Exploring the Interfacial Properties of two-Dimensional Materials and Van Der Waals Heterostructures

MAMTA

A thesis submitted for the partial fulfillment of the degree of

Doctor of Philosophy





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Dedicated to my beloved family

Declaration

The work presented in this thesis has been carried out by me under the guidance of Dr. Kiran Shankar Hazra at the Institute of Nano Science and Technology (INST) Mohali. This work has not been submitted in part or in full for a degree, a diploma, or a fellowship to any other university or institute. Whenever contributions of others are involved, every effort is made to indicate this clearly, with due acknowledgment of collaborative research and discussions. This thesis is a bonafide record of original work done by me, and all sources listed within have been detailed in the bibliography.

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In my capacity as the supervisor of the candidate's Ph.D. thesis work, I certify that the above statements by the candidate are true to the best of my knowledge.

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1D	1 dimensional
2D	2 dimensional
3D	3 dimensional
EBL	e-beam lithography
PVD	physical vapor deposition
СВМ	conduction band minimum
VBM	valence band maximum
AFM	Atomic Force Microscopy
MBE	molecular beam epitaxy
PLD	pulsed laser deposition
CVD	Chemical Vapor Deposition
PMMA	Polymethyl methacrylate
PL	Photoluminescence
MoO ₃	molybdenum trioxide
S	sulphur
FET	Field Effect Transistor
TMD	Transition Metal Dichalcogenides
MoS ₂	Molybdenum Disulfide
СВ	Conduction Band
VB	Valence Band
CPD	Contact potential difference
XPS	X-ray photoelectron spectroscopy
KPFM	Kelvin Probe Force Microscope
FM-KPFM	Frequency mode KPFM
AM-KPFM	Amplitude mode KPFM
DFT	Density Functional Theory
PID	Proportional Integral Derivative
E-beam	Electron Beam
QCM	quartz crystal monitor

ТМАН	Tetra Methyl Ammonia Hydroxide
SiO ₂	Silicon Dioxide
PDMS	Polydimethylsiloxane
HOPG	Highly oriented pyrolytic graphite
BP	Black Phosphorene
vdW	van der Waals
Α	A exciton
В	B exciton
Т	Trion
TBG	twisted bilayer graphene
TBTMDs	twisted bilayer transition metal dichalcogenides
FESEM	Field emission scanning electron microscopy

NOMENCLATURE

λ	Wavelength
0	Degree
Å	Angstrom
K	Kelvin
nm	Nanometer
μm	Micrometer
cm	Centimeter
mV	millivolt
φ _t	Work function of tip
φs	Work function of sample
ξ	surface Electric feild
φ _B	Schottky barrier height
eV	Electron volt
V _d	Applied biased at drain electrode
Ψ _{bi}	Built-in potential
W _D	Depletion width
N _D	intrinsic doping concentration
ϵ_{MoS2}	dielectric constant for multilayer MoS ₂
ρ_{MoS2}	screening length for MoS ₂
€0	permittivity of free space

ABSTRACT

Two-dimensional (2D) materials and their van der Waals heterostructures are viable candidates for futuristic nanoelectronics devices owing to their astonishing electronic, and optical properties. To advance the application of electronic devices based on 2D layered materials, it is essential to understand the fundamentals of electronic energy band alignment and charge transfer at the contacts and interfaces. So far band alignment at the contacts has traditionally been estimated analytically by following various transport models or measured indirectly from electronic response. However no direct experimental protocol was established so far to measure the crucial interface parameters at real condition of a contact/interface and estimate the deviation of these factors with ideal conditions. Thanks to 2D materials which can create a clear distinct, uniformly abrupt and non-diffusive interface (unlike bulk contacts) and enables us to probe the electrostatics at the nanoscale level exactly at the interface. We approached the Kelvin Probe Force Microscopy (KPFM) technique, an Atomic Force Microscopy (AFM) based advanced tool to probe the surface potential, to understand the electronic band alignments at the contact metal/2D interfaces as well as at the van der Waals heterostructures interfaces and applied the semi-classical electrostatic tactics to deduce interface parameters. For such nanoscopic measurements to investigate the spatial distribution of surface potential, MoS₂ is an appropriate candidate since it is a stable 2D semiconductor with high carrier mobility. Furthermore, we also examined the twisted MoS₂/MoS₂ homo-interface with hexagon morphology using room temperature µ-PL(Photoluminescence) which could be useful in the field of electronic devices based on twistronics. In addition to the band alignment at interfaces, we have experiences that MoS₂'s morphological shape can also modify its band structure. We employed low-temperature µ-PL to examine the influence of morphological shape on the optoelectronic properties of MoS_2 .

My first work focuses on the probing of energy band bending at the Au/ MoS_2 junction during current conduction in a bridge-type MoS_2 channel. MoS_2 flake was transferred on prefabricated Au electrodes to avoid the contamination caused by chemicals used in the lithography process. A thorough investigation of the surface potential during charge transportation revealed asymmetric contacts between MoS_2 and Source contact and Drain contact as well as Schottky behaviour at the MoS_2/Au interface. By varying the applied bias to MoS_2 channel, we have determined the interface parameters like built-in potential, surface electric field, and space charge density at Au/MoS_2 interface in non-equilibrium conditions. The experimentally determined depletion width is compared with analytically calculated depletion width and the difference between both attributes to local defects, contact area, and thickness variation of MoS_2 flake. The interface parameters and their variation with the current conduction can all be probed, opening the door to comparing and improving the performance of real devices against ideal ones.

In second project, we have probed the surface potential at the MoS_2/BP van der Waals p-n heterojunction constructed by the dry transfer method. By using the Kelvin probe force microscopy (KPFM) technique to measure the spatial distribution of built-in potential, builtin electric field, and depletion width, we are able to demonstrate the formation of the p-n junction at the $MoS_2/Black$ phosphorene (BP) interface and experimentally measure the band alignment under realistic circumstances. We have optimised the lift height of ~15 nm to get better resolved potential image. By changing the thickness of the MoS_2 flakes over a uniform thickness of BP flakes, the charge distribution at the MoS_2/BP interface has been modulated. The increase in the lateral built-in potential and lateral built-in electric field at MoS_2/BP interface is observed with increasing the thickness of the MoS_2 flake. Moreover, the Density Functional Theory (DFT) calculations have been done to validate the experimental findings.

