

Fabrication of Hetero-Structure and Characterization of HOPG/MoS₂

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By

John Regis

Registration Number: 20246718

Internship Supervisor

Dr. Aparna Deshpande



Indian Institute of Science Education and Research

Abstract

A heterostructure is a system composed of multiple layers of materials with different band gaps, lattice constants, or electronic properties, joined together to engineer new functionalities that no single material offers on its own. The hetero-structure, fabricated in this project, is a combination of HOPG (Highly Oriented Pyrolytic Graphite) and MoS₂ (Molybdenum Disulfide). 2D Heterostructures are important in physics since layered materials introduce new properties that are not generally seen in the bulk of the material.

The fabrication method used in this project is the Dry transfer of MoS₂ using PDMS film in exfoliated HOPG thin layers. The technique makes use of the Micro Manipulator table for the dry transfer. The objective of this project was to mechanically exfoliate graphene from Highly Oriented Pyrolytic Graphite (HOPG) and identify thin-layer flakes through an optical microscope, exfoliating MoS₂ in PDMS films directly and stacking the MoS₂ in the Graphene thin film, making a heterostructure of the same. Making

The characterisation part involves comparison of BULK HOPG / Bulk MoS₂ Heterostructure Bulk HOPG / Thin MoS₂ and then the graphene / graphene Heterostructure. The comparison is made by Raman Spectroscopy of all three. The peak comparison of all these three is the main objective.

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Chapter 1

Dry Transfer Method

1 Overview of Dry Transfer

1.1 P D M S

Polydimethylsiloxane, also known as dimethylpolysiloxane or dimethicone is polymer which have a lot of wide range application. Chemical structure of PDMS is $CH_3[Si(CH_3)_2O]Si(CH_3)_3$. In the dry transfer method, especially in this project, we used PDMS films to transfer MoS₂ flakes into the Si/SiO₂ substrate. The reason why PDMS is used for such transfer mechanisms is its unique mechanical property. PDMS is a viscoelastic material, such that, in high temperature/long flow it acts as a viscous liquid. While, in the low temperature it acts as a elastic solid. PDMS is non crystalline polymer which is why it has a non linear elasticity. PDMS has a low elastic modulus, meaning easy deformation. It is commercially available as big square strip, which has a non-adhesive layer on both surfaces. Removing the layer exposes the adhesive surface of PDMS which then we can use conveniently.

1.2 Micro Manipulator Stage for Dry Transfer

A micro manipulator stage is precision equipment used in various laboratory applications. It enables very precise movement in a very small lengths. In our case, micrometers. It has three motion, accessible by three knobs motion in X, Y plane and one that adjusts the height. It has an extended flat rod, which we use for fixing our glass slide by scotch tape and it can be moved, by loosening a screw, independently.

1.3 Method of flake Transfer

First, HOPG is exfoliated on a Si/SiO₂ substrate. I used both Scotch tape and blue tape for different samples. MoS₂ exfoliated on Scotch tape is pasted onto a PDMS film by simply pressing the tape onto the film, which is attached to a glass slide. Out of all the MoS₂ flakes that are stuck onto the PDMS, we pick suitable candidate flakes by analysing them with an optical microscope. The glass slide containing the PDMS is mounted on a micromanipulator stage by wrapping it with Scotch tape. Make sure the extended platform of the transfer stage is firmly screwed.

By placing the PDMS containing MoS₂ flakes under the microscope, we identify the flakes chosen for our transfer method. Keeping images at both 50× and 5× magnification makes it easier to locate the flakes: 50× provides detailed features of the flake, such as an approximate idea of the thickness, and 5× of the same flake helps with locating it.

By loosening the flat extended platform, the glass slide (PDMS) is moved out from the microscope vision and our Si/SiO₂ substrate is mounted. Same as the procedure mentioned above, we identify thin layer flakes out of which the heterostructure should be made. Now place the flake you have selected exactly at the middle of the crosshair under 50×, or whichever lens you prefer while transferring or conducting the transfer operation. Here I used the 50× lens. The reason is the placement of the crosshair changes a bit while changing the lens; hence 50× is preferred. After placing the Si/SiO₂ sample exactly at your preferred location, understand that the Si/SiO₂ substrate is mounted not using the standard glass slide but on the temperature-controlled glass slide, and an image of that is given below. Afterwards, the transfer plate is brought back and we place the MoS₂ flake exactly at the centre of the crosshair. It is very important that during this procedure the microscope knobs that control the position of the microscope-mounted sample should not be touched. Now we know that the MoS₂ flake and the HOPG flake are now aligned. If your microscope focus is adjusted for the substrate, the micromanipulator stage is brought down so that the entire procedure is visible. But it is possible that the focus of the microscope is adjusted to the PDMS sample above, and the microscope stage can be brought up to reach the PDMS slide. One could also change both the microscope stage and the micromanipulator by also changing the focus correspond-

