



3 Synthesis and Study of 2D Materials: Graphene

[Talk in YouTube](#)

Authors:

Bhuvan Prakash

Lalaji Memorial Omega International School

Esraaj Sarkar Gupta

Vidya Mandir Senior Secondary School

Mentors:

Prof. M S Ramachandra Rao, Professor in Department of Physics, IIT Madras

Kaushalya Kumari, Research Scholar, Department of Physics, IIT Madras

Ravindra Kumar, Research Scholar, Department of Physics, IIT Madras

Acknowledgements

We extend our heartfelt gratitude to IIT Madras, The Padma Seshadri Bala Bhavan Schools, The Agastya International Foundation, and Pravaha for affording us the invaluable opportunity to learn from esteemed professors and engage in this project. Our sincere appreciation goes out to the RSIC office bearers, Patrons, Coordinators, Chairmen, and members for their unwavering support.

We would like to convey our deep appreciation to our mentor, Prof. M S Ramchandra Rao from IIT Madras and his PhD students Kaushalya Kumari, Ravindra Kumar and Subhajit Chatterjee, for guiding us throughout this remarkable project and imparting knowledge on Synthesis and Study of Graphene.

Furthermore, we are immensely grateful to the various professors who delivered lectures on diverse scientific and mathematical concepts, patiently addressing our queries. We extend our thanks to all the faculty members at IIT Madras who, directly or indirectly, contributed to the realisation of this project.

1. Introduction

Graphene is a promising material that has gained immense research attention since 2004 when it was first synthesised by A. Geim and K. Novoselov. Derived from graphite, which is a layered, flaky allotrope of carbon, graphene is essentially a single layer of sp^2 hybridised carbon atoms bonded in a hexagonal lattice ($a = b \neq c$, where a , b and c represent the unit cell dimensions; $\alpha = \beta = 90^\circ$ and $\gamma = 120^\circ$, where α , β and γ represent the respective angles between the edges of the edges of the unit cell). Thus, graphite can be imagined to be composed of multiple layers of graphene stacked on top of each other, bonded by Van der Waals' Forces (VdW Forces), which can be determined by Eq (1) as shown below.

$$F_{VW}(r) = \frac{AR_1R_2}{6r^2(R_1 + R_2)}$$

... (1)

Here, r is the radius between spherical bodies 1 and 2, $F_{VW}(r)$ represents VdW Force as a function of r , $R_{1,2}$ are the radii of spherical bodies 1 and 2 respectively, and A is the Hamaker constant.

There are several ways in which this stacking can occur. In AAAA stacking, these layers are stacked right on top of each other, and consecutive graphite crystals are bonded through VdW Forces. In ABAB stacking, every other layer is bonded, as depicted in Figure 1.2 (a). Similarly, in ABCA stacking, every third layer is bonded, shown in Figure 1.2 (c).

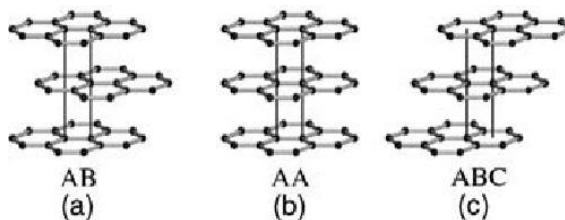


Figure 1.2: Stacking of graphite layers

R. Liu, L. Fang, Z. Tang "Synthesis of Carbon Nanowall by Plasma-Enhanced Chemical Vapor Deposition Method"
Journal of Nanoscience and Nanotechnology - 2014, 14(2):1647-57

Graphene is termed to be a 2D material. Unlike in mathematics where 2D implies that the object is completely planar i.e. that its thickness $z = 0$, in material sciences, any material with a

thickness that does not exceed 100 nm can be called a 2D material. A single layer of graphene has a thickness of $z \sim 1.1$ nm to $z \sim 3$ nm.

Graphene is currently of great interest to researchers due to the extraordinary properties it possesses. It has been observed to have a tensile strength of approximately 130 GPa, thus making it the strongest material ever tested, and a modulus of elasticity $Y = 1 \pm 0.1$ TPa. Apart from excellent mechanical properties, graphene also exhibits high electrical conductivity, which may reach up to 80 MS/m. This makes it more conductive than copper which has an electrical conductivity of $\sigma_{Cu} = 60$ MS/m. Graphene also exhibits high thermal conductivity, which is measured to be up to 5000 W/mK, all while being an optically transparent material. These properties make graphene a very viable and perhaps in some cases a better substitute for a multitude of materials used commercially today.

