force Microscope (AFM), which is invented by Binning, Quate and Gerber in 1986.[18]

The operation of AFM can be thought as feeling and scanning a surface by a fingertip. Here, for AFM, the meaning of “feeling” includes the interatomic forces, such as

chemical, electrostatic, magnetic and lateral forces. The scheme of an AFM device is shown in the Figure 2.3.

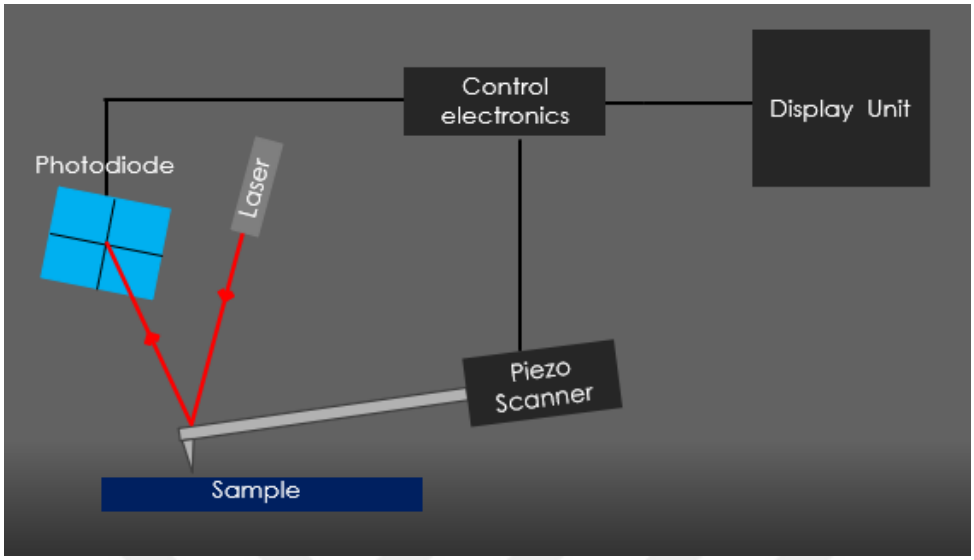

Figure 2.3 : Schematical representation of AFM.

In the scheme, we see a tip which is attached to a cantilever and the apex of the tip is the “fingertip” of the device. When the apex and the surface brought close to each other, interatomic forces emerge. Basically, we can consider the Lennard-Jones potential. When they are close enough, the atoms or molecules attract each other and if the apex get closer to the sample, they start to repel each other due to the Pauli exclusion principle. The attraction and repulsion diagrams related with Lennard-Jones potential is given in the Figure 2.4. As a choice, operation can be held in two modes: constant height and constant force. For both, a laser is directed on the cantilever’s reflecting surface and during the scan, due to the surface structure, cantilever is deflected and the deflection is detected by a four-quadrant photodiode. In constant height mode, the deflection error directly goes to the control electronics and displayed on a screen. In constant force mode, like an STM, we have a feedback loop that takes the error signal, which comes from the photodiode, and according to the amount of the deflection, z piezo move towards or backwards to keep the force constant, and the motion of the z piezo is displayed on the screen.

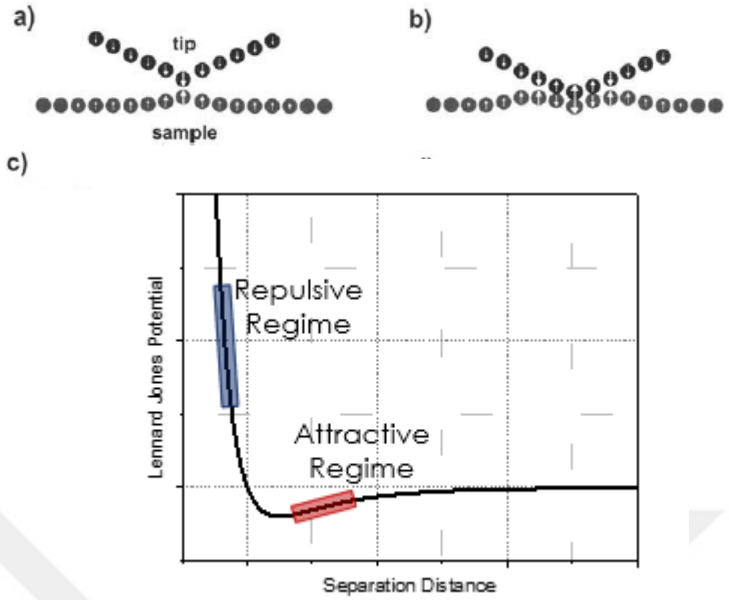

Figure 2.4 : a) and b) represents the attracting and repulsing situations between the tip apex and the sample, respectively [19] c) and shows the attractive and repulsive regions of the Lennard-Jones potential.

Apart from the constant height and constant force operations, there are two operation modes of AFM: static and dynamic modes. In static mode, cantilever raster scans the surface as explained above; however, in dynamic mode, cantilever is driven by an oscillation. This oscillation opens two other set of data: due to the changes on the surface, topological or chemical, the amplitude and the phase of the oscillation changes and these changes can be mapped as well as the topography map.

2.1.5 Friction force microscopy

Friction force microscope (FFM) is a static mode application of an AFM, in which the local frictional behaviour of a local surface can be observed. Cantilever deflection in lateral direction (torsional deflection) occurs differently when it comes to surface friction difference emerges. The torsional deflection can occur also in different situations, such has the surfaces with up-hill and down-hill slopes. This situation can be identified with line scans. In Figure 2.5, red lines represent the forward scan and blue lines represent the backward scan. Grey line shows the subtraction of backward line from forwad line and devided in 2. This yields zero for the deflection due to

topological height differences but if the deflection is due to the lateral forces, it gives non zero result.

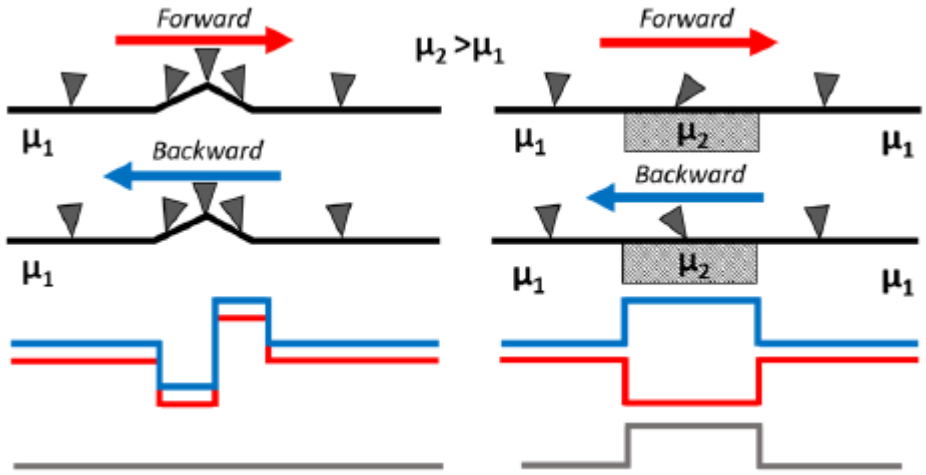

Figure 2.5 : Torsional bending with respect to different situations and their related line scans [20].

2.1.6 Stamping setup

Twisted samples are prepared with a homemade set-up. The layout of the set-up is shown in Fig.2.6. and the photographs of the set-up are shown in Figure 2.7 and Figure 2.8.

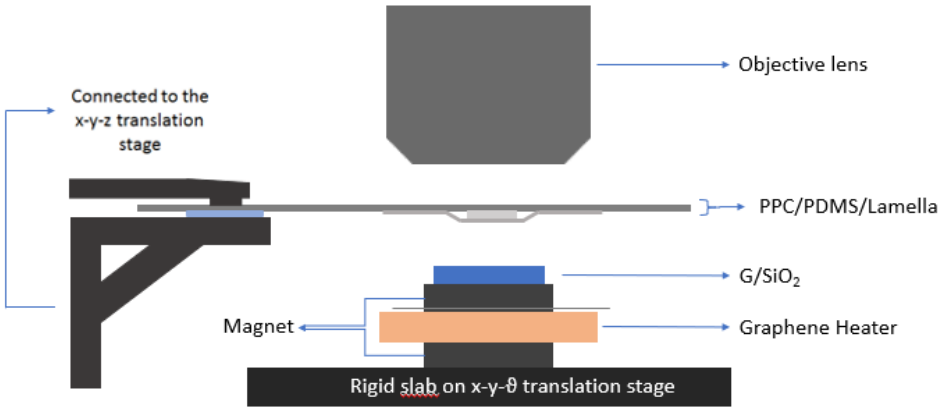

Figure 2.6 : Schematical representation of stamping setup.

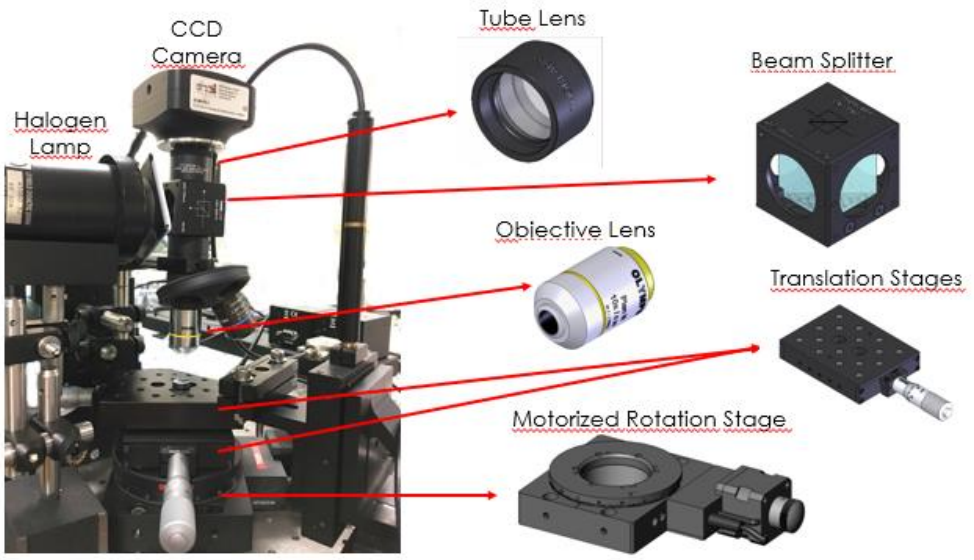

Figure 2.7 : Photograph of the imaging part of the stamping setup.