In the third project, we examined the twistronic of CVD-grown MoS_2/MoS_2 interface with hexagon morphology. We performed room temperature PL measurements and found the blue shift in the PL peak position at the interface. The shift in the PL energy attributes to the lattice strain induced by the angular shift between two flakes. We have measured the angle between two flakes with FESEM which is found to be 6.7 degrees. Deconvoluted PL spectra revealed unequal shift in the peak energy of A exciton, B exciton and trion at the MoS_2/MoS_2 interface. The energy shift in B exciton at the MoS_2/MoS_2 interface is more prominent. We observed an increment of ~19 meV in the spin-orbit coupling energy at the interface.

In addition, the optical properties of MoS_2 with a morphological hexagon shape have been explored in the fourth project. The Chemical Vapor Deposition (CVD) technique was used to synthesize the hexagon morphological shape of multilayer MoS_2 flake. Temperaturedependent PL studies reveal the red shift in PL owing to change in band gap due to semiconducting properties. Deconvoluted PL spectra demonstrate the change in PL intensity as well as PL red shift of trions, A exciton and B exciton. Variation in ratio of A exciton intensity to B exciton intensity with the temperature aids to calculate the fermi energy ~ 31 meV at room temperature which is quite low. High electron concentration of order ~ 1.5×10^{12} cm⁻² has been determined regardless of multilayer nature of MoS₂ hexagon. We observed enhancement in electron phonon coupling in the case of MoS₂ in hexagon morphology. The fitting parameters to change in PL peak energy with temperature determines the band gap~1.91 eV at absolute temperature which is high as compared to previous reports (~1.8 eV) for other morphological shapes. From line width variation with temperature, we are able to determine the exciton-optical phonon coupling strength. The valence band splitting energy is determined to be ~132 meV which doesn't vary significantly with the temperature.

Chapter 1

Introduction



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1.1 Aspects affecting charge transport in 2D materials

Modern nano smart devices necessitate high quality surfaces and interfaces due to their considerable impact on charge transport. Mainly, four components in current field effect transistor devices have a significant impact on their transport property:

- I. The material used for semiconducting channel
- II. The quality of the interface of the semiconductor channel with metal contact
- III. The interface of dielectric media with the semiconductor channel
- IV. The interface of two different semiconductors i.e., heterostructure interface



Figure 1.1 A large collection of two-dimensional layered materials with decreasing bandgaps from left to right and diverse electrical characteristics. Applications using 2D materials include a wide variety of radiation wavelengths, from the THz to UV spectrum¹.

Conventional bulk semiconductor possesses dangling bonds at the surfaces which hamper the device's performance due to the scattering of charge carrier. The devices can be further scaled down for better performance because 2D channels' ultra-thin thickness and dangling-bond-free surface provide superior gate electrostatics while also preventing the deterioration of carrier mobility². The two-dimensional layers promise the replacement of traditional silicon transistor devices in the future due to their exceptional electrical and optical properties. The essential materials required to make a transistor, such as metal, semiconductor, and insulator, are contained in the two-dimensional materials library. The bandgap of these materials can be tuned by changing the thickness and covering the whole electromagnetic spectrum making these materials flexible in electronic and optoelectronic device applications. The existing library, though, is still

insufficient to cover all applications. To expand the application of 2D materials devices or in search of multifunctional device based on 2D materials, either new twodimensional material can be discovered or modification (like doping, interface engineering etc.) can be done in existing 2D materials³.

1.1.1 Surface and interface studies on two-dimensional materials



Figure 1.2 Numerous techniques, including as sin, ion intercalation, heteroatom doping, defect engineering, and the creation of heterostructures based on them, can be used to modify the characteristics and catalytic activity of 2D materials⁴.

Surface and interface engineering can have a considerable impact on the energy level alignment⁵, gap states⁶, surface dipole⁷, and orbital interactions⁸, as has been thoroughly studied in organic electronics. Hence, these engineering techniques are essential for boosting the performance of electronic and optoelectronic devices⁹. 2D material's electrical structures and device performances are responsive to the different surfaces

since they are atomically thin layered materials. several surface modification techniques have been used in this context to enhance their functions and minimize their drawbacks¹⁰. By imparting point defects to the 2D materials¹¹ or by building a molecular self-assembly layer on top^{12, 13}, the surface functionalization can be accomplished. Nevertheless, a notable distinction between 2D materials and bulk systems is that they are usually supported on a substrate, creating an interface that may be modified by switching out substrates or through intercalation¹⁴. 2D materials' great electrical mobility and energy density in energy storage devices are made possible by their massive surface area to volume ratio and internal surfaces¹⁵. Since many of the atoms in 2D materials reside on their surface, atom substitute and covalent or non-covalent functionalization are more effective means of altering their physical and electrical characteristics^{16, 17}. For instance, the marginal density of states in graphene allows a small charge transfer to result in a significant shift in the chemical potential^{18, 19}. Moreover, the large specific surface area and strong surface activities of 2D layered material offer high potential for catalytic and gas-sensing applications²⁰. The benefits of engineering the features of 2D layered materials, such as the creation of lateral or vertical heterostructures, are illustrated via surface and interface modification²¹⁻²³. So, it is crucial to comprehend the atomic structures and interfacial features of these heterostructures in order to build 2D material-based electronics and enable a wide range of applications²⁴.

1.2 Metal/2D semiconductor interface

In any field effect transistor device, the interface of 2D semiconductors with the contact metal is an important part. The electronic properties of nano-electronic devices are significantly affected by the mechanism of charge injection at semiconductor/contact metal interface. Usually, conventional 3-dimensional semiconductor is covalently bonded with the contact metal due to the presence of dangling bond on 3-dimensinal semiconductor's surface. Nevertheless, the interface of 2D material with contact metal is formed by van der Waals interaction offering a tunneling barrier to charge carrier prior to Schottky barrier and resulting in high contact resistance²⁵. To achieve ohmic contacts, this van der Waals gap either can be avoided by fabricating edge contacts²⁶ or by choosing a contact metal forming covalent bond with 2D materials. Certain metals, such as Pd for WSe2²⁷, Ni for graphene²⁸, Mo for MoS2²⁹, and Ti for MoS2³⁰, can form covalent bonds to 2D surfaces, according to DFT simulations.



Figure 1.3 Band diagrams for each type of metal-semiconductor junction are shown in (a, b) for the bulk interface, (c, d) for the metal/2D semiconductor interface, such as the MoS2/Au contact, and (e, f) for the hybridization of the metal/2D semiconductor interface ³¹.