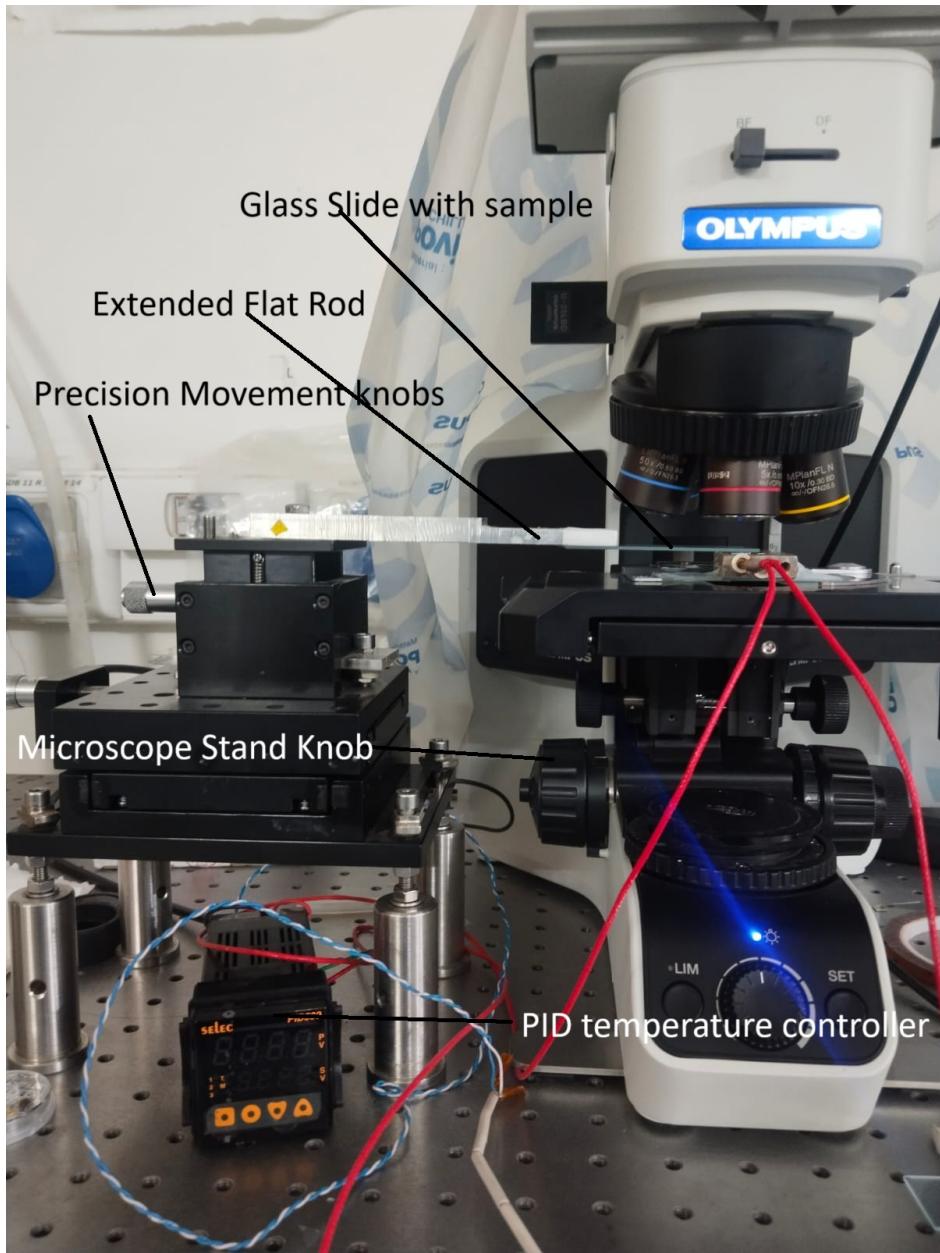


Figure 1: Parts of the micro manipulator stand

ingly. The reason why the visibility is kept is to enable us to find out if the two flakes we intend to stack misalign with each other and the fabrication quality of the heterostructure is compromised.

The next is to drop off the MoS₂ flake into the Si/SiO₂ substrate. One way of carrying out this procedure is to make sure two of our flakes are in contact, by looking at the meniscus formation. One major problem with the meniscus formation is that if the flake we wish to perform the drop-off on is far from the edge of the PDMS film (outer edge), the contact meniscus will not reach the flake, which will make the process of dropping off harder. From analysing the result of repetitive attempts of performing this operation, it is suggested to find the flakes which are closer to the outer edge of the PDMS, since they have a better chance of dropping off easily. Temperature is increased using the PID-controlled device; the temperature is set from 80,°C to 100,°C. Slowly retracting the micromanipulator stage or the microscope stage is done. After further inspection, the fabrication process is confirmed.

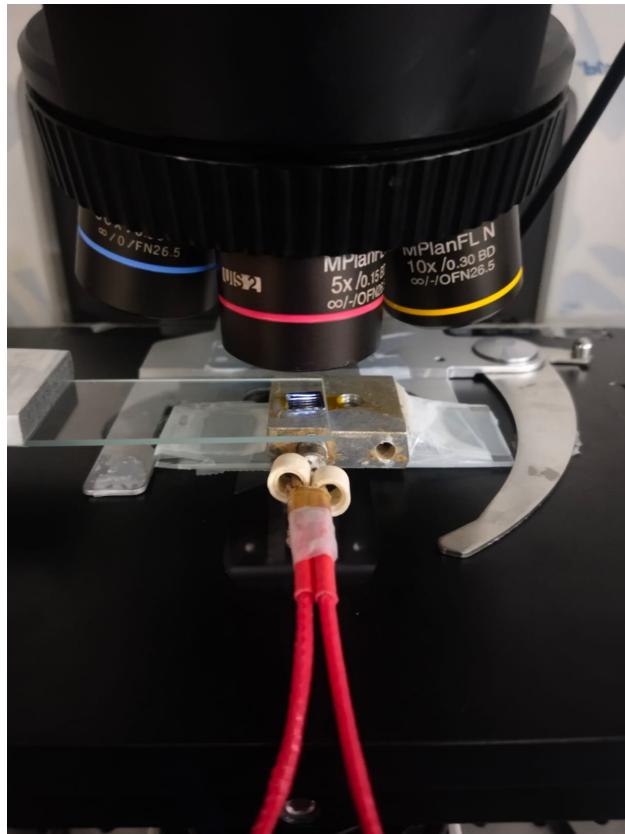


Figure 2: Dry transfer using Micro Manipulator stand.