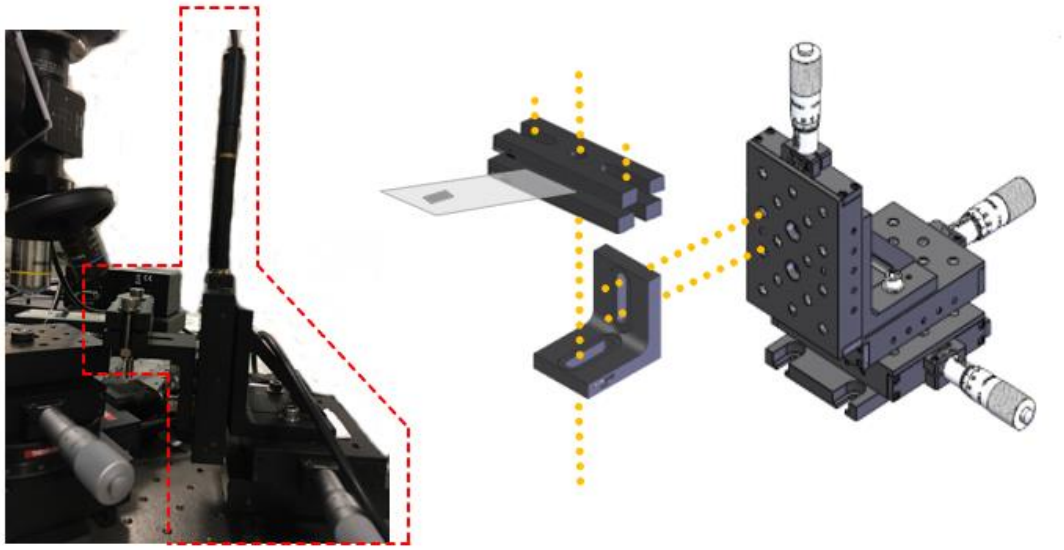

Figure 2.8 : Photograph of the stamp stage of the stamping setup.

The set-up basically consists two main parts: imaging part and the stamp stage. Imaging part is basically an optical microscope, which is shown in the Figure 2.6. A halogen lamp is used to give a proper illumination of the monolayer graphene regions. The 50-50 beam splitter enables to separate the light which is coming from the halogen lamp and it illuminates the sample, then the image goes to the CCD camera. Objective lenses are picked according to the working distances (distance between the lens and the sample); short working distance lenses are not useful since we need to put the stamp in between. So, the distance should be minimum 1 cm to give this freedom.

Sample stage is the combination of two linear translation stages to move te sample in x and y direction and a motorized rotation stage. Rotation is given by the controller to eliminate the human errors and to be able to give rotations with hight acurracy. The samples are glued on a magnet-heater-magnet sandwich to enable the heating of the sample during the pick-up and releasing processes. Magnets are strong enough to prevent unwanted sliding of the sample during the process. The heater is picked as graphene heater. The advantage of this selection is that it can be prepared with any size of choice and do not occupy large area and volume. The stamp is made with a stack of PPC film, PDMS mold and lamella, which are all transparent materials, picked to enable seeing the sample surface from above, the details of the stamp will be given in the next section. The stamp stage, shown in the Figure 2.7 is also a combination of linear translation stages. Stamps can move in x and y direction to align graphene regions with the stamp and z direction to able to perform pick up process. Z-stage is chosen to be motorized again to prevent unwanted sliding of the stamp. A right angle mount is attached on the z-stage and stamp is sandwitched between two slabs and attached on the eight angle mount. To ensure the stamp stands still, we used adhesive pads between the slabs.

2.2 Sample Preparation

2.2.1. Graphene

Graphene samples can be prepared by many different methods, but the main methods that we used were CVD and mechanical exfoliation.

Although CVD grown graphene has the advantage of large size, continuous sheet of graphene [21], the sheet is not only “monolayer” graphene. There are bilayer regions, multilayer regions, islands etc. on a single sheet. Especially, to make twisted bilayer graphene, monolayer is a necessity.

Mechanical exfoliation starts with cleaving an HOPG sample with a Scotch tape. Then, the material left on the tape is exfoliated for 3-4 more times. The details of mechaical exfoliation is explained in Appendix B. Further exfoliation damages the large areas of the material on the tape, so the chance of getting large area of monolayer is decreasing.

Then, the tape is pressed gently on plasma etched SiO_2 wafer with a fingertip. Plasma etching process improves the adhesion between graphene and the SiO_2 surface due to

removing the adsorbates from the surface [22]. For plasma etching, we put the wafers on a cleaned glass slide, then under 45 sccm Ar and 5 sccm O_2 flow, wafers are etched them for 90 s. Recently, 150 sccm O_2 plasma etching for 30s and 60 s were tried. These processes resulted in more monolayer graphene areas on the SiO_2 wafer. Following the plasma etching, to increase the contact, there are two methods to apply: first one is to heat the wafers (with tapes on top) on hotplate for 2 minutes at 100 ^{0}C, the second one is pressing and sliding a blade on the surface of the tape. Both methods give a better chance to get a larger monolayer graphene area on the wafer. Finally, the tape is peeled off from the surface.

2.2.2 Stamp preparation

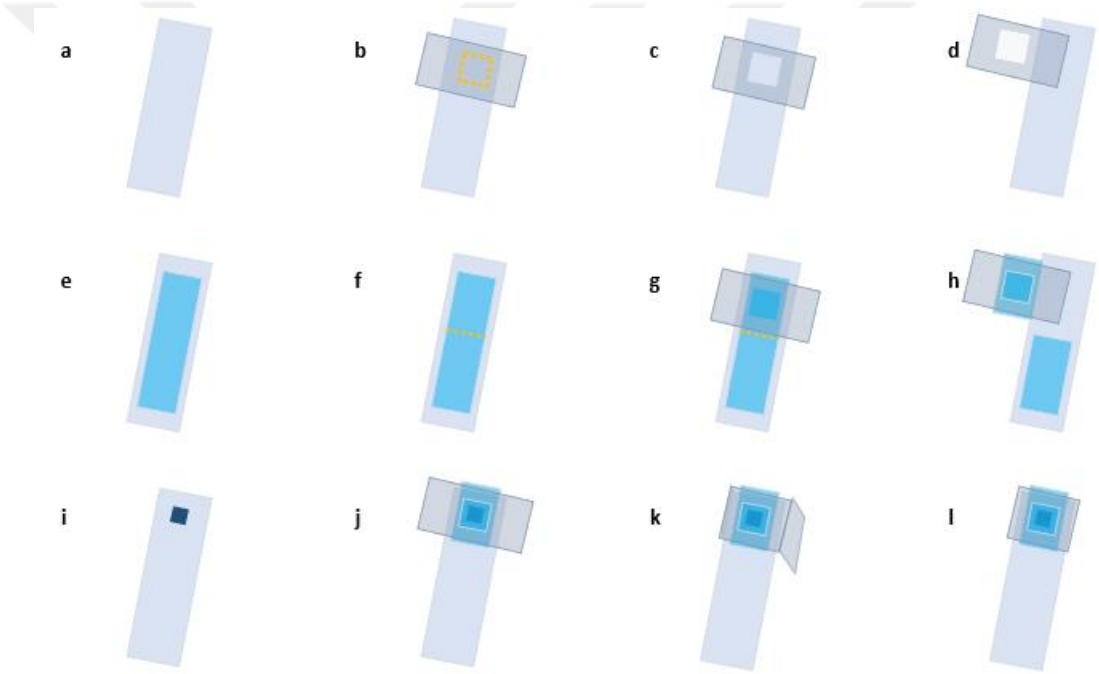

Figure 2.9 : Schematic representation of stamp preparation.

Stamp preparation method is shown step by step in the Figure 2.9. First, a glass slide is taken(Figure 2.9.a), then,a piece of Scotch tape is put on it (Figure 2.9.b), and cut a square window on it with a blade (Figure 2.9.c) and remove the tape (Figure 2.9.d). This tape serves as a frame for the PPC film. PPC films are prepared by drop casting the %15 by wieght PPC solution (in anisole) on a glass slide and put another glass slide and apply pressure on it, and then separate the glass slides and let them dry [23]. In Figure 2.9.e, PPC film represened by blue area on the glass slide. Then, a piece of the PPC film is cut (Figure 2.9.f) and frame tape is put on the PPC film (Figure 2.9.g)

and remove the film (Figure 2.9.h). Finally, a piece of PDMS mold (prepared with Sylgard 184 Silicone Elastomer Kit and 10:1 elastomer:hardener ratio, cured at room temperature for 48 hours) is put on another glass slide (Figure 2.9.i), and the PPC film is placed on top of the PDMS mold (Figure 2.9.j) and fix it with the tape from behind (Figure 2.9.k). Tape should not be too long, otherwise it blocks the view from behind and creates distortion for the imaging. And Figure 2.9.l shows the stamp.