1.2.1 Type of contact metal's geometrical configurations to 2D semiconductor

The electrodes to 2D materials can be designed in different geometrical configurations depending on the application. In general, top contact configuration is used in the devices which is easy to fabricate with lithography process. The top contact configuration makes good contact and is useful in transport applications. The 2D semiconductor can also be transferred on pre-fabricated metal electrodes (bottom electrodes)³²⁻³⁴ which are preferred if we are studying the effect of charge transport on the surface of 2D materials or if we want to study the applications of suspended 2D devices. It is well known that the edges of two-dimensional materials possess unique properties to their basal plan due to vacancies and dangling bonds at the edges. Hence the binding interaction of edges of 2D materials is proven to be better than the other configurations²⁷. Moreover, the edge contacts are necessarily good for multi-layered 2D material^{35, 36} because of the great conductivity anisotropy of 2D materials for in plane and out-of-plane directions. However,

experimentally it is difficult to fabricate purely edge contact therefore rarely reported experimentally³⁸. In general, the metal contact to 2D semiconducting device is a combination of edge contact and top contact. Due to the higher surface area, top contact contributes more than edge contact. In addition, the formation of edge contact is a challenging task. Therefore, the contact resistance at the interface can be reduced by various other methods rather than edge contacting.



Figure 1.4 Graphene-metal contact possibilities are shown schematically. (a) Devices with side contacts can be implemented as top or bottom-contacts. (b) End-contact or edge-contacted device ³⁷.

1.2.2 Energy band bending at metal/semiconductor interface

Depending on the type of semiconductor (n-type or p-type) and the work function of the semiconductor as well as contact metal, two types of contact were obtained named Schottky contact and ohmic contact as shown in **figure 1.5**. The desired contact can be made by just changing the contact metal having different fermi energy to the same 2D semiconductor. Charge transfer will occur as a result of the difference in work functions between metal and semiconductor, leading to the creation of depletion regions. An electric field is created at the interface as a result of charge flow between two materials and it resists further charge flow.



Figure 1.5 Metal-semiconductor heterojunction band structures. Schottky and Ohmic contacts are the two types of metal-semiconductor heterojunctions ³⁹.

Understanding the charge depleted area formed at the interfaces is crucial for comprehending charge transport in semiconductor FET devices. The understanding of charge transport has been evolved with the time from classical approach to quantum approach. Initially, classical model was introduced to explain the current versus voltage characteristics in the devices.



Figure 1.6 (a) Schematic representation of conventional *n*- channel MOSFET device where S is source, D is drain, V_S is source voltage, V_G is gate voltage and V_D is drain voltage (b) Graphical representation of output characteristics for the same where I_{DS} is drain to source current, V_{GS} is gate to source voltage and V_{DS} is drain to source voltage.

Fig. 1.6(a) is showing the scheme for conventional n-channel Metal oxide semiconductor field effect transistor (MOSFET) and fig. 1.6(b) is showing the graphical picture of the output characteristic of the MOSFET device. The classical approach uses two separate functions to interpret the current response in active and saturation region of MOSFET. For the short channel MOSFET, the electric field across the channel is large for even V_{DS} =1 V and velocity of charge carriers saturates in saturated region resulting the saturation of current $^{40}\!\!.$ While for longer channel MOSFET even at higher V_{DS} the electric field remain moderate across the channel depicting that saturation is not due to velocity saturation of charge carriers in fact reason for saturation is the pinch off near the drain. However, simulation studies on short channel MOSFET shows that velocity of charge carriers is not saturating in the high electric field across the channel ⁴¹. The classical model also lacks the explanation of subthreshold region and depletion charges in MOSFET^{42, 43}. To explain the saturation current at higher voltages, subthreshold region and depletion charges in MOSFET the semi classical electrostatic approach has been applied⁴⁴. We employed the KPFM methodology as a direct experimental measuring tool and applied the semi-classical electrostatic approach for analytical calculations to address the shortfall of classical approach. Until yet, the depletion region formed at interfaces has been examined applying the classical approach for analytical calculations which is indirect measurements of depletion region parameters hence the method doesn't give precise values for the interface parameters at the real condition, instead it estimate the parameters in ideal condition only. In case of field effect transistors, electrostatics define the control of terminal voltages on source-to-channel barrier. For 3D semiconducting FET channel, the solution to Poisson equation as⁴⁵

$$\nabla . \dot{D}(x, y, z) = \rho(x, y, z)$$
$$\nabla^2 \psi(x, y, z) = -\frac{\rho(x, y, z)}{\epsilon_s}$$

where ~D represents displacement vector, ρ represents charge density, and ϵ_s denotes the dielectric constant of the semiconductor. ϵ_s is supposed to be uniform throughout the semiconductor. We will examine 1D electrostatics in the direction normal to the channel to make understanding easier. We consider $\psi(y)$ vs y at a point in the middle of the channel where the influence of the source and drain potentials are small, allowing 2D effects to be disregarded. The Poisson equation can be solved conveniently and

qualitatively using energy band diagrams. Also, we'll look at how a gate voltage affects the relationship between energy and position relative to the depth of the semiconductor channel. The relation between conduction or valence band energy and surface potential is given as,

$$E_C(y) = E_{C0} - q\psi(y)$$
$$E_V(y) = E_{V0} - q\psi(y)$$

where E_{C0} and E_{V0} are constants and q is electronic charge. For ideal conditions if gate voltage is not applied i.e., at $V_G = 0$, the flat band condition should occur. However, in real scenario, the flat band doesn't exist at $V_G = 0$ in fact $V_G = V_{FB} = \phi_{MS}/q$ is needed to obtain flat band condition. A negative electrostatic potential is generated in the oxide and semiconductor, causing the bands to bend upward, when a negative gate voltage is applied.

In this case, the surface potential will be negative, $(\psi(y = 0) = \psi_S < 0)$. Due to the valence band's upward bend towards the Fermi level, the hole concentration increases near the oxide-semiconductor contact. Near the surface, there is a positive net charge. This accumulation charge is located extremely near the semiconductor's surface.



Figure 1.7 Band bending diagram for three different gate voltages. (a) flat band (b) Accumulation of majority carriers and (c) depletion or inversion of charge carriers.

The bands bend downward when a positive gate voltage is applied because it induces a positive electrostatic potential in the semiconductor and oxide and $(\psi(y = 0) = \psi_S > 0)$,

the surface potential is positive in this case. Because the valence band deviates from the Fermi level, the concentration of holes falls. As a result, a depletion layer forms with a thickness of W_D and a negligible hole concentration of $\rho_0 \ll N_A^-$. If the band bending is not excessive, the electron concentration will also be low and the sole charge at the surface will come from the ionized acceptors in the depletion area. When the band bending is significant enough, the electron concentration starts to increase close to the surface. Current flowing through a FET device is caused by this inversion layer of mobile carriers.