Optical Microscope Analysis of Heterostructures

2 Optical Microscope Images

Optical Microscope Images of the flakes after the dry transfer. Some of them are thick layers and are not good candidates for Hetero structures. By analyzing the thickness and

2.1 Hetero structure 1



Figure 3: Optical Image of two bulk flake after dry transfer

Two overlappingn flakes can be seen. One is an HOPG flake another is MoS₂. Both, from optial analysis itself can be seen that, are bulk flakes

not thin layers. Hence we can deduce that it is not suitable for a good heterostructure.

2.2 Hetero structure 2

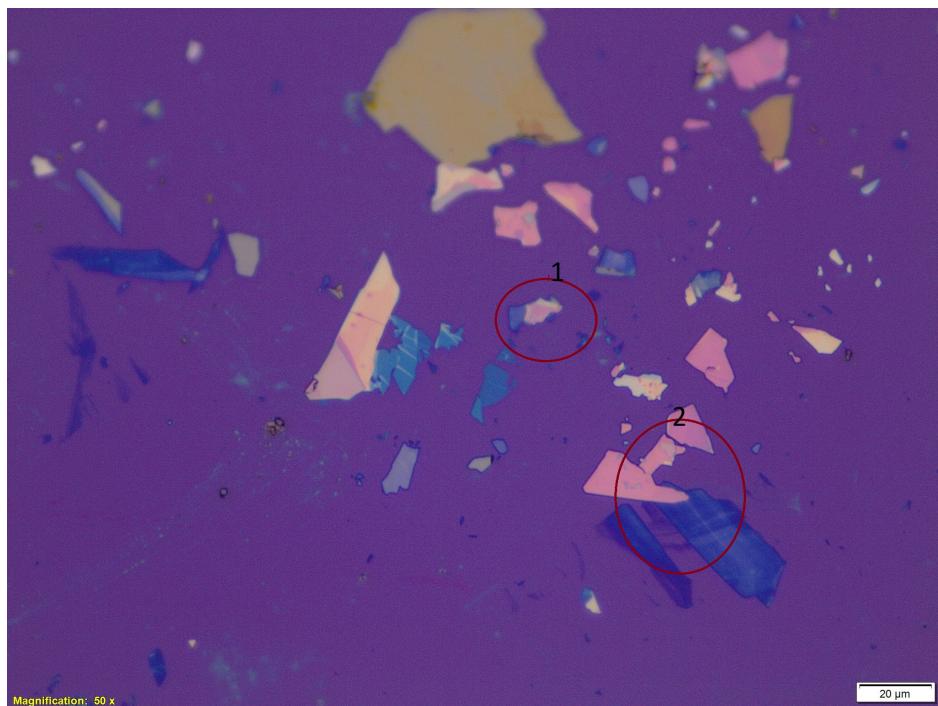


Figure 4: Two Overlapping Flakes 1 , 2

The heterostructure could not be successfully formed because, although the graphene flake was thin, the transferred MoS flake turned out to be comparatively thick, leading to an unsuccessful attempt.

2.3 Hetero structure 3

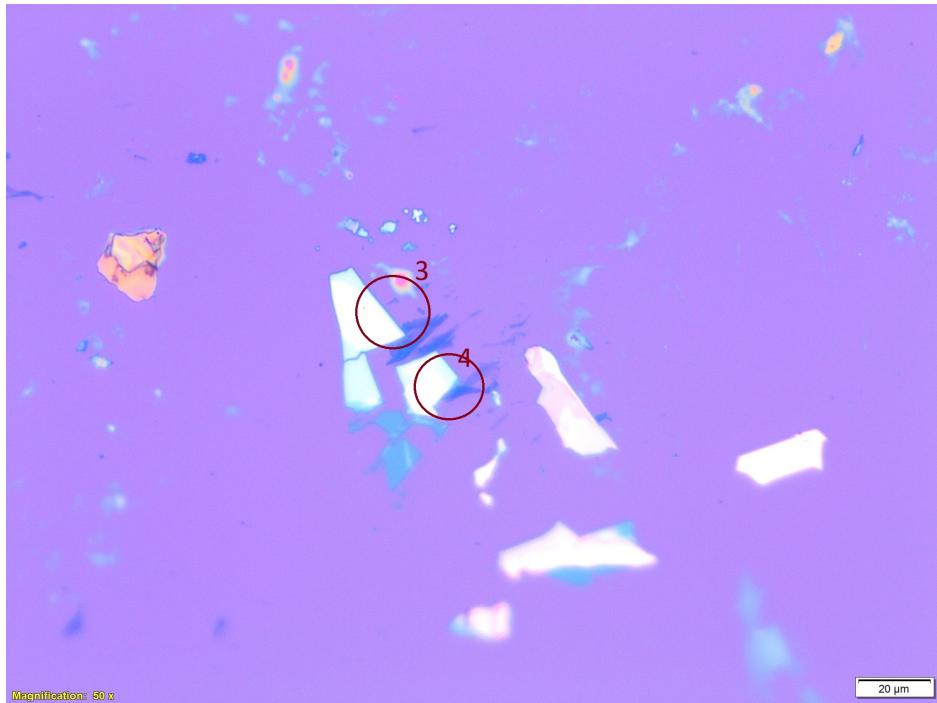


Figure 5: Two overlapping flakes 3 and 4

The heterostructure could not be successfully formed because, although the graphene flake was thin, the transferred MoS flake turned out to be comparatively thick, leading to an unsuccessful third attempt.