2.2.3 Twisted bilayer graphene preparation

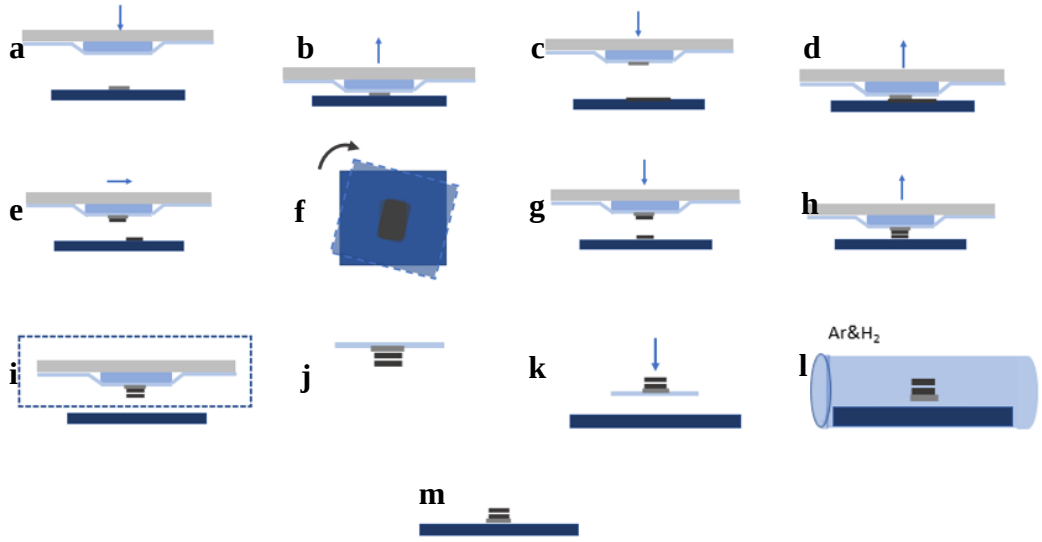

Figure 2.10 : Tear and Stack Technique.

The twisted bilayer graphene samples are prepared with the stamping setup with tear and stack technique [24]. First step is preparing graphene and hBN samples with mechanical exfoliation. Step by step explanation of mechanical exfoliation of graphene is shown in Appendix B and for hBN, mechanical exfoliation is explained in Appendix C. After mechanical exfoliation, the tape residues on graphene samples are cleaned with annealing them in Ar and H_2 atmosphere, 300 sccm and 100 sccm respectively, at 450 ^{0}C.

The second step is pickin-up the hBN and graphene layers of the stack. Schematical representation of each step is shown in the Figure 2.10. As in the Fig 2.10a and 2.10b, the hBN flake (which was prepared by mechanical exfoliation) is picked up with the PPC/PDMS stamp. Fig. 2.10c shows the hBN flake, picked up by the stamp is aligned with the graphene. By changing the focus of the microscope, the alignment can be achieved. As in Fig. 2.10d, by using the motorized z stage, the hBN flake is pressed on graphene and pulled back. Thanks to van der Waals interaction, graphene region

which is in contact with hBN is teared and rest of the graphene remains. Then, as in the Fig. 2.10e, the sample stage is slided and realigned with the rest of the graphene on SiO_2 wafer. Finally, as in Fig. 2.10f, graphene sample is rotated and In Fig. 2.10g and 2.10h, the stack on the stamp is pressed on top of the remaining part of the graphene and pulled back again.

The final step is transfering the stack on a clean SiO_2 wafer. The final stack shown in Fig. 2.10i. Then, The PPC film is peeled from PDMS (Fig. 2.10j), and the PPC film and the stack is transfered on SiO_2 wafer, as in Fig. 2.10k. This way, TBG will be looking upwards. Later, the final product is annealed in Ar and H_2 atmosphere, 300 sccm and 100 sccm respectively, at 450 ^{0}C again to get rid of the PPC film (Fig. 2.10.l) [23]. The TBG sample with a precise rotation is shown in Fig. 2.10m.

3. RESULTS AND DISCUSSION

3.1 First Pick-up Experiment

First attempt of picking up a graphene flake was achieved by a flake of Bi_2Te_3 crystal. This selection was made because it was known that Bi_2Te_3 is another van der Waals crystal and van der Waals interaction between the layers can pick up the graphene. First experiments held at ambient conditions and without heating because of the former preparation technique of PPC films; these films were prepared by spin coating the PPC on a glass at 4000 rpm for one minute. Since they were very thin, the PPC became distorted, even glued on the SiO_2 wafer at very low temperatures, such as 25 ^{0}C and 30 ^{0}C. So, this procedure did not incuded heating the samples. The Bi_2Te_3 crystal is brought on top of a monolayer graphene region, pressed for two minutes and drew back. In Figure 3.1, the process can be seen. The images were taken with a hand microscope (Dyno Lite) instead of the CCD camera because of the limitations of objective lenses. Figure 3.2 shows the graphene flake before and after the pick-up experiment.

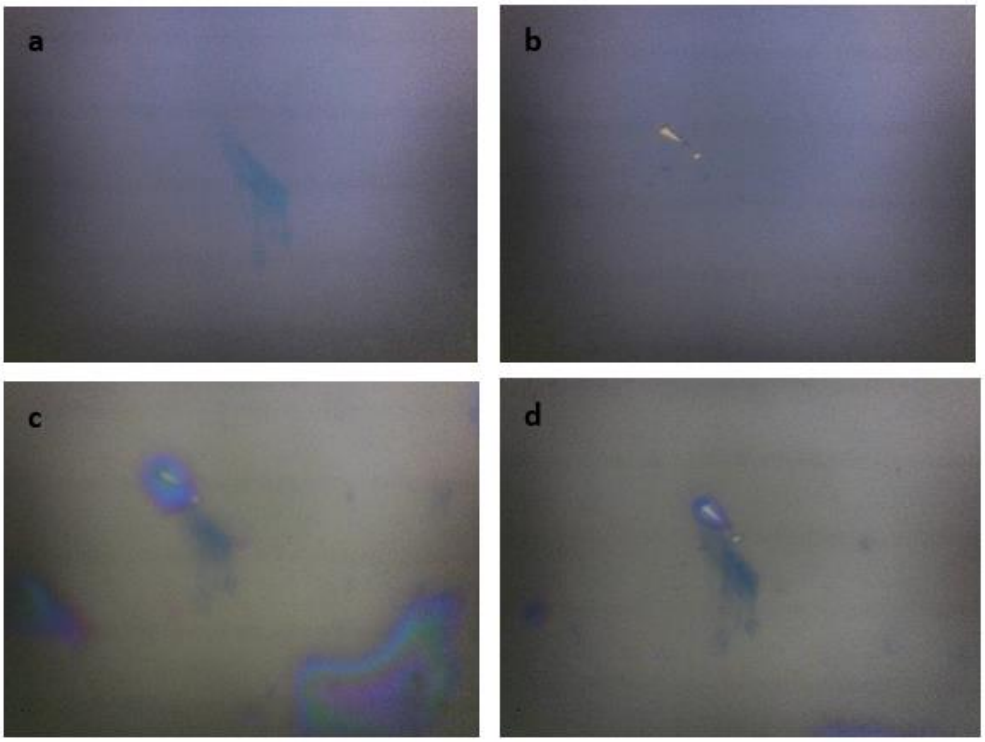

Figure 3.1 : a) and b) graphene and Bi_2Te_3 flakes before they brought in contact, c) the image after the contact is achieved and d) shows the further pressing and waiting process.

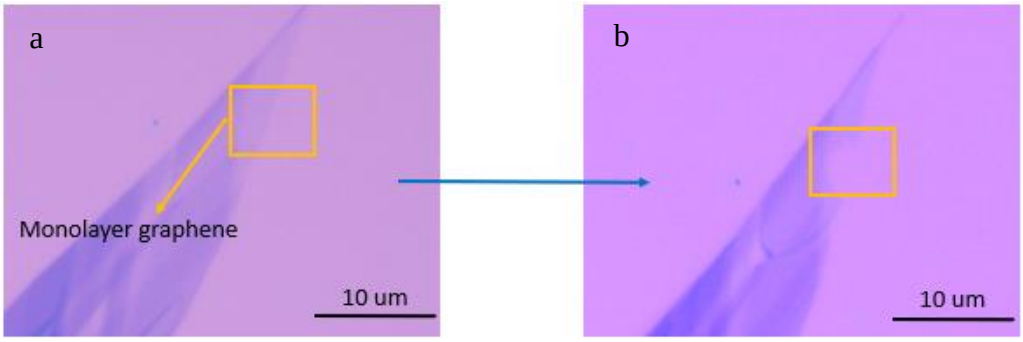

Figure 3.2 : a) Before and **b)** after images of the graphene flake, it is observed that in the area where Bi_2Te_3 brought in contact, tearing occurred.

The configuration of the system during this procedure was giving poor quality in imaging, and the sample had to be taken to another optical microscope to see if the pick-up procedure was succesful. So, I could not pick-up the second layer graphene because the position and the alignment of the graphene flake would be changed after the putting the sample to the set-up. But, we observed that picking-up the graphene was possible with the Bi_2Te_3.

During the procedure, we did not use a graphene sample which is not prepared with the plasma etching of SiO_2 wafer; so, the ambient condition was enough to tear the graphene and separate it from the SiO_2 wafer. After the arrival of hBN crystals, we also started using the plasma procedure as a part of graphene sample preparation. Plasma procedure cause graphene adhere more on SiO_2 wafer and heating the graphene samples was necessary to the pick-up procedure. The PPC we used is not resistant to the heating, as explained above. So, we tried pick-up procedure without heating but we saw that it was not possible after many unsuccesful attempts.