1.2.2.1 Depletion approximation

When the device is biased in depletion, a very excellent solution of the electrostatic potential and electric field against position can be easily extracted. With a p-type semiconductor, the bands bend downward in depletion, and hole concentration is negligibly small for $y \leq W_D$. The electron concentration is also low because the conduction band is still much above the Fermi level. Therefore, the space charge density is given as

$$\rho(y) = -qN_A \qquad y < W_D$$



Figure. 1.8 Depletion mode illustration of metal oxide semiconducting device (a) Energy band diagram (b) Electric field vs position.

The depletion approximation is frequently quite accurate and is sufficiently straightforward to allow for analytical solutions. By resolving the Poisson equation, we may determine the electric field in the depletion area as

$$\xi(y) = \frac{qN_A}{\epsilon_s}(W_D - y)$$

The significant quantity we observe is the value of the electric field at the surface of the semiconductor as

$$\xi(y=0) = \frac{qW_D N_A}{\epsilon_s}$$

The electrostatic potential can be derived from electric field as follow

$$\psi(y) = -\int_{\infty}^{y} \xi(y') dy'$$

The potential drop across depletion width is ψ_s which is given as

$$\psi_s = \frac{1}{2} \epsilon_s W_D$$

Furthermore, the depletion region and the charge in the depletion region is analytically derived as

$$W_D = \sqrt{\frac{2\epsilon_s \psi_s}{q N_A}}$$
$$Q_D \approx \sqrt{2q N_A \epsilon_s \psi_s}$$

We can calculate the depletion width, charge in depletion width, and electric field in depletion width if we know the surface potential of a semiconductor.

1.2.3 Engineering of contacts to two-dimensional materials

The fabrication of transparent or ohmic contacts between semiconductors and metallic electrodes for the effective injection of charge carriers into the conduction channel is one of the core aspects of semiconductor device research⁴⁶. The atomically flat and dangling bond free surfaces of 2D materials offer the potential of ohmic contact with the contact

metal in contrast of conventical 3-dimensional semiconductor channel⁴⁷. Although 2D materials are atomically thin, conventional device production methods, like e-beam lithography (EBL) and physical vapor deposition (PVD) of metals, can eventually destroy their crystal structure, leading to substantial Schottky barrier or interfacial states at 2D/metal contacts⁴⁸⁻⁵⁰.



Figure. 1.9 *Ohmic contact engineering of 2D materials with various methods* ⁴⁶.

The scientific community has made sincere attempts to lower contact resistance at the junction of contact metal and 2D material to establish ohmic contacts. The contact engineering can be done by means of tunning energy band alignments which can either be done by choosing contact metal with appropriate work function⁵¹ or by changing the thickness of 2D materials⁵² because band gap of 2D material is

thickness dependent⁵³. Another method to engineer contacts interface with 2D material is dponig. In order to regulate 2D/metal energy level alignment in a controlled manner, surface charge transfer doping has been shown to be a successful and non-destructive doping strategy^{54, 55}. Moreover, multiple crystalline phases exist in two-dimensional layered materials, including the metallic octahedral (1T) and distorted octahedral (1T') phases, as well as the semiconducting trigonal prismatic (1H or 2H) phase. The semiconducting prismatic (1H or 2H) phase can be converted into 1T or 1T' metallic phase by various techniques⁵⁶⁻⁵⁹ to engineer metal/2D semiconductor interface to get an ohmic interface. The undesirable interfacial states at metal/2D junction cause interfacial fermi level pinning⁶⁰, which hamper the performance of 2D material based devices. To avoid the interfacial states, a buffer layer⁶¹⁻⁶³ (metal, semiconductor, or insulator) of another 2D material is inserted between the contact metal and 2D channel. The atomically flat interface of the 2D channel with buffer 2D layer results in efficient charge carrier injection at the contacts. Via the van der Waals integration of 3D metal layers onto 2D materials as contacts^{47, 64}, several approaches have recently been developed in order to retain the 2D lattice and eliminate interfacial stresses or residues during device construction. Moreover, one-dimensional (1D) edge contact can permit a stronger orbital overlap at the 2D/metal interface in comparison to 2D devices with top contact geometry because dangling bonds are present at the 2D edges⁶⁵. This causes the Schottky barrier to become narrower and makes carrier insertion easier.

1.3 2D/2D interface of Van der Waals heterostructures

In contrary to the covalent bonding at traditional epitaxial interfaces, the comparatively weak van der Waals forces between the layers in 2D material heterostructures greatly relax the restrictions of lattice-matching, eventually aiding a wider heterostructure phase space⁶⁶. Van der Waals's interaction between the layers of 2D dimensional materials exhibits the possibility to tune the electronic and optical properties by making the heterostructures of two different 2D materials and gives the flexibility to use a single device for many applications^{67, 68}. The quality of the Van der Waal interface

largely influences the performance of the nanoelectronics devices. The interface quality mainly depends on the method of synthesis of van der Waals heterostructures.

1.3.1 Types of 2D/2D heterostructures on the basis of band alignment

Van der Waals heterostructures can be divided into three categories: type I (symmetric), type II (staggered), or type III(broken) depending on the band alignment⁶⁹. Each one of these band alignments have a specific use to support various device types. The bandgap of one semiconductor is inside the bandgap of another semiconductor in type I alignment, which causes both electrons and holes in the first narrow energy band gap semiconductor to relax. Because it confines electron and hole pair inside the narrower bandgap semiconductor, it is regularly utilized in light-emitting diodes for increased light illumination efficiency. In contrast, type II alignment compels electrons and holes to reside in distinct semiconductors because both the conduction band minimum (CBM) and valence band maximum (VBM) is higher or lower than the other⁷⁰.



Figure.1.10 Probable band alignments for a heterojunction of two semiconductors.

The manufacturing of rectifying diodes with photovoltaic effects is made possible by the separation of electron-hole pairs in type II aligned heterostructures, which is typically used for photoelectric detectors that convert incident light into electrical signals⁷¹. A semiconductor with type III band alignment has a bandgap that is outside of that of the other and a CBM that is lower than the other semiconductor's VBM. In comparison to the bulk semiconductor, there is no longer any prohibited gap at the interface. Tunneling field-effect transistors with high current densities benefit from this type III band alignment⁷².

1.3.2 Methods to assemble 2D van der Waals heterostructures

Van der Waals heterostructures construction can be done with various methods which involve mechanical stacking, liquid-phase exfoliation, chemical vapor deposition (CVD), molecular beam epitaxy (MBE), and pulsed laser deposition (PLD). However mechanical stacking and CVD methods are widely preferred to grow van der Waals heterostructures.