2.4 Hetero structure 4

Observing that, thinner layer of MoS₂ was slipping off from the desired position several times, I decided to make a lateral heterostructure and connect it with gold connections using the method photolithography.

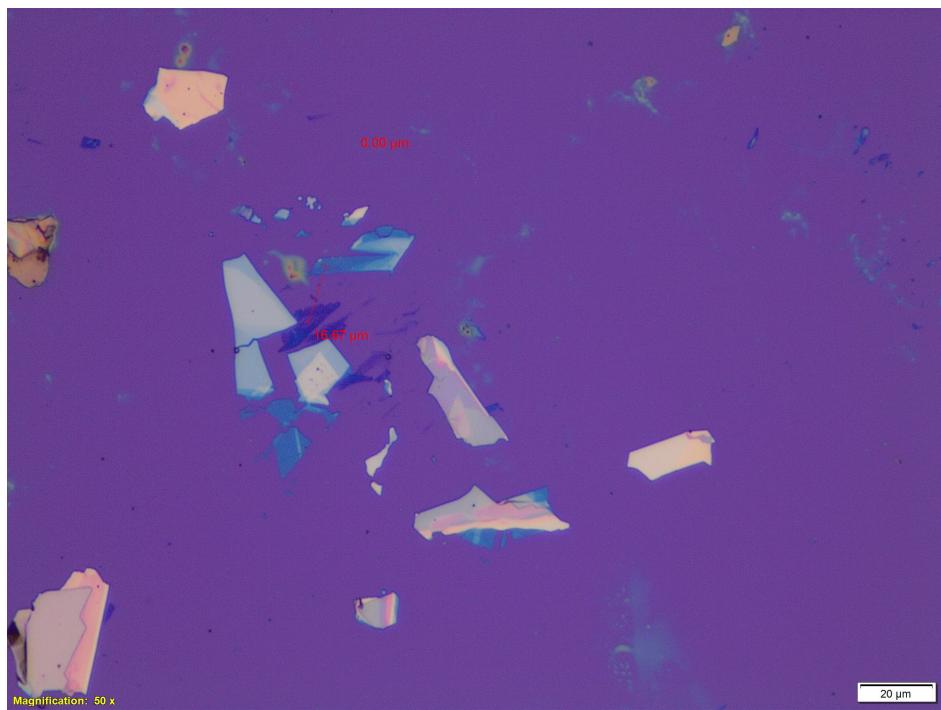


Figure 6: Two thin layers of MoS₂ flake with a red line indicating the connection that have to make for lateral Heterostructure.

Raman Spectroscopy

3 General Overview of Raman Spectroscopy

To estimate the number of graphene layers, we often use Atomic Force Microscopy (AFM), and to confirm the results, Raman spectroscopy is also used. That's why it is important to understand the basic ideas behind Raman spectroscopy. To learn more, I read a few research papers that explain how Raman spectra can be interpreted, especially for graphene, and I've noted down the important points from those readings.

Raman spectroscopy is a useful and widely used method to study materials without damaging them. It is especially helpful in both laboratories and real-world settings. This technique was first developed in the early 20th century by scientists C. V. Raman and G. S. Landsberg. However, it became more commonly used after lasers were introduced later in the century. Raman spectroscopy helps scientists understand materials in greater detail, especially carbon-based ones like graphite. Over time, it has become valuable in many industries, including food and textiles. Compared to other methods like infrared spectroscopy, Raman spectroscopy has some key benefits — for example, water does not interfere much with the results, which makes it suitable in situations where other methods fail. It has even been successfully used to monitor processes like fermentation in real-time. Still, it has some challenges, such as difficulty in analyzing the data accurately and the problem of certain strong signals, like those from carbon particles, hiding other signals. Researchers are actively working to solve these issues. This review looks at how Raman spectroscopy is used to study different materials and explains the science behind how it works, helping readers understand its broad potential and current developments.

When light interacts with matter, it can be absorbed, passed through (transmitted), or scattered. Absorption happens when the energy of the

light exactly matches the energy gap between two electronic states. Scattering, however, does not need this energy match as it happens when light hits a molecule and briefly disturbs its electrons, creating what is called a virtual state. This state does not last long, and the system returns to a real energy level and releases a photon. If the released photon has the same energy as the incoming one, it is called Rayleigh scattering which is also known as elastic scattering. But if the energy changes either increasing or decreasing, it is called Raman scattering which is also known as inelastic scattering. When the scattered photon has less energy, it is called a Stokes shift, and if it has more energy, it is called an anti Stokes shift. The difference in energy is known as the Raman shift. The strength of Raman signals also depends on how the molecules are distributed across energy levels, which follows a rule called the Boltzmann distribution. At room temperature, more molecules are in the ground state, so Stokes scattering is stronger than anti Stokes. If the incoming light matches a real energy level, the signal is much stronger and this is called Resonance Raman scattering. Still, Raman scattering is very weak overall and only about one in one hundred million photons shows this effect, so instruments use filters to remove stronger background signals like Rayleigh scattering. The intensity of the Raman signal also depends on factors like the number of molecules, the incoming light intensity and frequency, and how easily the molecule's electrons can be disturbed which is known as polarizability. However, using higher energy light to increase signal strength can also damage the sample, so there is a trade off to consider in real applications.