This project aims at synthesising, isolating and characterising graphene crystals produced from graphite crystals via top-down synthesis methods. The characterisation of prepared crystals are to be done by Raman Spectroscopy, Atomic Force Microscopy and Scanning Electron Microscopy.

2. Synthesis of Graphene

There are two broad categories of the methods of synthesising graphene: top down and bottom up. In top down synthesis methods, graphite crystals are broken apart (exfoliated) until single or multilayered graphene is obtained. In bottom up synthesis, graphene is synthetically produced and directly deposited onto a substrate.

In this project we looked into two top-down methods of exfoliation where graphite crystals were separated into layers by overcoming the VdW bonds that held these layers together to synthesise single layered graphene. As we discussed previously, this stacking of layers can occur in three ways: AAAA, ABAB, ABCA. It is clear that VdW Forces between bonded layers is the highest in AAAA stacking and least in ABCA stacking, as depicted in Figure 1.2. Since we have shown previously that VdW Force is a function of radius (r), and that it is inversely proportional to the square of r . Thus we can theoretically determine that separation of graphite into graphene could best be done in graphite crystals with ABCA stacking. Thus, ideally, we would like to carry out the exfoliation on graphite crystals with ABCA stacking.

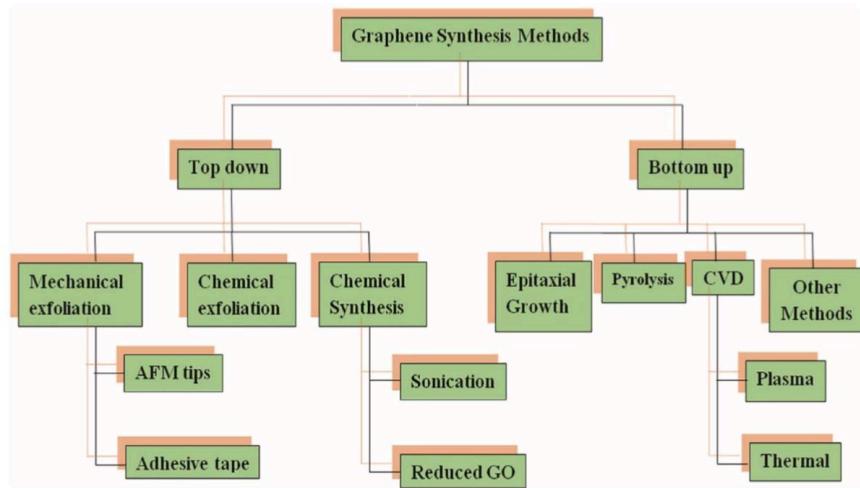


Figure 2.1: Different methods of synthesis of graphene

M. Skoda, et al., Graphene: one material, many possibilities—application difficulties in biological systems, *J. Nanomater.* 2014 (2014), 890246.

2.1 Mechanical Exfoliation

Mechanical exfoliation is a top down synthesis method for the production of small graphene crystals, first used by Andre Geim and Konstantin Novoselov back in 2004 to make the first samples of graphene. This method involves the repeated removal of layers of graphite crystals to obtain a single layered crystal using an adhesive. A highly oriented pyrolytic graphite (HOPG) crystal is used. This process is rather unreliable and may require multiple attempts to produce an acceptable sample of graphene. Mechanical synthesis allows us to acquire exfoliated crystals of graphene without significant amounts of contamination, thus bypassing the need for a post-synthesis cleaning process. The procedure also only requires easily available equipment and apparatus.

Graphite crystals were placed on scotch tape and exfoliated by the repeated peeling of multilayered graphite crystals to obtain single layered and multilayered crystals. Exfoliated crystals are then placed on silicon substrates coated with a 90 nm or 200 nm layer of silicon dioxide. The procedure was repeated to produce 8 prepared substrates.



Figure 2.2: Mechanical exfoliation of graphite

2.2 Chemical Exfoliation

Graphite can also be exfoliated in its liquid phase by chemical exfoliation. Chemical exfoliation involves the dispersion of graphite powder in a solvent such as ethanol. Graphitic solutions are prone to the agglomeration of graphite particles. To prevent agglomeration, an anti-agglomerant is introduced to the graphite solution. Alternatively, stirring or ultra-sonication could theoretically be used to prevent this phenomenon.