1.3.2.1 Transfer techniques

The pre-exfoliated 2D flakes were transferred to a substrate by means of a polymer carrier to assemble 2D van der Waals heterostructures for device applications. Numerous transfer methods have been developed throughout time to achieve contamination-free van der Waals interfaces. However, wet-transfer and dry-transfer are mainly two transfer techniques being utilized to fabricate 2D van der Waals heterostructures. The frequently used wet transfer method is PMMA (polymethyl methacrylate) carrying layer transfer. Dean et al. invented the PMMA carrying layer transfer technique, which they used to create the high mobility graphene/hexagonal boron nitride (h-BN) heterostructure on the typical SiO2 substrates⁷³. The polymer assist transfer method requires chemicals which hamper the quality of van der Waals heterostructure. A viscoelastic stamp-based all-dry transfer technique was created by Castellanos-Gomez et al. Since there are no wet chemical steps involved in this technique, it has been proven to be particularly favorable for fabrication of devices with freely suspended 2D materials as well as transfer speed⁷⁴. The contamination at the van der Waals interface in case of dry transfer method is lesser but it still not provides contamination free interface leaving room of plenty to advance the contamination free transfer of 2D materials.

Wet transfer method (a) 3 2 (1)Water-soluble Immerse in layer water PMMA Si/SiO Align 5 (4) 6 Glass Slide Bring in Release contact slowly

(b) Dry transfer method



Figure. 1.11 (a) PMMA involved wet transfer method. The chosen flake is exfoliated onto a Si/SiO2 substrate that has been covered in PMMA and a water-soluble polymer layer (1). After that, the stack is submerged in water so that the water-soluble layer can disintegrate, leaving the PMMA layer holding the flake floating on the water's surface (3). With the flake pointing down, the PMMA is then affixed to a glass slide that is attached to a micromanipulator (4). The flake is brought into contact with the target substrate after being aligned with it using a microscope (5). The flake is transferred by carefully removing the PMMA from the finished substrate. (b) the dry transfer method. The exfoliated flake is placed on a PDMS stamp (1), which is then fixed to a glass slide attached to a micromanipulator (2). The flake could be brought into touch with the end substrate (3) by aligning it under a microscope (4). The PDMS stamp (5) can be slowly peeled off, allowing the flake to be placed on the substrate (6) ⁷⁵.

1.3.1.2 Deposition techniques



Figure. 1.12 (a) Diagram of one-step CVD growing process for 2D heterostructures. The vertical heterostructure created by a single step of CVD development is shown schematically in (b) and optically in (c), respectively. The schematic and optical images of the in-plane lateral heterostructure created by the one-step CVD growth are shown in (d) and (e), respectively ⁷⁶.

Researchers are trying to grow the large area 2D flakes and their van der Waals heterostructures to make them applicable on large scale. Mechanical exfoliations lack the large area exfoliation of 2D material. CVD (Chemical Vapor Deposition) is more reliable technique to grow the scalable area of 2D flakes and their van der Waals heterostructures⁷⁷. There are typically two methods for building 2D van der Waals heterostructures. One strategy involves growing 2D materials in heterostructures directly using a one-step CVD process, while another involves growing 2D materials consecutively on top of other 2D materials. Based on stacking two types of heterostructures can be grown using CVD method i.e., lateral heterostructures and vertical heterostructures.

By adjusting the heating temperature, Gong et al. realized the fabrication of vertical and lateral heterostructures of WS₂/MoS₂ using a one-step CVD technique⁷⁶ while h-BN/Gr heterostructures were created by Liu et al. using a two-step CVD technique⁷⁸. It was recognized that the formation of vertical and lateral heterostructures offered a favorable environment due to its potential scalability and higher reproducibility than mechanical exfoliation. Vertical van der Waals heterostructure. Involves the van der Waals epitaxy between the layers and can be synthesized with Chemical vapour deposition, Physical vapor deposition, and dry transfer method of mechanical exfoliation.



Figure. 1.13 Schematic illustrating the creation of lateral and vertical heterostructure using transition metal dichalcogenides (TMDs): (a) The first TMD layer on the base. (a) The construction of a second TMD layer using a first TMD layer. (c) Two different forms of TMDs build lateral heterostructure. (d) Vertical heterostructure is constructed using two types of TMDs⁷⁹.

On the other hand, lateral heterostructures are covalently bonded with each other through the edges and can only be grown using chemical vapor deposition method and Physical vapor transport methods^{80, 81}.

1.3.3 Engineering band alignment at van der Waals interfaces

The band alignment modification at van der Waals interface is a typical task and viable to realize superior performance multifunctional devices. The electrical and optical properties of the van der Waals heterostructure devices can be controlled by tuning the band alignment at the van der Waals interfaces. External factor like strain and electric field has been found to impact the band structure of van der Waals heterostructures. Strain perturbs the crystal lattice of 2D material which modifies its band structure. Volume changes cause energy band locations to shift, and diminishing crystal symmetry causes band degeneracy splits. MoSe2/SnS2 heterojunctions can be used in a wider range of applications since type-I, type-II, and type-III band alignment can be obtained under various electric fields and in-plain biaxial strain⁸². The band structure of MoS₂/WS₂ van der Waals heterostructure is found to be altered when tensile and compressive strain is introduced in the system⁸³. It has been demonstrated that straining up the BP- MoTe₂ heterostructures from 3.1% to 4.8% leads the CBM (Conduction Band Minima) and VBM (Valence Band Maxima) of the BP sublayer to deviate from those of the MoTe2 sublayer, causing type-II to type-III band alignment conversion⁸⁴. Apart from strain, the external electric field can also tune the band alignment at the

interface of van der Waals heterostructures^{72, 85}. In case of $MoTe_2/WSe_2$, it is observed that with the application of electric field stronger than an optimum value, type II band alignment shifts into type I band alignment⁸⁶. A remarkable shift from type-III to type-II band alignment was achieved when a positive electric field was applied, dragging the band edges of the WTe₂ layer down while dragging the HfS₂ layer up⁸⁷.



Figure. 1.14 The relationship between the $MoSe_2/SnS_2$ heterojunctions' band gap and (a) the external E-field and (b) the in-plane biaxial strain. Under external E-fields of (c) 0.06 V/Å and (d) 0.16 V/Å, the band structures and matching band alignments are shown ⁸².