3.1 Graphene and Graphene-Like Materials

The Raman spectrum of single layer graphene has two main peaks: the G peak around 1582 cm^{-1} and the 2D peak around 2700 cm^{-1} . These peaks help us study the structure of the graphene sheet. Graphene with defects also shows a D peak, which mainly appears at armchair edges due to how light scatters. Zigzag edges show a weaker D peak because of their shape and surface roughness.

Temperature also affects the Raman bands. At lower temperatures, the G band splits, and at higher temperatures, its position shifts downward. These changes reverse when the sample is heated and cooled. The number

of layers in a graphene sample can be estimated by comparing the height of the G and 2D peaks. A high G to 2D ratio suggests more layers. The shape and position of these peaks also change depending on how many layers there are because the electronic structure and vibrations evolve. Some studies use the G peak and the silicon peak in the Raman spectrum to count atomic layers on a silicon surface. Others have explored how certain chemicals like PMMA affect the strain in graphene and shift its Raman peaks. One interesting finding is that the width of the 2D peak becomes narrower when the electron mobility is higher. The D to G peak ratio however stays the same. This means Raman spectroscopy can help study how well electrons move in graphene. In summary the G D and 2D peaks in the Raman spectrum give valuable information about the structure thickness defects and electronic behavior of graphene.

In the Raman spectrum, graphene exhibits a single sharp 2D peak at around 2700 cm^{-1} that is significantly more intense than the G peak at 1580 cm^{-1} , with the 2D intensity roughly four times that of the G peak. In contrast, graphite shows a broader and weaker 2D band, split into two components and having only about half the intensity of the G peak. The shape and intensity of the 2D peak are strong indicators of the number of layers: single-layer graphene has a single symmetric 2D peak, bilayer graphene shows a broader 2D band with four components, and multilayer graphene gradually resembles bulk graphite. The D peak, which appears at edges or in the presence of disorder, is absent in the central region of the sample, confirming minimal defects. These features allow Raman spectroscopy to reliably identify the number of graphene layers and their structural properties.

3.2 MoS₂ and MoS₂-Like Materials

The Raman spectrum of MoS₂ is dominated by two first-order vibrational modes that are extremely sensitive to the number of layers: the in-plane E' (often denoted E_{2g}¹) mode near 384 cm^{-1} and the out-of-plane A'₁ (A_{1g}) mode near 403 cm^{-1} . These peaks arise from the characteristic lattice vibrations of the molybdenum and sulfur atoms and provide a reliable and non-destructive method for determining the thickness of MoS₂ flakes.

In monolayer MoS₂, the E' mode is slightly upshifted and the A'₁ mode

is slightly downshifted due to the absence of interlayer interactions. As additional layers are introduced, interlayer coupling stiffens the A'_1 mode (shifting it upward) and softens the E' mode (shifting it downward). As a result, the frequency separation between the two modes increases systematically from monolayer to bulk. Typically, monolayer MoS₂ shows a peak separation of $\sim 18\text{--}20\text{ cm}^{-1}$, bilayer and trilayer samples show $21\text{--}24\text{ cm}^{-1}$, and bulk MoS₂ exhibits a separation of $25\text{--}26\text{ cm}^{-1}$. This monotonic evolution makes the $E'\text{--}A'_1$ difference an effective fingerprint for layer number.

Defect-activated modes such as the LA(M) peak in the $230\text{--}260\text{ cm}^{-1}$ range appear when sulfur vacancies, grain boundaries, or edge disorder are present. A high LA(M)/ E' intensity ratio indicates increased defect density, whereas pristine regions exhibit very weak defect peaks.

The Raman modes of MoS₂ also respond to external conditions. Increasing temperature causes a redshift of both the E' and A'_1 peaks, whereas cooling reverses the shift. Mechanical strain affects the in-plane E' mode strongly while shifting the out-of-plane A'_1 mode much more weakly, allowing Raman spectroscopy to distinguish strain from doping. Chemical residues such as PMMA induce compressive strain and shift the peaks upward.

An important observation is that the linewidth (FWHM) of the A'_1 mode narrows when the carrier mobility increases, making the A'_1 width a useful probe of electronic quality. Meanwhile, the intensity of defect-related peaks remains largely unchanged by mobility. Thus, Raman spectroscopy provides insights not only into layer number and structural quality, but also into strain, doping, and charge transport properties in MoS₂.

In summary, monolayer MoS₂ shows $E' \approx 384\text{ cm}^{-1}$ and $A'_1 \approx 403\text{ cm}^{-1}$ with a separation of about 19 cm^{-1} , along with a strong 2LA(M) mode near 450 cm^{-1} . As the number of layers increases, the A'_1 peak shifts upward, the E' peak shifts downward, and their separation increases toward the bulk value. These Raman signatures make it straightforward to determine the number of layers and assess the structural, vibrational, and electronic behavior of MoS₂ flakes.

Preparation of connection between two flakes

4 Photolithography

Photolithography is a pattern-transfer technique used extensively in micro- and nanofabrication to define precise structures on a substrate. It relies on the interaction between light and a photosensitive polymer, known as a photoresist, to selectively expose and develop regions according to a predefined mask pattern. The method is widely used for fabricating electronic devices, sensors, contacts on 2D materials, and complex microstructures due to its scalability, reproducibility, and high spatial resolution.