Chemical exfoliation aims at breaking the Van der Waals' bonds present between each layer of carbon atoms bonded in their hexagonal lattice to produce single layered graphene. This is done by allowing electrolytes to dissociate in the solution. Since $\Delta H_{\text{mix}} < 0$ for electrolytes, they release some energy upon being dissociated in the solution. This energy is thus used to break the VdW bonds between the layers of graphite, leaving us with graphene powder. Chemical exfoliation involves post-synthesis cleaning steps in order to separate the graphene powder from the reagents used in the process.

We were unable to carry out a chemical exfoliation process due to the lack of required reagents and time.

2.3 Commercial Methods of Preparation

The methods of synthesis mentioned above are rather rudimentary and are not expected to yield defect free single layered graphene crystals. Commercial graphene sheet synthesis requires dedicated and expensive equipment. While many industries have been able to produce

large sheets of graphene using other electrochemical and pyrolytic synthesis methods, defect free graphene sheets with the extraordinary properties mentioned previously are extremely hard to produce. So far, the largest sheets of near-perfect graphene have been no more than 10 mm x 10 mm in size, produced by Graphene Platform™.

3.Characterisation of Graphene

3.1 Raman Spectroscopy

A Raman Spectrometer is a device which operates on the principle of the Raman Effect and is used to identify the chemical composition of samples. It generally consists of a monochromatic laser, an optical filter and a charge coupling device (CCD).

The sample is hit by the monochromatic laser which thus absorbs energy to excite its electron to a virtual energy state. When the electron gets de-excited, it emits light of the same wavelength to return to its ground state. However, sometimes it may release photons of different wavelengths. The emitted light is passed through an optical filter, which filters out the light of the same wavelength as that of the laser. This ensures that only Raman Scattered light is allowed to then hit the CCD detector. The photons that hit the CCD detector are thus used to construct an emission spectrum. The peaks of the generated emission spectrum are then studied to identify the composition of the given sample.

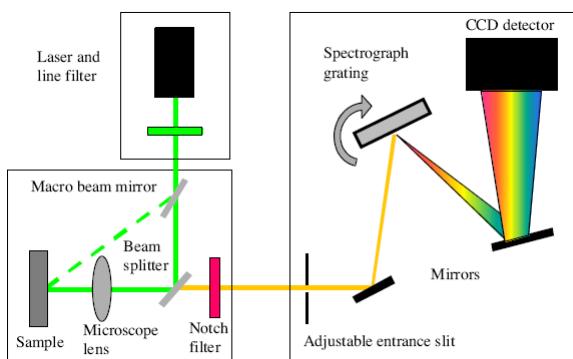


Figure 3.1: Raman Spectroscopy Primer
An Introduction to JASCO Raman Spectrometers and the Raman technique

Graphite crystals that were optically identified to be thinner than most others were analysed using Raman Spectroscopy. Graphite crystals always seem to have a non-zero graphene peak,

ignoring noise. A crystal is termed to be a graphene crystal if its graphene peak (2700 cm^{-1}) is higher than its graphite peak (1600 cm^{-1}). Defect peaks are also seen, which is thought to be caused by impurities from the preparation process. A peak from the residue of glue that was used during exfoliation was also seen.

3.2 Atomic Force Microscopy (AFM)

Atomic force microscopy (AFM) allows us to map the topology of objects with a resolution of roughly 1 nm. While there are many kinds of AFM, we chose to use non-contact AFM (nc-AFM) due to the rough nature and large range of sizes of our crystals. An atomic force microscope has a few major parts, which include a needle (4) with a tip mere nanometers thick (as depicted in Figure 3.3.2) mounted on a cantilever (1). The needle is brought close to the object (6) without contact, reaching a distance $d \sim 5\text{ \AA}$, at which point Van der Waals' Force is noticeable.

The cantilever is then oscillated with a known, constant frequency by a piezoelectric element (3). The VdW force acting on the tip of the needle changes the amplitude or frequency of oscillation. A laser is used to direct light onto the cantilever that is then reflected and received by a photodiode (5), which interprets the changes in oscillation. This then allows the device to compute the distance between the needle and the sample, which is then used to map the topology of the sample under study. The device also ensures that the distance between the needle and sample is always kept at a constant d , and the height of the needle is adjusted as the topology of the sample varies.