1.3.4 Tunning electronic band structure with the twisted 2D interfaces

The interlayer interactions of 2D materials are significantly affected by the misalignment of the two lattices. For illustration, a minor twist angle might be utilized to tailor the valley dynamics by regulating the intervalley momentum separation between layers. The emergence of superconductivity and insulating behaviour in twisted graphene bilayers is evidence that the twistronic has a significant impact on the system's transport properties^{88, 89}. The fundamental behaviour of twistronics is this universal angle dependence, which is fascinating, especially the interesting and dramatic behaviour for small angles.



Figure. **1.15** (a-d) Atomic structure diagrams of a monolayer of MoS_2 and bilayers with twist angles of 0°, 15°, and 60°. (*e*–*h*) optical reflection images of twisted bilayers and a monolayer of MoS_2 corresponding to respectively (*a*–*d*) at 10 µm scale bar ⁹⁰.

These fields are promising in multifunctional devices, or getting several diverse uses at different twist angles in a single device, due to getting different electrical properties at different twist angles.

1.4 Effect of morphological shape on electronic band structure

The electronic band structure of 2D material is morphological shape dependent which can be promising candidates for optoelectronic devices. The mechanical exfoliation does not lead to desirable morphological geometry. However, the CVD method provides the ability to control the morphological shape and flake area by optimizing the growth parameters. Triangular shapes are the most common morphological shapes for two-dimensional materials synthesized using the CVD process because they need the least amount of energy of formation. Nonetheless, it has been shown that two-dimensional materials can have morphological geometries other than triangle shape by adjusting the growth parameters of the CVD process or by selecting the substrate on which the sample grows⁹³⁻⁹⁵. Theoretical investigations demonstrate that a variety of catalytic activities as well as necessary electrical and magnetic properties are achievable for 2D materials by altering the chemical potential through edge state control^{91, 96, 97}. Even the basal plane of the CVD-grown MoS₂ hexagon can be activated for the hydrogen evolution reaction by modifying the morphological shape⁹⁸.



Figure. 1.16 (a) MoS_2 domains' magnetic properties and shape at various chemical potentials ⁹¹. (b) Evolution of shape of MoS_2 by changing the concentration of MoO_3 powder in CVD process ⁹².

There is still lot of room to examine the electrical and optical properties of different morphological shapes of two-dimensional materials because the majority of studies to date have concentrated on the synthesis aspect. Moreover, in 2D materials, the bound electron-hole pair (excitons) has significant role in optically controlled valleytronic devices⁹⁹. Thus, it is crucial to explore how morphological shape affects excitonic dynamics. In our work we have investigated the excitonic dynamics of CVD grown hexagonal geometry of MoS₂.

1.5. Thesis layout

In order to apply devices in real condition, the real conditions figure of merits for 2D interfaces as compared to ideal one estimated from conventional techniques and excitonic properties of 2D materials are necessary to be known. Band alignment at the

interfaces has previously been assessed indirectly from electronic response or analytically predicted by following different transport models. However, no direct method of experimentation has yet been developed to measure the critical interface parameters at a contact or interface in real conditions and quantify the variation from the ideal scenario. In order to understand the electronic band alignments at the contact metal/2D interfaces as well as at the van der Waals heterostructures interfaces, we confronted the Kelvin Probe Force Microscopy (KPFM) technique, an advanced tool based on Atomic Force Microscopy (AFM). We then utilized the semi-classical electrostatic approach to figure out interface parameters.

The chapters in this thesis are organized as

Chapter 2: The synthesis methods and experimental setup used to carry out the research work given in the thesis are described in the second chapter of the thesis. The 2D materials and van der Waals heterostructure are created using the dry transfer technique and CVD method. The surface potential of the sample is measured using the KPFM method, and the band gap studies are investigated using μ -PL(μ -Photoluminescence). The excitonic behaviours are investigated using the low temperature μ -PL. Primary characterization tools like Raman and Atomic force microscopy (AFM) are also discussed in this chapter. The experimental set-up used for device fabrication are also deliberated.

Chapter 3: I investigate the energy band bending that occurs at the Au/MoS₂ junction when current is conducted in a bridge-type MoS₂ channel. To prevent contamination from solvents used in the lithography process, MoS₂ flakes were placed on prefabricated Au electrodes. An in-depth examination of the surface potential during charge transport showed asymmetric contacts of source and drain electrode with MoS₂ in addition to Schottky behaviour at the MoS₂/Au interface. We determined the interface parameters such as built-in potential, surface electric field, and space charge density at Au/MoS₂ interface in non-equilibrium circumstances by modulating the applied voltage to MoS₂ channel. The difference between the experimentally determined and analytically obtained depletion widths is attributed to local defects, contact area, and thickness variation of the MoS₂ flake. By probing the interface parameters and how they change with current conduction, it is possible to compare and enhance the performance of actual devices with ideal ones. **Chapter 4:** The surface potential distribution at the MoS_2/BP van der Waals p-n heterojunction created using the dry transfer technique was investigated in this chapter. We demonstrate the formation of the p-n junction at the $MoS_2/Black$ phosphorene (BP) interface and experimentally measure the band alignment under realistic conditions by measuring the spatial distribution of built-in potential, built-in electric field, and depletion width via the Kelvin probe force microscopy (KPFM) technique. For a better resolved potential picture, we have optimum the lift height of about 15 nm. The charge distribution at the MoS_2/BP interface has been modified by adjusting the width of the MoS_2 flakes over a uniform thickness of BP flakes. As the MoS_2 flake thickness is increased, a rise in the lateral built-in potential and electric field is seen at the MoS_2/BP interface. Additionally, computations using the Density Functional Theory (DFT) have been performed to verify the experimental results.

Chapter 5: In this chapter, we looked at the twistronic of a hexagon-shaped CVDgrown MoS_2/MoS_2 interface. We conducted PL measurements at room temperature and discovered the blue shift in the PL peak location at the interface. The lattice tension brought on by the angular shift between two flakes is what is responsible for the change in the PL energy. We used Field emission scanning electron microscopy (FESEM) to determine the angle between two flakes and discovered that it is 6.7 degrees. Uneven change in the peak energies of the trion, B exciton, and A exciton at the MoS_2/MoS_2 interface was seen in the deconvoluted PL spectra. At the MoS_2/MoS_2 interface, the B exciton's energy change is more pronounced. The spin-orbit coupling energy at the interface increased by about 19 meV, as seen by our observations.