4.1 Photo Lithography Procedure

The process typically begins with thorough substrate cleaning to remove particles, organic contaminants, and residual moisture. This step is crucial because any impurity can prevent uniform adhesion of the photo resist. After cleaning, a thin film of photoresist is deposited onto the substrate using spin coating. Spin coating ensures that the resist spreads evenly due to centrifugal forces, producing a uniform thickness controlled by the spin speed and resist viscosity.

Following deposition, a soft-bake step is performed to evaporate excess solvent from the resist and improve adhesion. The substrate is then aligned with a photomask containing the desired pattern. During exposure, ultra-violet (UV) light passes through transparent regions of the mask and interacts with the photoresist. In a positive photoresist, illuminated regions become more soluble in the developer, whereas in a negative photoresist,

the exposed regions crosslink and become less soluble. This contrast between exposed and unexposed areas allows precise transfer of the mask geometry onto the substrate.

After exposure, the substrate undergoes development in a chemical solution that selectively removes either the exposed or unexposed regions, depending on the resist type. This step reveals the patterned resist profile, effectively creating a temporary protective stencil. The developed pattern can then be used for metal deposition, etching, or other fabrication processes. When metal is deposited, the unwanted regions are later removed using a lift-off process, leaving behind well-defined contacts or structures.

Finally, a post-bake or hard-bake step is often applied to improve the durability and temperature stability of the patterned resist. Throughout the procedure, resolution and pattern fidelity depend on factors such as resist thickness, exposure dose, wavelength of light, substrate surface quality, and mask alignment accuracy. Despite its limitations—such as diffraction effects and the requirement for cleanroom environments—photolithography remains the most widely used and reliable technique for creating microscale device architectures.

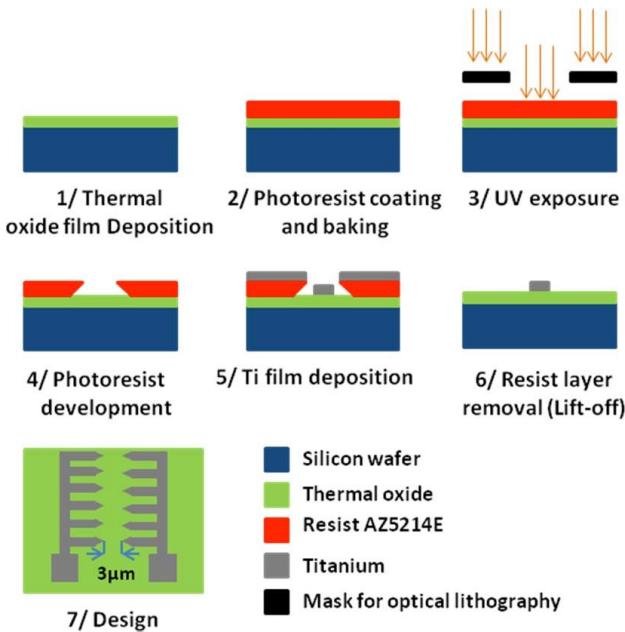


Figure 7: PhotoLithography Process

4.2 Brief Overview of CleWin Software

CleWin is a computer-aided design (CAD) tool widely used in microfabrication and photolithography for creating precise mask layouts. It is essentially the drafting software of cleanroom technology: engineers use it to design patterns that will later be transferred onto substrates using lithographic processes.

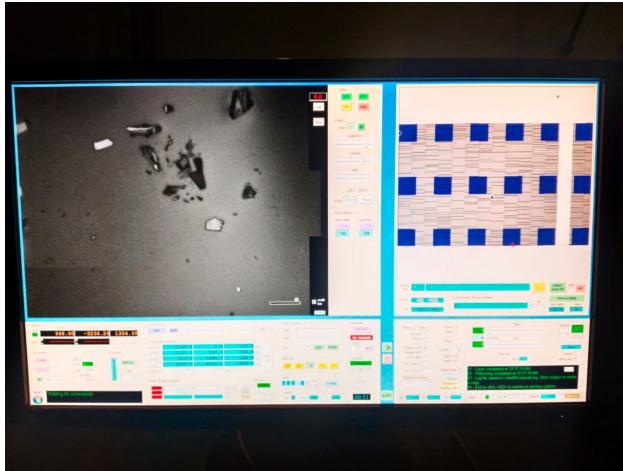


Figure 8: Screen Shot of the Software

CleWin supports multi-layer mask design, allowing users to draw, modify, and organise structures such as contact pads, electrodes, waveguides, nanowires, and MEMS/NEMS components. Each layer can be assigned specific process attributes (e.g., deposition, etch, lift-off), helping users visualize the full device stack.

The software provides sub-micron resolution drawing tools, Boolean operations (union, subtraction, intersection), grid snapping, and geometry-manipulation functions that make layout design efficient and accurate. It also supports industry-standard file formats such as GDSII, enabling compatibility with mask writers and e-beam lithography systems.

CleWin includes DRC (Design Rule Checking) to ensure that spacing, linewidths, and alignment constraints meet the fabrication facility's specifications. It also supports alignment mark generation, which is essential for multi-step lithography involving multiple masks.

In practice, CleWin acts as the bridge between concept and fabrication: it converts device ideas into mask patterns that can be directly used for photolithography, e-beam lithography, UV exposure tools, and other pattern-

transfer processes. Because of its simplicity, low learning curve, and strong cleanroom adoption, it remains a standard layout editor in many academic and industrial microfabrication labs.