3.2 STM Investigation of CVD Grown Graphene

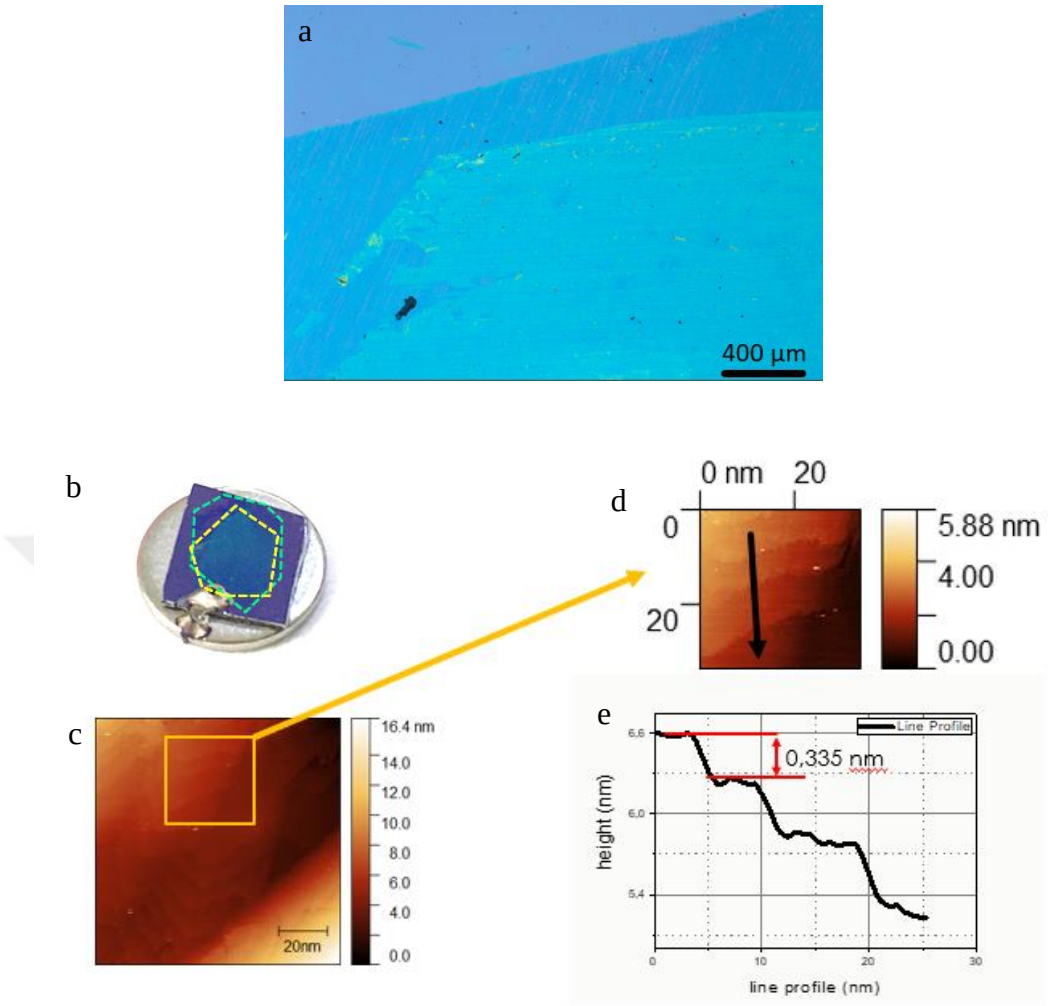

Figure 3.3 : a) Optical microscopy image of a twisted bilayer graphene, prepared by PMMA mediated transfer method on SiO_2, b) STM data of the same sample and c) is its zoomed in image. Red arrow indicates the line scan and the height profile according to the line scan is shown in d.

In the Figure 3.3a, optical microscopy image of fabricated twisted bilayer graphene in arbitrary rotation angles, is shown. Figure 3.3.b is the photograph of the sample; green dashed lines whow the first, yellow dashed lines show the second layer of graphene. This sample was prepared with PMMA mediated transfer method (see Appendix A). The copper foils have rough surfaces and because the approximate angle between the two layers is 65^0. As in the Figure 3.3.b, the sample is attached on a metal sample holder with a silver paste, also, the silver paste is spread on a side of a sample, without damaging the sample, and made sure that she silver paste is also touches to the sample holder which enables the flow of the tunnelling current. Figure 3.3c shows the STM topographical image of the same sample. The data is taken nearly at the center of the sample. Here, a multi-layered structure of graphene is observed. The line scan is taken

for step height measurements in Figure 3.3.d and the Fig 3.3.e shows the relevant step height of the layers. The measured step height is consistent with the HOPG interlayer distance, which is 0.335 nm.

STS data for three different samples; TBG, monolayer graphene and HOPG, are shown in the Fig. 3.4. TBG and monolayer graphene samples were prepared with PMMA mediated wet transfer method. In Figure 3.4.a, STM data of TBG is shown and the purple dot is the data point where we take the STS measurment. At this point, surface is flat and there is no layered structure. In Figure 3.4.b, STM data of HOPG is shown and the blue dot is the data point where we take the STS measurment and in Figure 3.4.c, STM data of monolayer graphene is shown and the black and red dots are the data points where we take the STS measurments.The black and red lines show the I-V curve of a monolayer graphene sample on different points. Purple and green lines show the I-V curve of TBG sample, at the purple dot, backwards and forwards respectively and the blue line shows the I-V curve of HOPG. It is shown that HOPG has the lowest conductivity while the TBG has the highest, even though we cannot control the angle between the layers. For monolayer graphene sample, I-V curve gave a high conductivity as well, it might be due to a local effect.

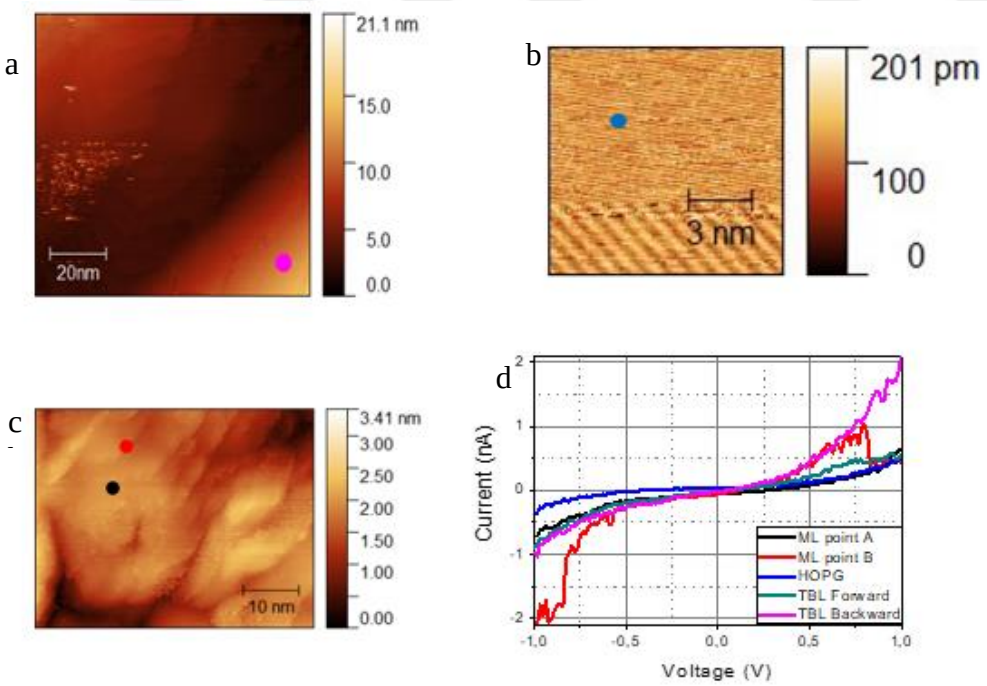

Figure 3.4 : a) and c) STM data of twisted bilayer graphene and monolayer graphene, respectively. Both are prepared with PMMA mediated method, b) STM data of HOPG surface, d) shows the STS I-V curves indicated with the same colours in a,b and c.

3.2 AFM Investigation of Graphene and hBN Samples

We investigated mechanically exfoliated graphene and hBN samples with dynamic mode AFM. Green dashed box on AFM data shows where we took the histogram for monolayer graphene on SiO2 wafer and yellow dashed box shows the area where we took the histogram for determining the interlayer distance of graphene. The height of graphene on SiO_2 is found to be 0,85 nm in average and the step height of the layers of graphene (0,335 nm expected) is found to be 0,44 nm in average**.**

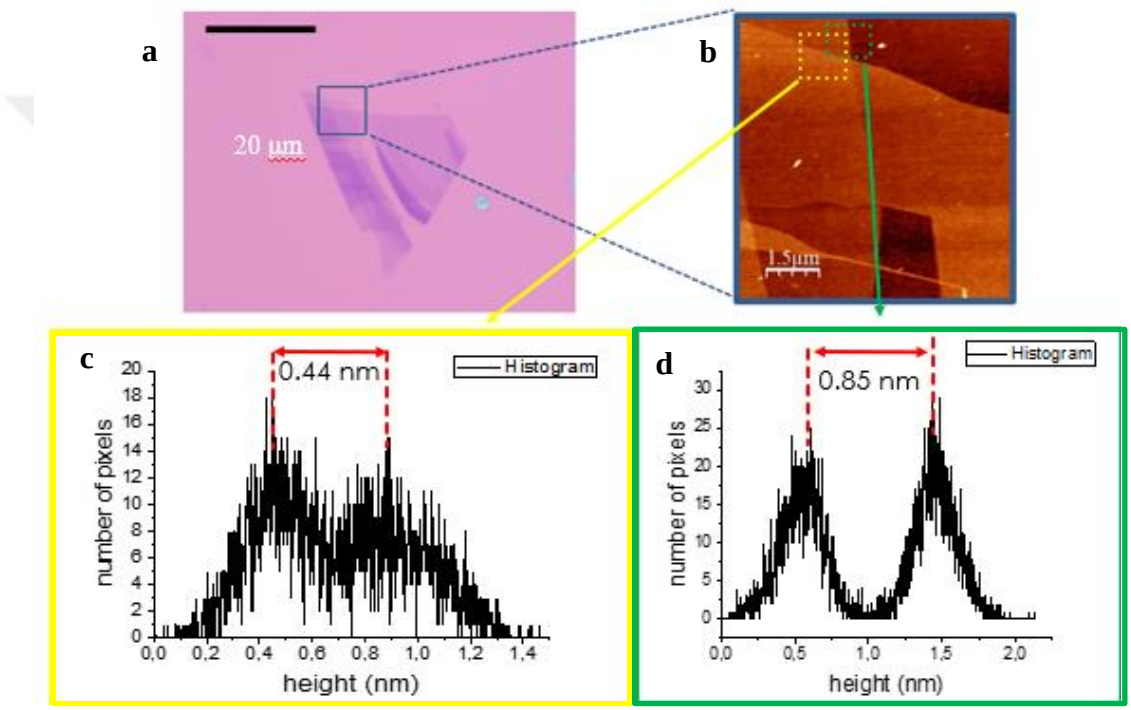

Figure 3.5 : a) Optical microscopy image and b) AFM image of a graphene flake on SiO2 wafer. The scale bar on optical data shows 20 µm and AFM data is taken in the square region indicated with a blue box. c) and d) shows the histograms indicated with the yellow and blue boxes.