Chapter 6: In this chapter, the optical characteristics of MoS_2 with a morphological hexagon shape were also investigated. The hexagonal morphological form of multilayer MoS2 flake was created using the Chemical Vapor Deposition (CVD) method. Studies on PL that are temperature-dependent show a red shift in PL as temperature rises due to a change in band gap brought on by semiconducting characteristics. Deconvoluted PL spectra show the trions', A exciton's, and B exciton's, PL luminosity and PL shift has been changed with the temperature. The fermi energy, which is quite low at 31 meV at room temperature, can be calculated using variations in the ratio of A exciton strength to B exciton intensity with temperature. The electron concentration of order ~ 1.5×10^{12} cm⁻² has been obtained irrespective of multilayer nature of MoS₂ hexagon. In the instance of MoS₂ with a hexagonal morphology, we noticed an improvement in electron phonon coupling. The band gap at absolute temperature is determined by fitting

parameters to the variation in PL peak energy with temperature, and it is determined to be 1.91 eV, which is high compared to earlier reports (1.8 eV) for other morphological shapes. We can calculate the exciton-optical phonon coupling strength from line width change with temperature. The valence band splitting energy, which is estimated to be around 132 meV, is not greatly affected by temperature.

Chapter 7: This chapter represents the summary of the research work discussed in the thesis as well as the future scope.

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Chapter 2

Experimental set-up details



This chapter describes the basic experimental tools to synthesise and characterise twodimensional layered materials and their van der Waals heterostructures.

2.1 Synthesis technique

Two-dimensional materials can be synthesised using various techniques, including topdown and bottom-up procedures. I have employed a few techniques in my work, listed below.

2.1.1 Micromechanical exfoliation

To achieve the highly crystalline and pure form of 2-dimensional materials, the micromechanical exfoliation technique is employed, which is a top-down method. Bulk crystal is placed in scotch tape and exfoliated numerous times to obtain a thinner flake of 2D materials. As shown in the schematic, after thinning the bulk crystal, the flakes are transferred to the desired substrate (SiO₂, Au, ITO, Si, etc.) and can be seen in an optical microscope. This technique allows us to get monolayer, bi-layer, tri-layer, and few-layer flakes. The limitation of this method prevents its widespread application since we cannot control the morphological size and shape of 2D flakes.



Figure. 2.1. Optical images of mechanical exfoliation of a single crystal of twodimensional material¹.

2.1.2 Chemical vapour deposition technique

This technique compromises the crystallinity of 2-dimensional materials but is helpful for low-cost, large-area production. The CVD system we have in our lab is one zone CVD system, which is made up of an alumina tube. It has a proportional-integral-derivative (PID) controller and can operate up to 1000 °C. The quartz tube is thus inserted into the alumina tube. The precursor, molybdenum trioxide (MoO₃), which was kept in the heating zone (at the centre of the quartz tube), and sulphur (S), which was

placed in the lower temperature zone (i.e., end side of the quartz tube). Couplers with gas inlets fix the quartz tube's inlet and outlet, and a bubbler is connected to the quartz tube's outlet. Argon (Ar) gas is used to cleanse the quartz tube for five minutes before beginning the deposition. In this method, metal and ligand precursors are heated at various temperatures before reacting in the vapour phase. Figure 2.2 shows the CVD reaction's schematic. Ar gas is introduced into the high-temperature tube from the left side, carrying evaporated sulphur atoms (kept at the left end side) towards the MoO₃ precursor. Sulfur atoms and evaporated molybdenum oxide combine to form a film of MoS2 on a substrate set above a crucible of MoO₃. The temperature was set for MoS2 deposition to rise at a rate of 600 °C per hour and hold at 800 °C for 10 minutes in an argon atmosphere. MoO3 powder in the heating zone begins to melt when furnace temperatures hit 800 °C, and at the same time, S at the low temperature begins to evaporate. The vapour sources of S and MoO₃ to form MoS₂.



Figure.2.2. Schematic diagram of CVD reaction in one zone CVD system for growing MoS_2

It is well-known that the properties of two-dimensional materials depend on the size, phase, morphology and interface present, etc. All these factors can be controlled by tunning the CVD growth parameters hence tunning the properties of 2-dimensional materials^{2, 3}. It is crucial to understand the general principles of CVD reaction, i.e., the influence of growth parameters such as the precursor, substrate, gas flow pressure, and substrate temperature on mass and heat transfer, interface interactions, and hence the growth of the 2D materials. Besides growing 2D materials and van der Waals heterostructures, twisted 2D materials have grown successfully with the CVD method⁴.

2.1.3 Dry transfer technique

Dry and wet transfer are two basic techniques for fabricating van der Waals heterostructures. A dry transfer is advantageous over wet transfer due to wrinkle free and polymer-contamination-free interface of heterostructures. Castellanos-Gomez et al. stacked 2D material heterostructures utilising PDMS rather than the wet transfer method⁵. The dry transfer technique also transfers 2D flakes of pre-fabricated electrodes to make suspended devices. Generally, a PDMS thin film transfers a 2D flake from scotch tape to the desired substrate.



Figure 2.3 Scheme representing dry transfer method.

Initially, a 2D flake of one material is transferred on a substrate to form a heterostructure of two different two-dimensional materials. A 2D flake of another material is then transferred to PDMS thin film from scotch tape with mechanical exfoliation. PDMS thin film on the glass slide is kept upside down on the transfer setup, and the desired 2D flake is aligned with the bottom flake, which was previously transferred on the substrate. The alignment of both flakes is assisted with the help of an optical microscope. The upper flake on PDMS was slowly moved downwards with the micromanipulator till it makes contact with the bottom flake. The substrate was kept at 40 degrees Celsius, and PDMS thin film peeled off slowly, leaving a heterostructure on the substrate.



Figure 2.4. Image of 2D flake home-made transfer set-up

2.2 Optical Characterization

An optical microscope of high resolution confirms the first confirmation of the 2-D flake. The flake's location, area, and thickness can be estimated with the help of an optical microscope. Further, primarily characterisation has been done in the same place.

2.2.1 Raman Characterization

Raman is a fingerprint and the most reliable technique to confirm layer numbers in the case of 2D materials. Besides primary characterisation, Raman can detect the defect states, doping and strain at the interfaces, etc^6 . Typically, the Raman effect can be explained with two popular theories. One is the classical theory of the Raman effect, and another is the quantum theory of the Raman effect.



Figure 2.5. Schematic representation of Raman scattering process.
2.2.1.1 Classical Theory of Raman effect

Classically, light is an electromagnetic wave propagating in one direction with an alternating oscillating electric and magnetic field which oscillate perpendicular to each other and the direction of propagation. The oscillating electric field intensity of E is given as

$$E = E_0 \cos(2\pi\nu' t) \tag{1}$$

where *E* denotes the electric field intensity at time t, E_0 represents the amplitude of the electric field component, ν' indicates the electromagnetic wave frequency.