4.3 Contact made between MoS₂ and HOPG Flake

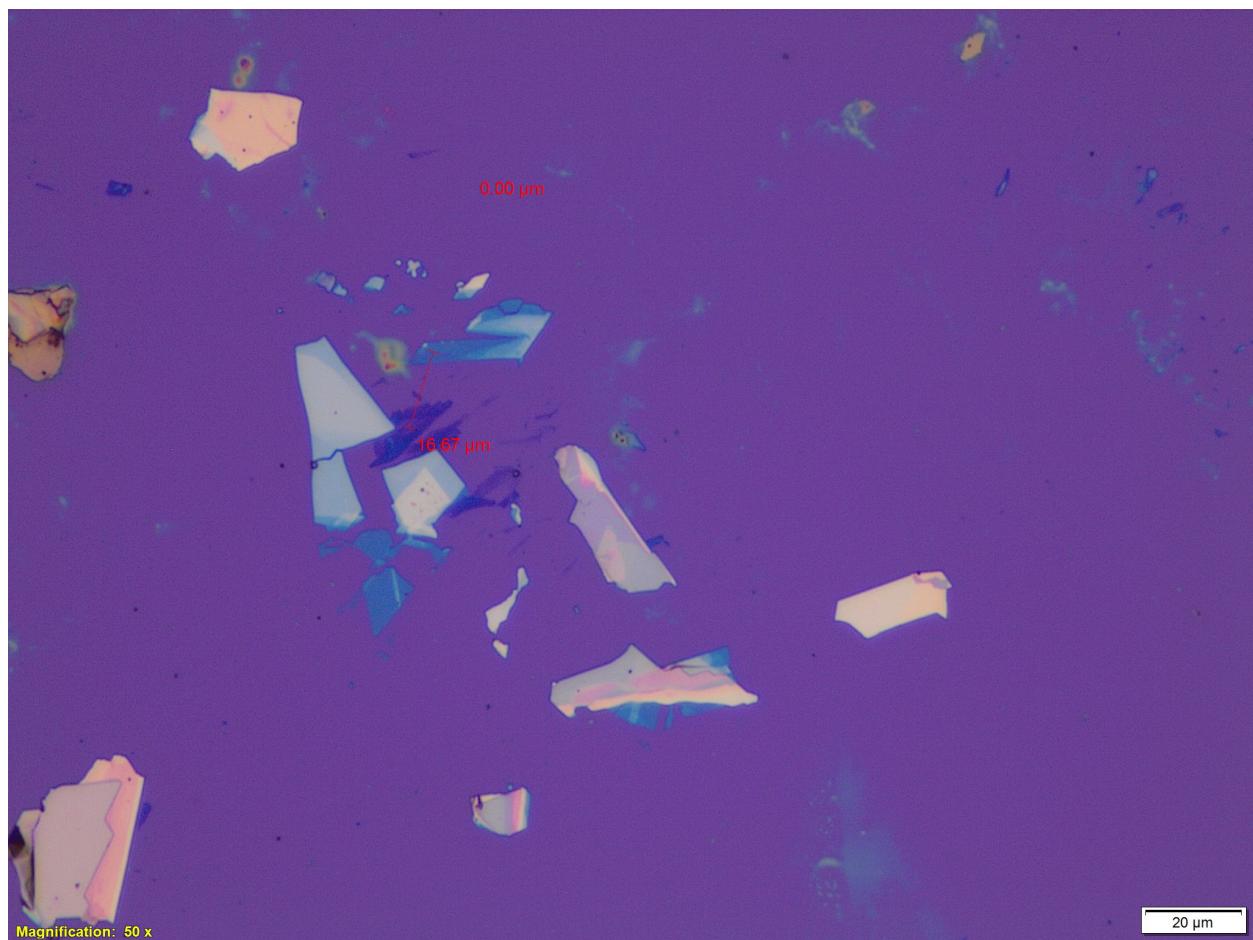


Figure 9: Enter Caption

Two thin flakes of HOPG and MoS₂ are laterally placed side by side, $\approx 16 \mu m$ located through the CleWin software and an electrode connection is made. Two make a four-probe connection or a two probe connection largesr pads/contacts should be made in order to connect it to a IV measurment device.