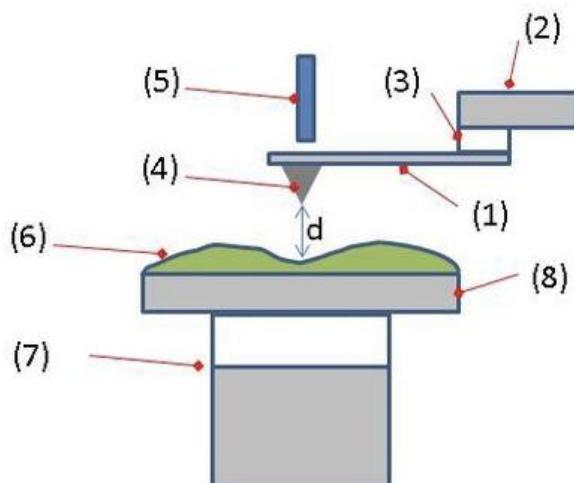


Figure 3.2: Major parts of AFM

https://en.m.wikipedia.org/wiki/Atomic_force_microscopy

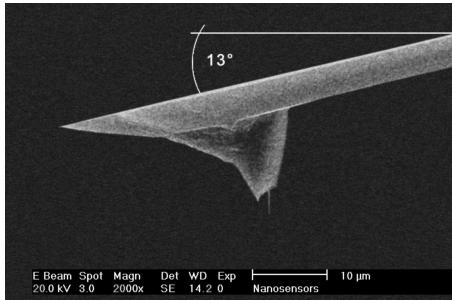


Figure 3.2.1: Needle mounted on cantilever

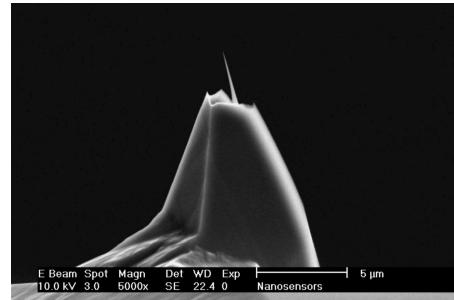


Figure 3.2.2: Needle Tip

[Reference 7]

Since VdW Force is incredibly weak compared to most other forces, nc-AFM is very prone to errors. Thus, to ensure that error is avoided in the computing of VdW Force, the same region is mapped consecutively by the nc-AFM: forward reading and backward reading. Only if the topology in both the readings match, the data is said to be accurate. Occasionally, the forward and backward reading data may not match, in which case the data is deemed to be inaccurate and is thus discarded.

Crystals of graphene are studied using non-contact AFM, which allows us to determine the dimensions of the crystal and yield the following images. The thickness of crystals is measured by measuring the difference in height between the substrate surface and the highest point of the crystal.

3.3 Scanning Electron Microscopy

SEM is used to image the sample surface through detecting different signals generated from the impact of focused highly energetic electrons at the sample surface.

A SEM generally consists of an electron source, Anode, Condenser lens, Objective lens, Scan coil and the detectors. The electron source is sealed inside a special chamber to preserve vacuum and protect it against contamination, vibrations, and noise. Electromagnetic lenses are used in SEM instead of glass lenses, as electrons cannot pass through glass. The Electromagnetic lenses are made up of coils of wires inside metal pole pieces. The magnetic field generated when current is passed through the coil is used to control the path of the electron beam.

The interaction of electrons within a sample can generate many different types of electrons, photons, or radiations. In the case of an SEM, the two types of electrons used for imaging are backscattered and secondary electrons. Backscattered electrons belong to the primary electron beam and are reflected back after elastic interactions between the beam and the sample. Whereas, secondary electrons originate from the atoms of the sample, they are a result of inelastic interactions between the electron beam and the sample. The image of the sample is obtained when these electrons are detected.

Scanning Electron Microscope

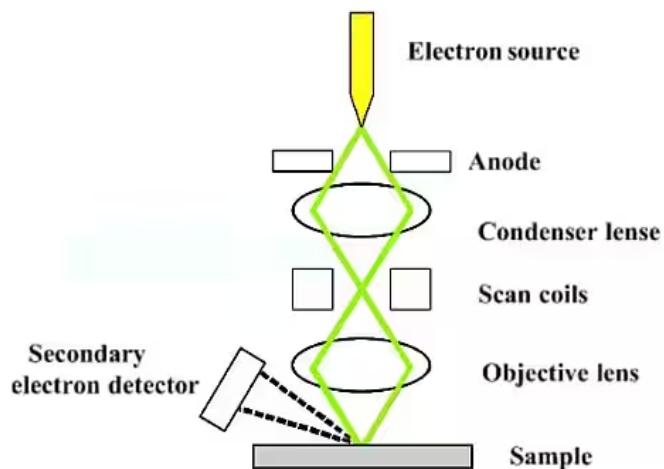


Figure 3.4: Components of SEM

<https://www.thermofisher.com>

4. Results

Out of two of our exfoliated samples, two were selected and studied using the characterisation techniques discussed above. Let us name them Crystal 1 (C_1) and Crystal 2 (C_2).