The graphene samples were exfoliated from Grade-3 HOPG and transfered on plasma etched SiO_2 wafer. The plasma etching parameters are 50 W, 90 s, Ar (45 sccm) and O_2 (5 sccm) flow. Plasma etching process cleans the wafers delicately, and this is one of the reasons for graphene to hold on to the surface of the wafer. Also, we think that the process “activates” by removing some of the oxidized layers and opens some holes (because of the “mechanical” cleaning of argon) on the surface and graphene holds on to these defects. In figure 3.6, one of the holes which was created by the plasma ething

is shown and it is investigated with AFM. That surface also cleaned with the same parameters which are mentioned above. The depth of the hole specified in the purple dashed square is approximately 5.7 nm.

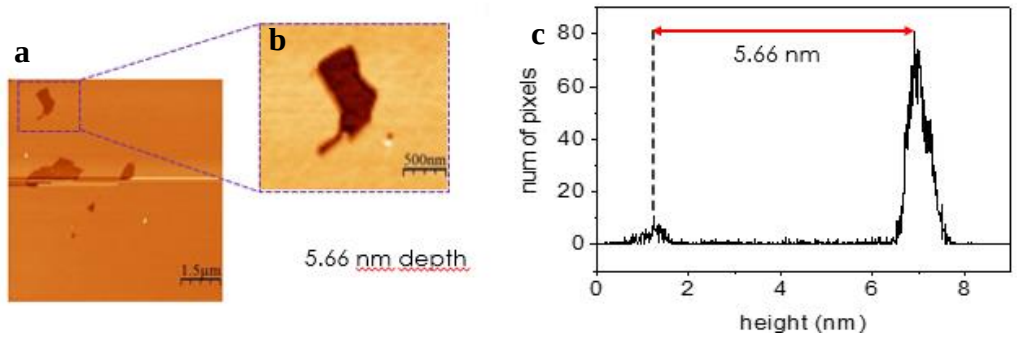

Figure 3.6 : a) AFM data of some holes which are opened because of plasma treatment on SiO2 wafer, b) zoomed in AFM data and **c)** is the related histogram of the data on b.

The hBN flakes which are exfoliated from 2D Semiconductors Large Area crystals are found to have clean and flat surfaces, which are suitable for tear and stack graphene. In the Figure 3.8, optical and AFM data is shown. This flake is chosen to estimate the approximate height of hBN flakes. hBN flakes can be acquired with many different heights with mechanical exfoliation method. and since it is a transparent crystal, different colours can be seen for different heights. As observed in the Figure 3.7, different numbers of layers can give different coours on the same flake under the optical microsope. The height of the the flake in Figure 3.8 is found to be approximately 25 nm.

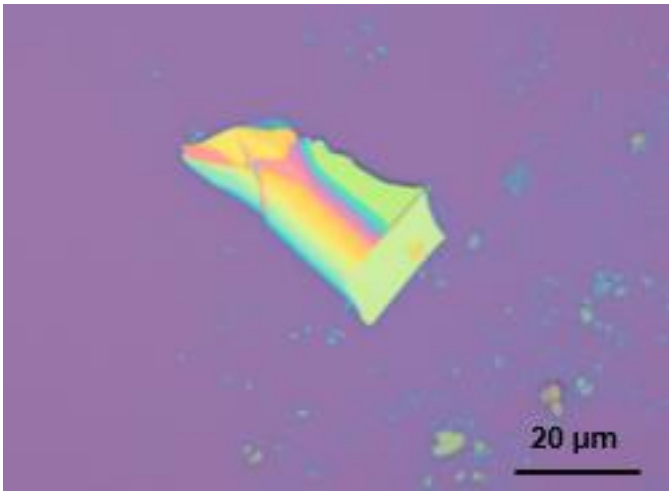

Figure 3.7 : Optical Microscopy image of a single hBN flake, which has varying number of layers.

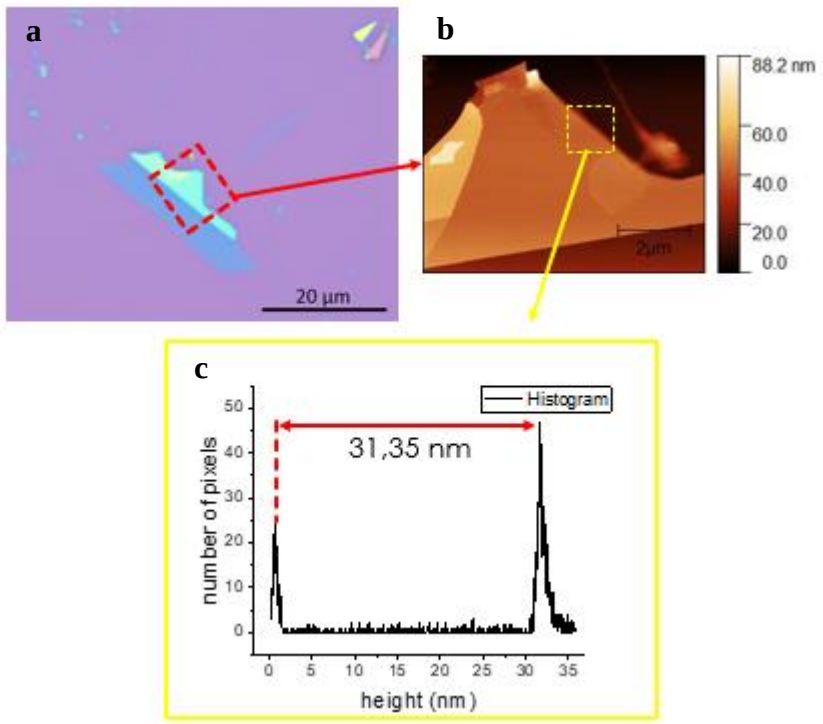

Figure 3.8 : a) Optical Microscopy image of an hBN flake, b) AFM data taken in the area indicated with a red box in a, c) histogram of the area indicated with yellow dashed square.

3.3 FFM Investigation of Twisted Bilayer Graphene

We aimed to investigate the friction behavior of twisted bilayer with respect to their twist angle. However, this stands as a future plan for the project. To understand the friction behaviour, we need a set of experiments ahead. For this purpurpose, firstly, we need to understand the friction behavior of monolayer graphene and hBN on SiO_2 wafer alone. Then, we need to compare them with the situation where the numbers of layers are increasing for both materials. Later, after we pick up graphene with hBN and hBN is our new substrate, we need to understand the friction behavior of graphene on hBN and compare with graphene on SiO_2. Increasing number of layers can be another parameter here, so this situation also will be compared as well. Finally, friction behavior of twisted bilayer graphene will be examined for different twist angles.

4. CONCLUSION

In this study, we aimed to investigate the electronical and mechanical studies of twisted bilayer graphene samples. For this purpose, built a home-made stamping setup from the scratch, which can be used to prepare twisted bilayer graphene samples with controlled twist angle. Graphene and hBN samples are investigated with optical microscopy and AFM. Also, effects of plasma etching of SiO_2 wafers are observed. We used Bi_2Te_3 crystal as a proof of concept for pick-up experiments at the beginning and we observed that pick-up can be done with this set-up. After acquiring hBN crystals, we had difficulties of picking-up the samples, which was related to the plasma etching process. Plasma etching of SiO_2 wafers caused graphene stick on the wafer, so heating was needed. But at this point, we observed that our PPC was not heat resistent, so these experiments should be done with another polymer which is heat resistant. So, twisted bilayer graphene samples are still tried to be prepared. These samples will be investigated with AFM, FFM and Scanning Spreding Resistance Microscopy as a future work. We are expecting to see different friction behaviors of these samples with respect to twist angle. Also, we were able to prepare twisted bilayer graphene samples with PMMA mediated wet transfer method. Despite the inability to control the twist angle with this method, our STS experiments showed that twisted bilayer graphene samples showed a better conductivity than HOPG and monolayer graphene.

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APPENDICES

APPENDIX A: PMMA Based Transfer Method of Graphene

APPENDIX B: Mechanical Exfoliation of Graphene

APPENDIX C: Mechanical Exfoliation of hBN

APPENDIX A

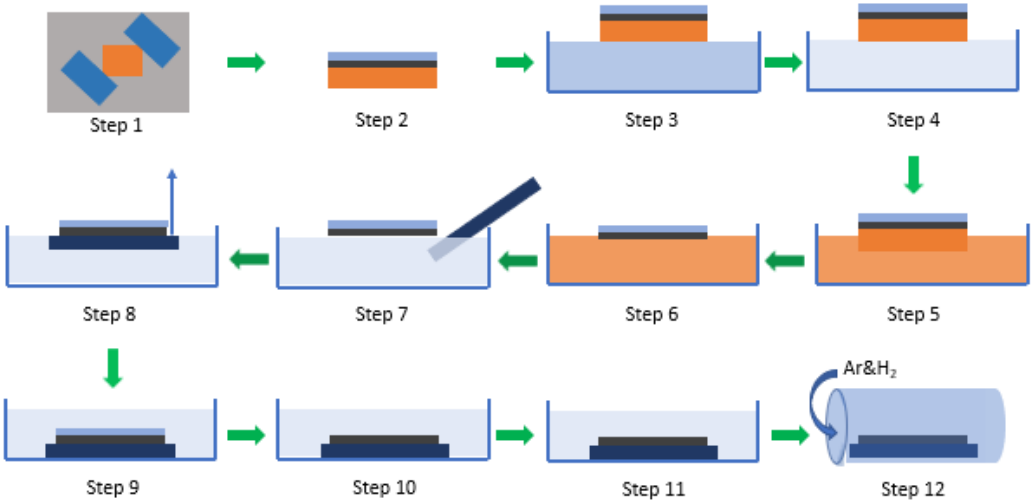

Figure A.1 : Schematical representation of PMMA based graphene transfer.