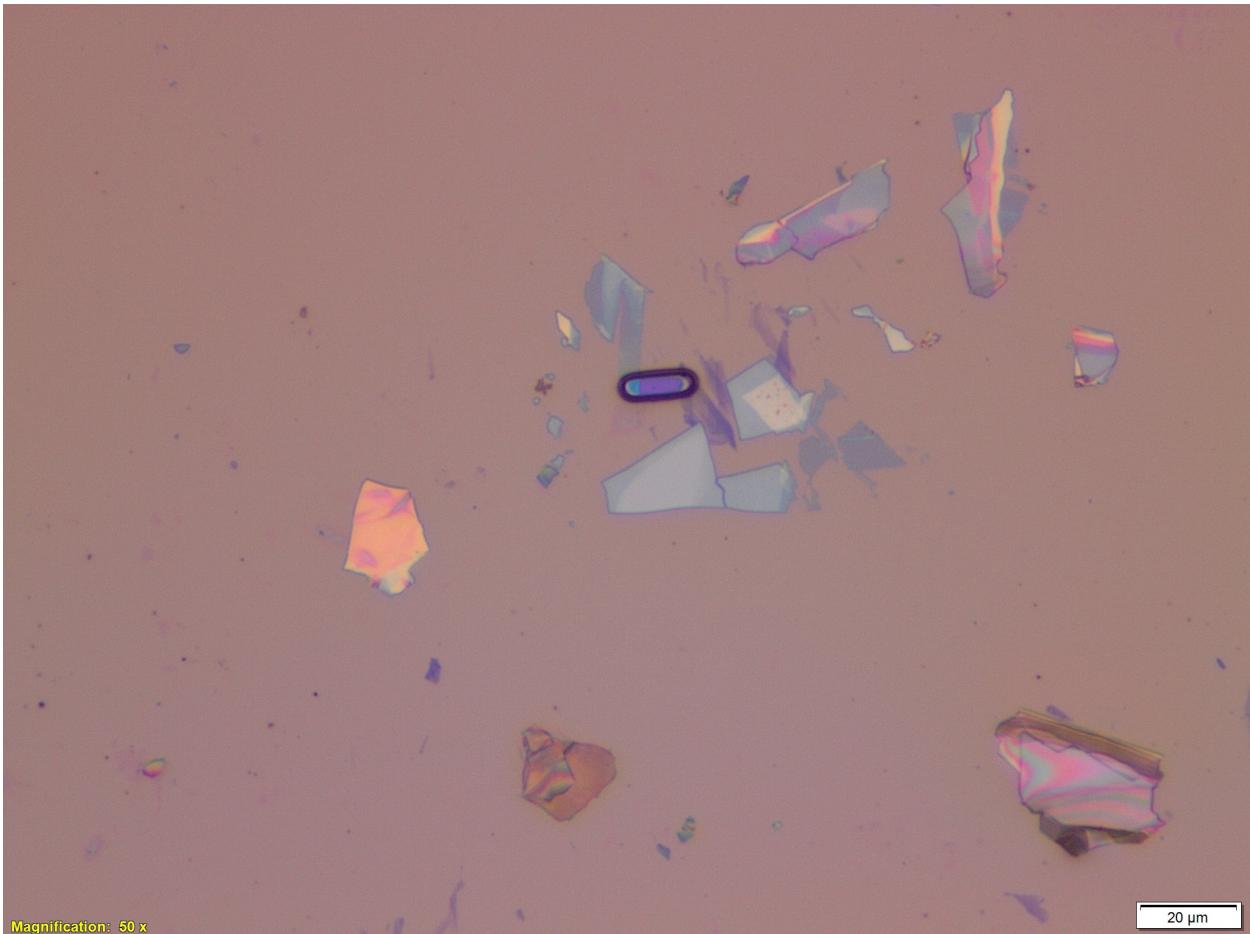


Figure 10: After the Polymer coat

This is an image of two flakes HOPG flake and a MoS₂ flake after a polymer coat, the exposed light have created a non-polymer area in such a way that, it connects both flakes (*i*) and (*ii*). This is done by positive photoresist photolithography.

Summary of the Project

5 A brief Summary of the Semester Project

In this work, a lateral heterostructure was prepared by placing a thin graphene (HOPG) flake next to a MoS flake on a Si/SiO substrate using a dry-transfer method. Unlike vertical heterostructures, where one layer is stacked on top of another, a lateral heterostructure forms when two different 2D materials lie side by side on the same plane and share a clean boundary. This type of structure is useful because it allows direct comparison of material properties and makes device fabrication easier, especially for transport measurements.

The preparation began by exfoliating both MoS and HOPG using Scotch tape. The MoS flakes were transferred to a PDMS film, while the HOPG flakes remained on the Si/SiO substrate. Under the optical microscope, the graphene flake selected for the process appeared thin, clean, and extended over a suitable area. The MoS flake chosen on PDMS also had a clear shape and could be positioned accurately. Both samples were placed on a micromanipulator stage, which allowed slow and precise alignment of the two flakes.

To control adhesion during transfer, a small heating plate was used beneath the substrate. The temperature was kept low enough to avoid damaging the materials but high enough to help the PDMS release the MoS smoothly. With the help of the micromanipulator, the MoS flake was slowly lowered until it touched the edge of the graphene flake. The contact line where the two materials met formed the lateral junction. Because both flakes were on the same plane, no stacking was required, and the interface formed naturally during the release process.

After the transfer, optical microscope images showed the two flakes lying adjacent to each other, forming a clear boundary. The graphene re-

gion had a lighter contrast, while the MoS region appeared darker, allowing easy identification of the interface. Even though some regions of MoS were slightly thicker, the lateral arrangement remained intact because this method does not depend strongly on vertical alignment. The main requirement is a clean edge on both flakes, which was achieved during exfoliation.

This lateral heterostructure can now be used for further steps, such as making contact pads through photolithography or measuring Raman spectra across the interface. By comparing the Raman peaks of MoS, HOPG, and the junction region, it is possible to study strain, defects, and the quality of the interface. The optical contrast confirms that the two materials are clearly separated but are in close enough contact to act as a lateral heterojunction.

Overall, the dry-transfer method using the micromanipulator, PDMS film, and a controlled heating stage allowed the successful formation of a lateral heterostructure between MoS and graphene. This structure is suitable for device fabrication and further characterization

Acknowledgment

6 Acknowledgment

I would like to express my sincere gratitude to Dr. Aparna Deshpande, my supervisor, for her continuous guidance, support, and encouragement throughout this work. Her insights and advice were invaluable at every stage of the project.

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I especially acknowledge Prashant Sir for his support and guidance during the lithography process. His expertise greatly helped in executing the fabrication steps smoothly.

Finally, I extend my appreciation to everyone who contributed directly or indirectly to the successful completion of this project.