Studying C_1 and C_2 under the Raman Spectroscopic produced the following Raman Spectra where three major peaks are observed. The first peak, occurring at roughly 500 cm^{-1} is the silicon peak (Si peak), present due the nature of our substrate. The second peak, termed the G peak, occurs around 1600 cm^{-1} denoting the presence of graphite. The last peak, called the 2D peak, represents single layer graphene. Smaller peaks present in the spectra are expected to be due to noise, defects and other impurities (such as the glue used for mechanical exfoliation).

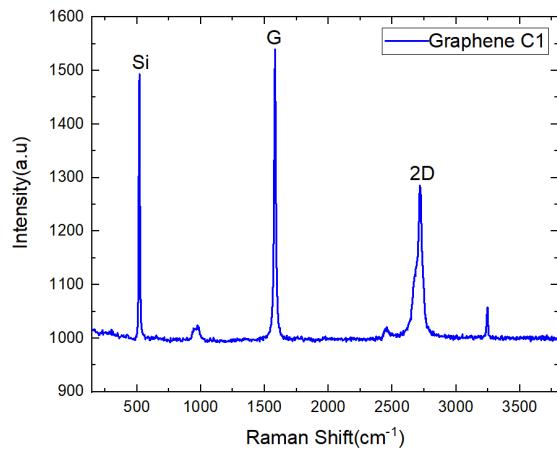


Figure 4.1.1: Raman Spectrum of C₁

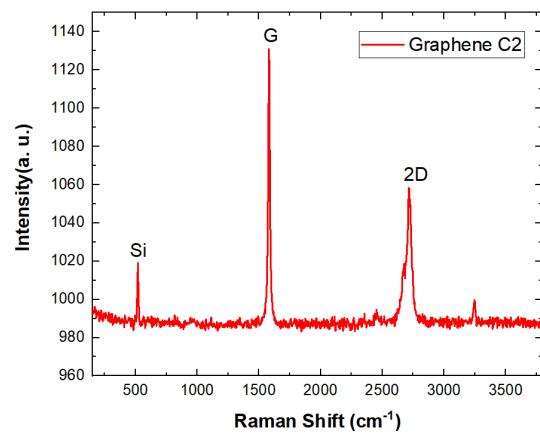


Figure 4.1.2: Raman Spectrum of C₂

As depicted in the Raman Spectra (Figure 4.1.1) above, C₁ has a significant difference between its G and 2D peaks, indicating that the selected crystal has a very low amount of graphene compared to graphite. We thus classify C₁ to be a graphite crystal. Similarly C₂ has a G peak that is higher than its 2D peak. Although the difference between the peaks is much lower, we cannot classify C₂ to be a graphene crystal yet since graphene crystals are expected to produce a Raman Spectrum where the 2D peak is higher than the G peak.

Analysing the crystals under an AFM, we are able to obtain their topology and thickness.