Step 1: CVD grown graphene on copper (G/Cu) is flattened with a glass fixed onto a substrate such as glass or aluminium oxide plate with Scotch tape.

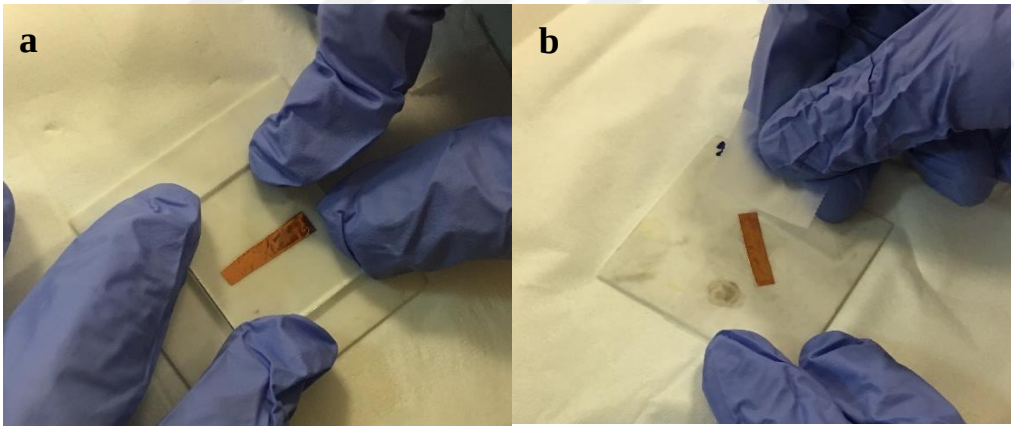

Figure A.2 : a) Flattening the copper foil with a glass, b) fixing the sample with Scotch tape.

Step 2: PMMA solution (%4, dissolved in acetone) is drop casted and spin-coated on G/Cu, then left for curing at RT for 12 hours. For samples with the dimensions 2cm x 2cm, 2500 rpm is more supporting and for bigger samples, 4000 rpm is more convenient to let PMMA to cover the whole sample. For the spin coating procedure, it is better to give 200 rpm/s acceleration before it reaches to the desired spin value and 200 rpm/s decceleration after the coating is done. After curing, graphene is taken from the aluminum plate with a razor by cutting the taped parts.

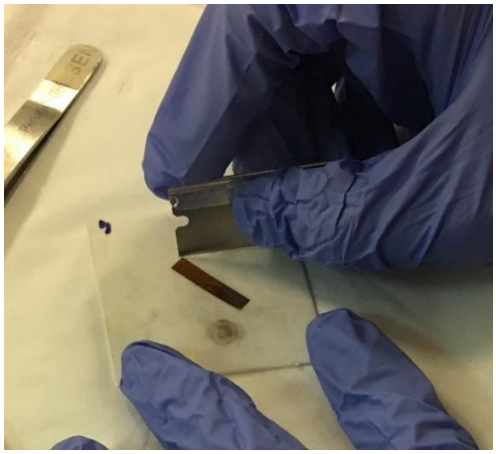

Figure A.3 : Cutting the samples taped sides.

Step 3: Since graphene is grown on both sides of copper, PMMA/G/Cu stack is put on nitric acid (1:3 DI water, diluted) to perform backside etching. Here, you need to use a tweezer which can be used with nitric acid. When the bubbles are seen under the copper foil, the sample is taken onto DI water.

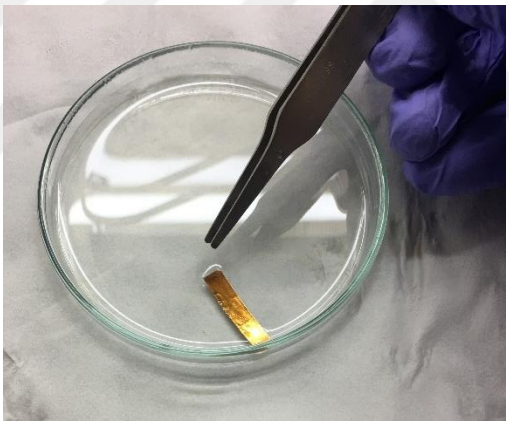

Figure A.4 : Backside etching in nitric acid.

Stage 4: PMMA/G/Cu stack is rinsed in DI water 3 times.

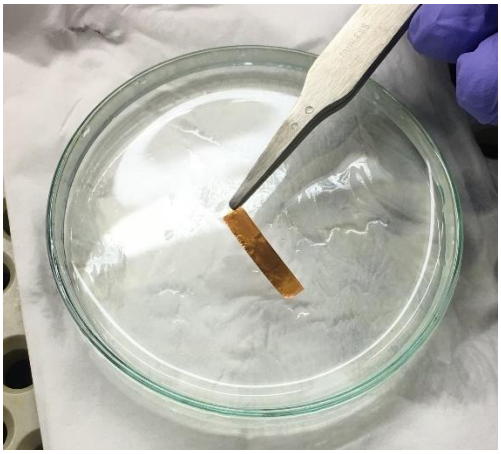

Figure A.5 : Schematical representation of PMMA based graphene transfer.

Stage 5 & 6: PMMA/G/Cu stack is transferred on 0.5 M $FeCl_3$ solution in a watchglass until copper is etched. After all copper is etched, wait for an additional hour to make sure that it is completely etched. Since $FeCl_3$ etches metals, carbon or ceramic tip tweezers are used during this process. Then, FeCl3 is rinsed 3 times in DI water.

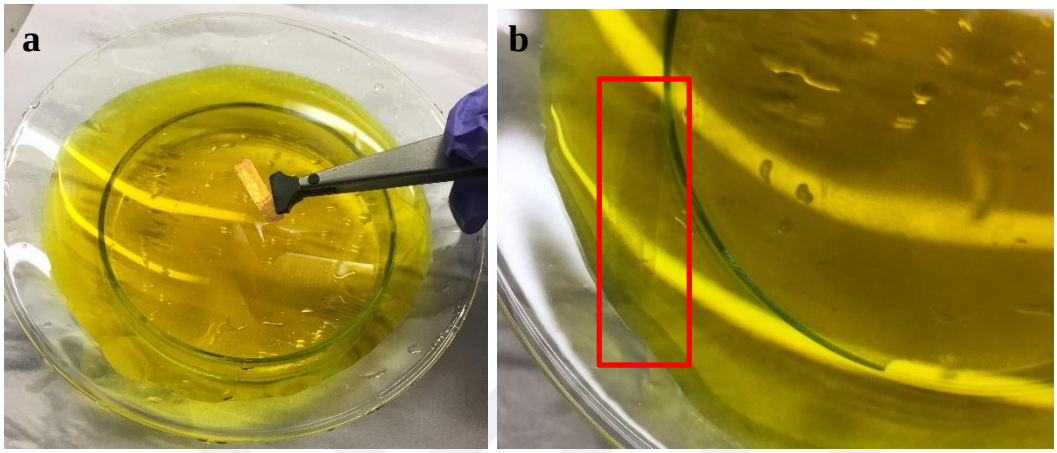

Figure A.6 : a) Putting PMMA/G/Cu on $FeCl_3$ solution, b) PMMA/G stack

Then, the floating PMMA/G stack is taken with a smaller watch glass and FeCl3 is diluted with in DI water. Then the small portion on the watchglass with the sample is poured on DI water carefully. This is repeated 3 times.

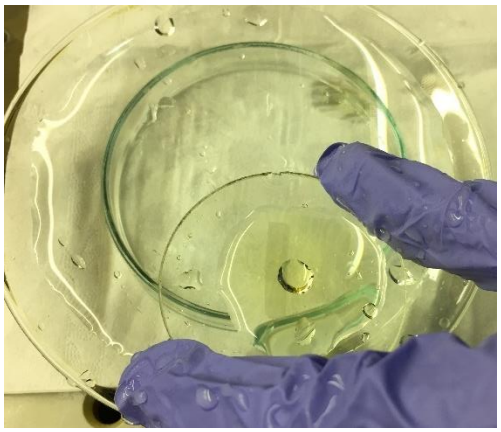

Figure A.7 : Diluting $FeCl_3$ solution.

Step 7 & 8 : Swimming PMMA/G stack is fished with the target substrate (here, quartz plate was used) and N_2 blow drying is applied to remove the water at the interface, also to increase the contact between graphene and the substrate. The sample is left in dessiccator for 12 hours.

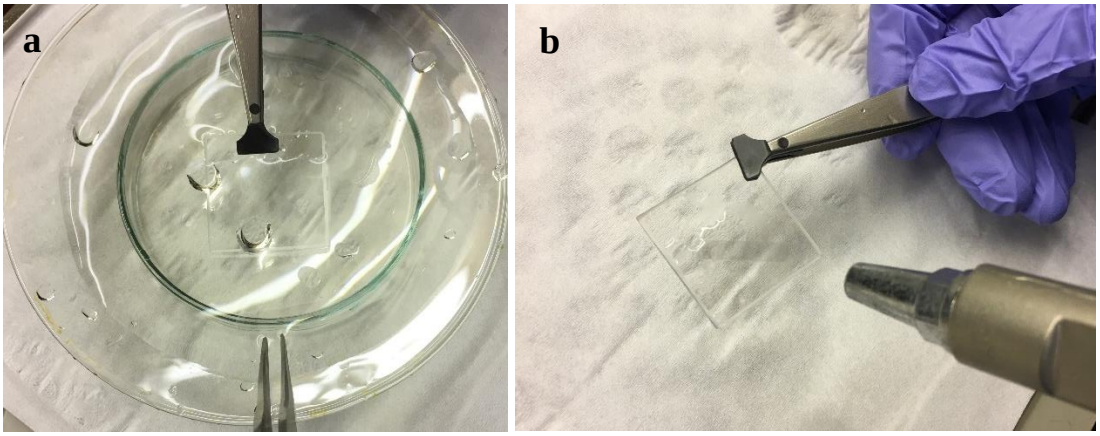

Figure A.8 : a) Fishing the PMMA/G, b) N_2 blow drying the sample on the left.

Step 9: The sample is put in acetone to remove PMMA layer for an hour.

Step 10: The sample is put in IPA to remove accetone residues for half an hour.

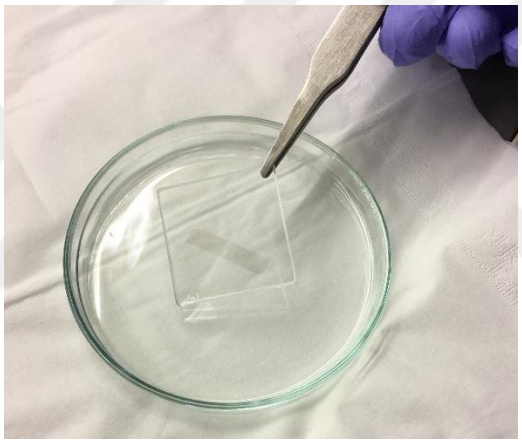

Figure A.9 : Putting the sample in acetone bath.

Step 11: The sample is put in DI water for half an hour to remove IPA residue.

Step 12: For further residue cleaning (e.g. to increase the graphene quality for making graphene based devices), the sample is annealed at 450^0C in furnace in Ar&H_2 atmosphere. The flow rates are 300sccm for Ar and 100sccm for H_2. Annealing time can be set as 3 hours.

APPENDIX B

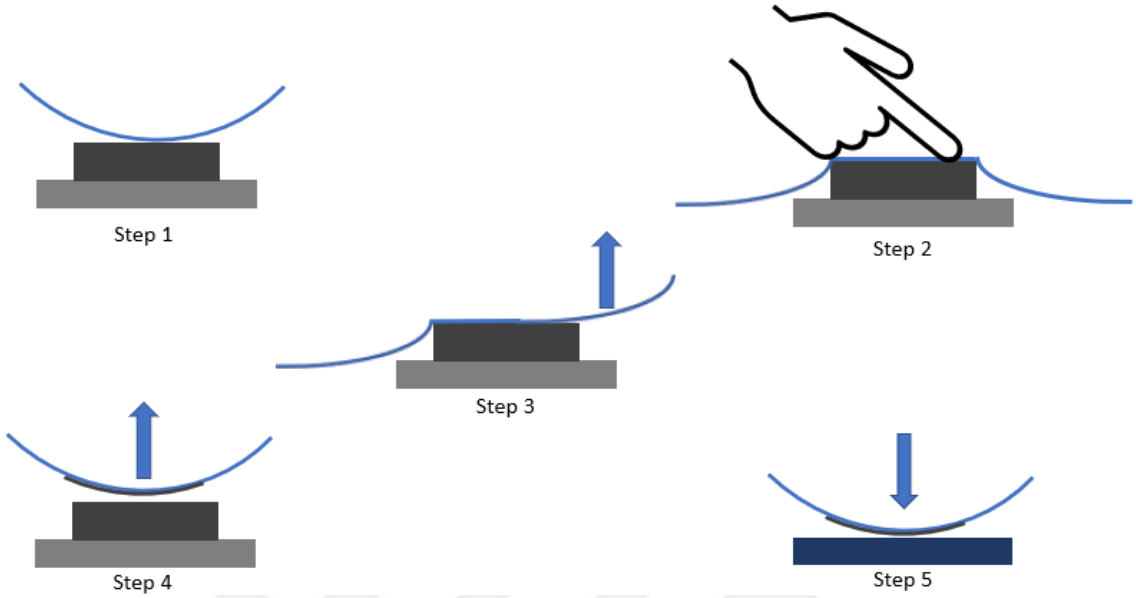

Figure B.1 : Schematical representation of mechanical exfoliation of graphene.

Step 1: Put Scotch Tape onto HOPG sample. Sample needs to be held by a substrate (Gel Pack or some vaccum underneath).

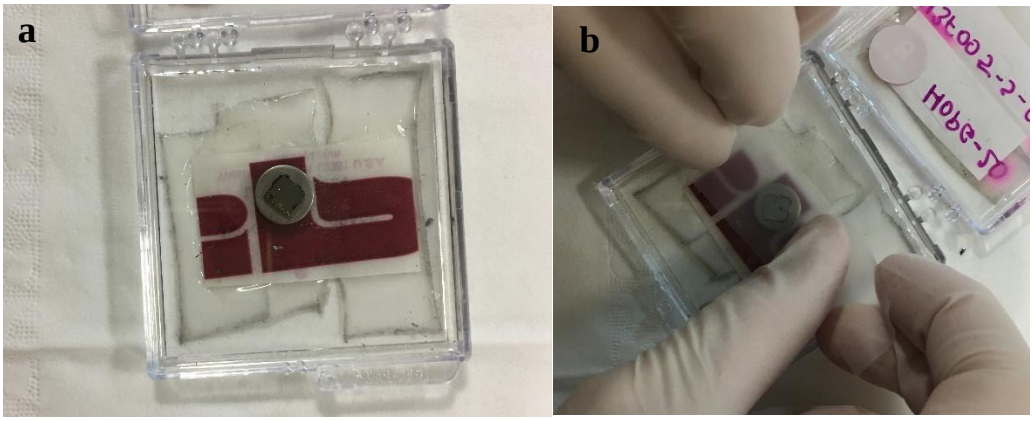

Figure B.2 : a) HOPG sample on a Gel-Pak, b) and putting the scotch tape on HOPG.

Step 2: Press gently on the tape to increase the contact.

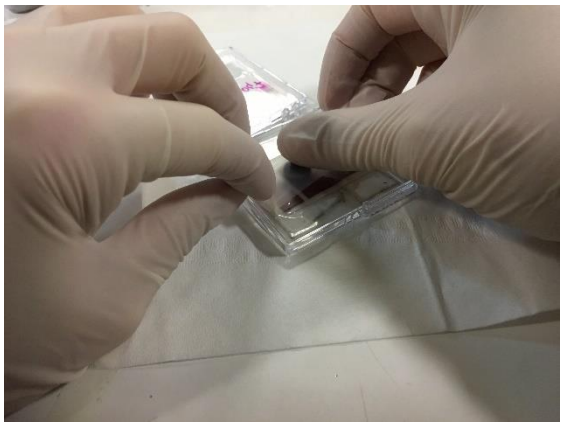

Figure B.3 : Pressing on the tape gently.

Step 3 and 4: Detach the tape from HOPG sample and exfoliate the HOPG on the tape.

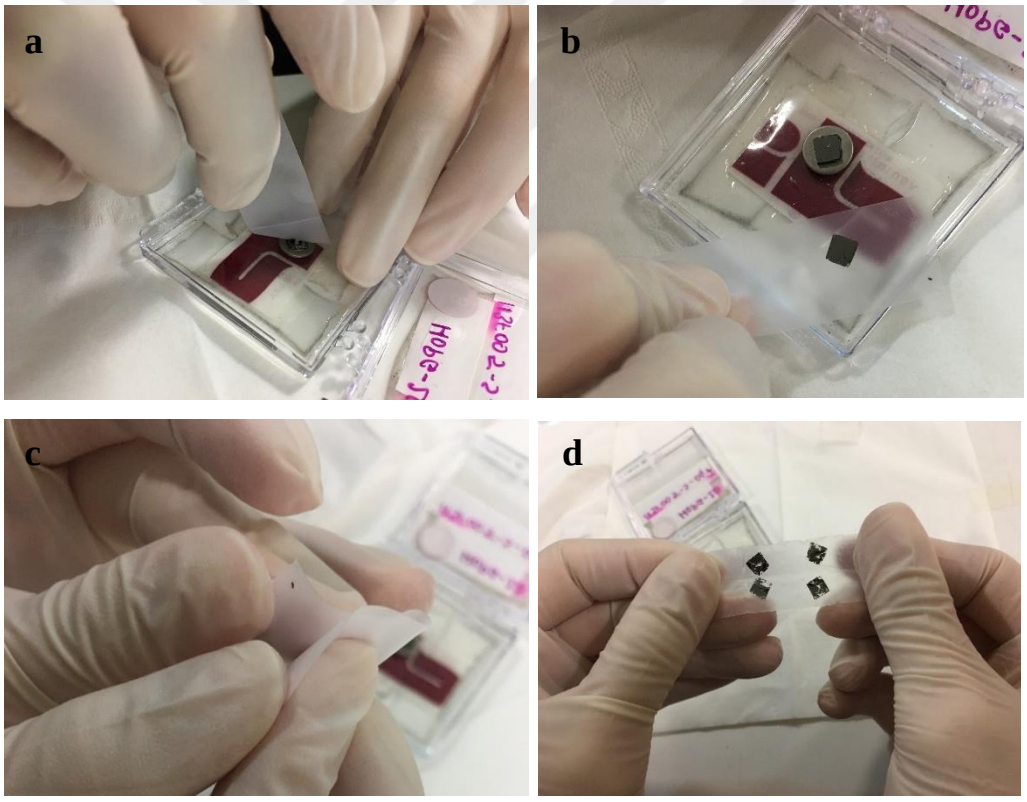

Figure B.4 : a) removing the tape b) cleaved HOPG on the tape, c)and d)exfoliating the cleaved HOPG.