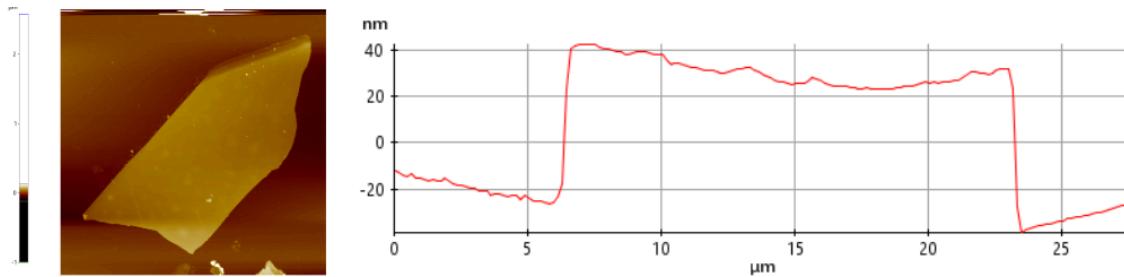


Figure 4.2.1: Topology of Crystal 1

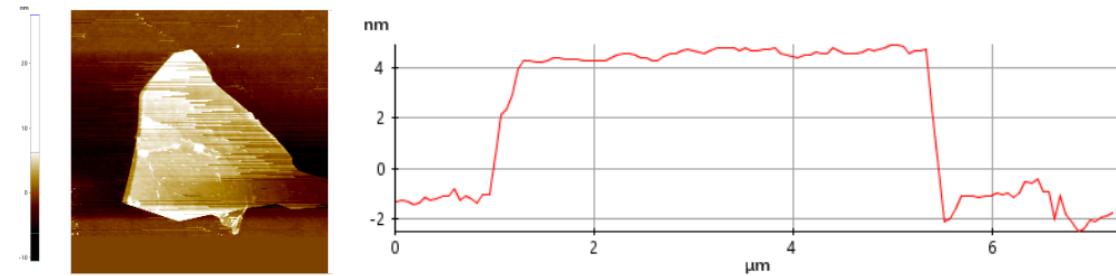


Figure 4.2.2: Topology of Crystal 2

As depicted in Figure 4.2.1, we see that C_1 has a thickness of roughly 60nm. Multilayered graphene crystals are not expected to exceed a thickness of 10 nm (with single layered sheets ranging from 1.1 nm - 3 nm). We can thus determine that C_1 is most definitely a graphite crystal. Observing C_2 in Figure 4.2.2 we see that its maximum thickness $z \sim 6$ nm. Since it has a thickness $z < 10$ nm, we can determine C_2 to be a multilayered graphene layer.

Several crystals were viewed under the SEM, allowing us to image the transparency of two multilayered graphene flakes, as shown in Figure 4.3. Although we cannot completely determine if the imaged flakes are that of graphene or graphite, transparency is an indicator of a small number of layers. It is possible that the flakes depicted in Figure 4.3 are multilayer graphene crystals. In Figure 4.3.2, a completely transparent flaky edge is visible towards the left of the crystal.

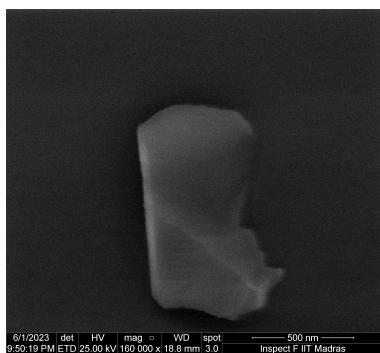


Figure 4.3.1: Multilayered Graphene

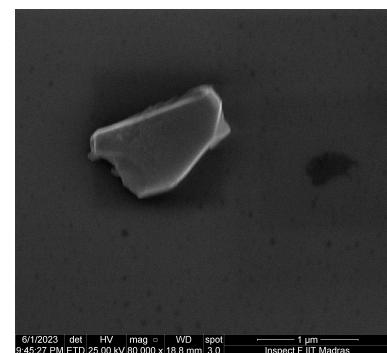


Figure 4.3.2 : Multilayered Graphene

In Figure 4.4 we can see two other crystals alongside a transparent crystal (located at the centre of the image). The large, black crystal, at the top of the image visually resembles an unexfoliated graphite crystal, while the opaque crystal is expected to be a much thinner, partially exfoliated graphite crystal.

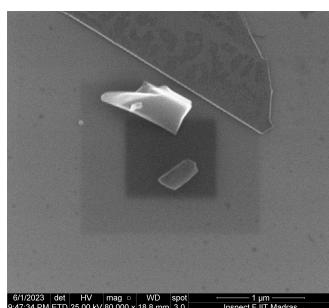


Figure 4.4: Graphene flakes of different thicknesses

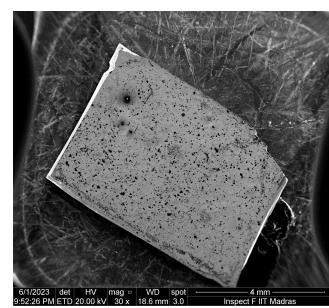


Figure 4.5: Graphene flakes on Silicon substrate

In Figure 4.5, we have an image of one of the many substrates we coated with mechanically exfoliated graphite / graphene crystals.

5. Concluding Remarks

We investigated two methods of synthesis of graphene. We prepared graphene with mechanical exfoliation and characterised it with Raman Spectroscopy, Scanning Electron Microscopy and Atomic Force Microscopy. We were able to obtain mechanically exfoliated multilayered graphene crystals with thicknesses that did not exceed a thickness of 10 nm from graphite crystals. There are more detailed investigations to be carried out in the near future.

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