Step 5: Bring the tape with cleaved HOPG layer and put on top of the cleaned target substrate and apply pressure with heating the sample, finger, side of a blade etc…

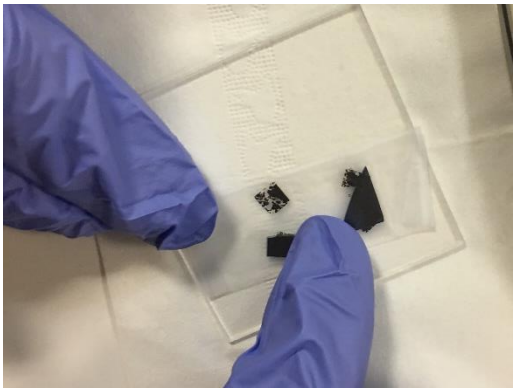

Figure B.5 : Pressing gently on the tape which is attached to the SiO_2 wafer.

Step 6: Remove the tape from the substrate

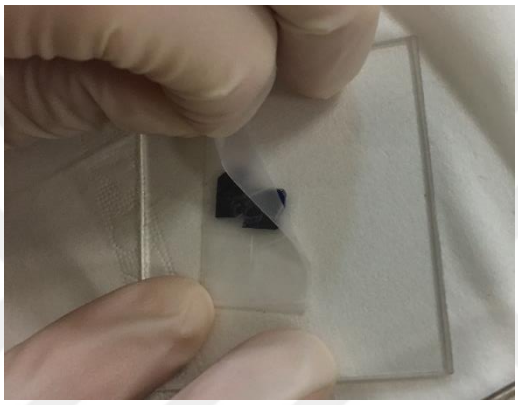

Figure B.6 : Removing the tape from the SiO_2 wafer.

For further cleaning, to get rid of the tape residue from the sample, anneal the samples at 450^0C in furnace in Ar:H_2 (300:100 sccm) atmosphere for 3 hours.

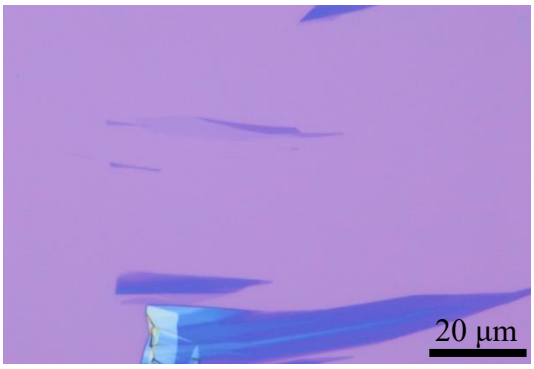

Figure B.7 : Mechanically exfoliated graphene sample.

APPENDIX C

Step 1: hBN samples are also prepared with mechanical exfoliation method, explained in Appendix B, but for hBN, it starts with dropping the hBN flakes on a Gel-Pak.

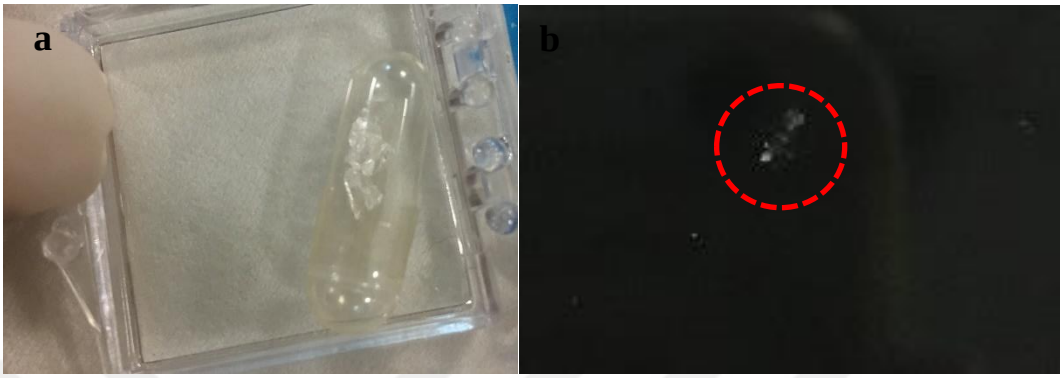

Figure C.1 : a) hBN large area crystals in a capsule, purcashed from 2D Semiconductors, b) the dropped small pieces of crystals on a Gel-Pak in red dashed circle.

Step 2: Take the piece of crystal, which is dropped on the Gel pack, with a small touch of Scotch tape. It is important to be gentle for not leaving tape residue on the Gel-Pak.

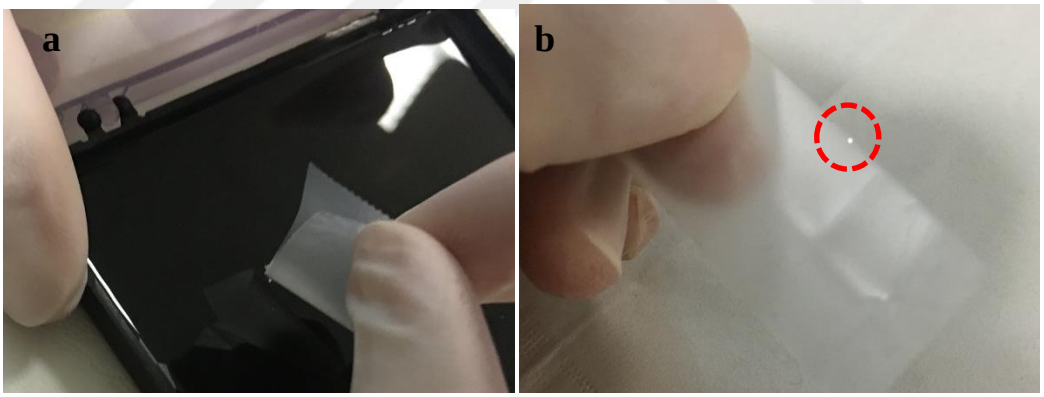

Figure C.2 : a) Taking a piece of small flake, b) flake is shown in red dashed circle.

Step 3: After taking the flake from Gel-Pak, start exfoliating the flake using the whole area of the tape.

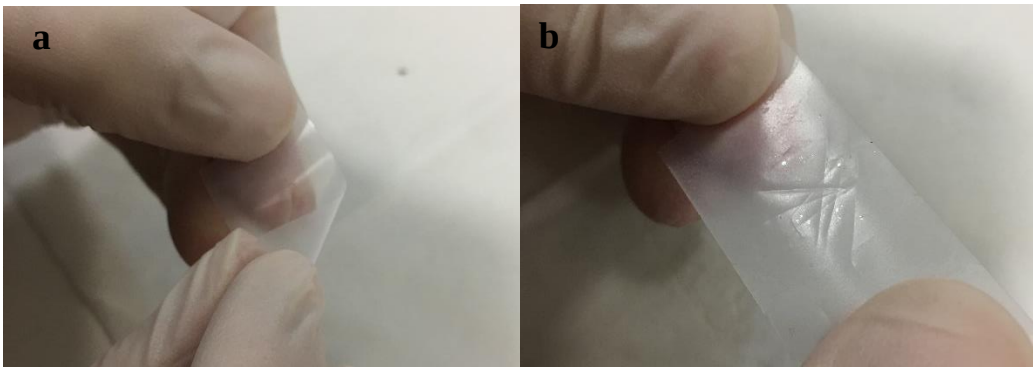

Figure C.3 : a) Exfoliation of hBN flake, b) exfoliated hBN flakes on the tape.

Step 4: Put the tape in contact with a SiO2 wafer and press gently on the tape. Then remove the tape from the wafer with no further treatment.

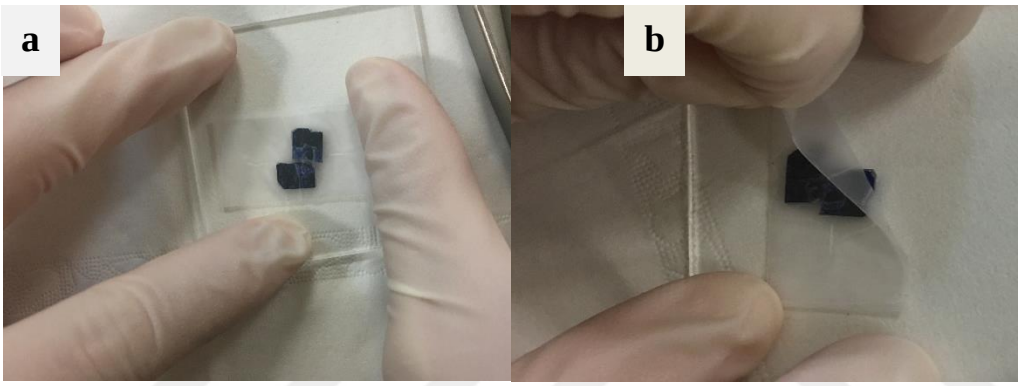

Figure C.4 : a) Putting the tape on the SiO_2 wafer, b) removing the tape.

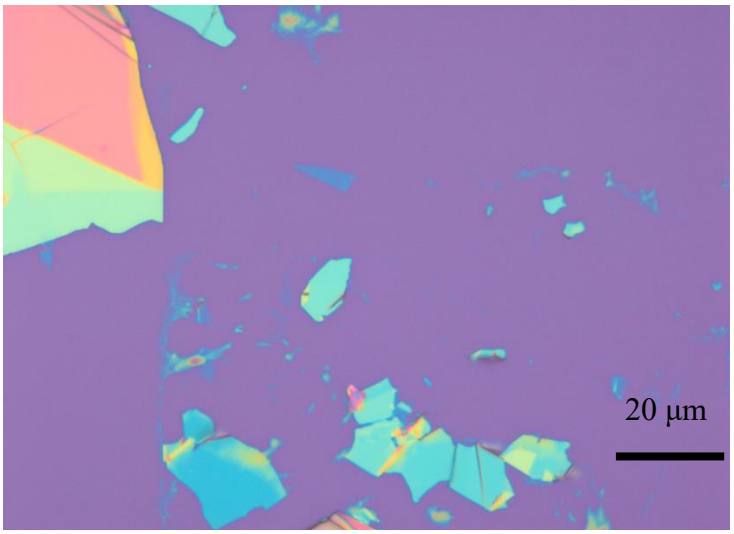

Figure C.5 : Mechanically exfoliated hBN sample, hBN flakes are in different sizes and thicknesses…

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