When an oscillating electromagnetic wave strikes a sample molecule, it distorts the electron cloud and thus induces the electric dipole moment μ ,

$$u = \alpha E \tag{2}$$

where α is the polarizability of the molecule, which is a property of the molecule. Polarizability measures the strength of a molecule to get polarised under the influence of an applied field.

For Raman scattering to happen, the polarizability should change during molecular vibrations. Taking the example of a diatomic molecule showing the change in polarizability with molecular vibrations, Taylor's expansion of polarizability with neglecting higher-order power terms is

$$\alpha = \alpha_0 + \left(\frac{d\alpha}{dq}\right)_0 q$$

(3)

where α_0 denotes the polarizability of the sample molecule at the equilibrium position, q represents the vibrational coordinate, and $\left(\frac{d\alpha}{dq}\right)_0$ denotes the first-order derivative of polarizability w.r.t q at the equilibrium position. Using equations (1) and (3), equation (2) can be written as

$$\mu = \left[\alpha_0 + \left(\frac{d\alpha}{dq}\right)_0 q\right] E_0 \cos(2\pi\nu' t)$$
$$= \left[\alpha_0 + \left(\frac{d\alpha}{dq}\right)_0 q_0 \cos 2\pi\nu t\right] E_0 \cos(2\pi\nu' t)$$
$$= \alpha_0 E_0 \cos(2\pi\nu' t) + \left(\frac{d\alpha}{dq}\right)_0 q_0 E_0 (\cos 2\pi\nu t) (\cos 2\pi\nu' t)$$

Above equation can be written as

$$\mu = \alpha_0 E_0 \cos(2\pi\nu' t) + \frac{1}{2} q_0 E_0 \left(\frac{d\alpha}{dq}\right)_0 \left[\cos 2\pi(\nu' + \nu)t + \cos 2\pi(\nu' - \nu)t\right]$$

the first term of the above equation $\alpha_0 E_0 \cos(2\pi v't)$ shows scattering with the same frequency as that of incident electromagnetic wave and is called Raleigh scattering. The second term with frequencies v' + v, which is higher than the incident frequency, shows showing anti-stokes line. The third term, with frequencies v' + v, which is lower than the incident frequency, shows showing stokes line. The necessary condition to get the Raman signal is $\left(\frac{d\alpha}{dq}\right)_0 \neq 0$ change in polarizability w.r.t. vibration of the molecule⁷.

2.2.1.2 Quantum Theory of Raman effect

In the quantum approach, the light consists of photons having energy E as

$$E = hv$$

where h represents the plank's constant and ν is the frequency of the light.

Rayleigh scattering is elastic scattering in which the frequency of scattered photons remains the same as that of the incident photons; only the direction of scattered photons changes. While Raman scattering is inelastic scattering in which the frequency of scattered photons changes due to energy transfer between the incident photon and the molecule.

The sample molecule is in a ground electronic state, at first vibrational excited or ground vibrational state. The energy of an incident photon is not sufficient to excite the molecule to a higher electronic excited state, but it is much less than the energy required to excite vibrational energy level; therefore, photon will raise the molecule to a quasi-excited state which is a virtual energy level, not a fixed energy level. Quasi-excited state of the molecule is unstable, and to get stability, it will release energy and jumps to the ground electronic state by emitting photons in four possible ways. Suppose molecules relax their energy to the same vibrational level at which they are situated before excitation. In that case, they emit a photon with the same energy as the incident photon called Raleigh scattering. If molecule release their energy to a higher excited vibrational energy level than they were situated before excitation, they emit photons of frequency as

$$v_s = v_o - \frac{E_1 - E_0}{h}$$

Where v_s denotes Stokes frequency, v_o represents the frequency of incident photons, E_1 is the energy of excited vibrational energy levels, E_0 is the energy of ground vibrational level and *h* is planks constant.

Similarly, if molecule release their energy to lower vibrational energy states than they were situated before excitation, they emit photons of frequency as

$$v_{aS} = v_o + \frac{E_1 - E_0}{h}$$

Where v_{aS} is anti-stokes frequency, Stokes and anti-Stokes lines are Raman scattering. The difference in the frequency of Stokes lines and Raleigh lines is equal to the frequency difference between anti-Stokes lines and Raleigh lines, but the intensity of Stokes lines is greater than the intensity of anti-Stokes lines. This is because of Boltzmann's distribution law which states that the population at the ground state is higher than the first excited state⁷.

2.2.2 Photoluminescence (PL) Characterization

PL is a non-contact and non-destructive technique to probe electronic structures in twodimensional materials. This technique helps to determine the bandgap, impurities level and defects in low dimensional materials⁸. The photoexcitation process occurs when incident light (photons) interacts with a material. This excitation mechanism drives electrons and holes into the conduction and valence bands.



Figure 2.6. The schematic of the band diagram of quasiparticles in 2D materials can be observed from PL. The orange circle indicates electrons, while sky blue is an indication hole.

The photons released as a result of the electrons and holes recombining after relaxing in the conduction band are detected in the form of PL. The PL of 2D materials is associated with quasi-particles like excitons, trions, etc⁹.

These quasi-particles in 2D materials can even be observable at room temperature, irrespective of 3D materials. The quasi-particle exciton is an electrostatically bound electron-hole pair. The exciton further lowers its energy to form a trion by combining either one hole or one electron. We have used the WITEC alpha 300R Raman spectrometer equipped with a 532 nm Nd-YAG laser with a 1 μ m spot size to carry out the PL measures. Furthermore, the PL fit is deconvoluted to detect excitons and trions.

2.2.2.1 Low-temperature PL measurements

The excitonic physics of 2D materials can be better understood at low temperatures. To understand the dynamics of exciton at low temperatures, we have used Lowtemperature.



Low temperature vacuum stage

Figure 2.7. Schematic representation of low temperature PL set up.

PL set up of Linkam HFS600E-PB4. The sample was kept in a continuous vacuum of $\sim 10^{-3}$ mbar during the measurements. The 2D flake is locally identified with a long-distance objective of 50X. The temperature of the stage is controlled with the software. A liquid nitrogen cryostat is employed for cooling in our system. 532 nm laser line excites the cooled sample, and an optical interface is used to couple the PL to a spectrometer.

2.3 AFM Characterization



Figure 2.8. Schematic diagram representing AFM system.

Nanoscale characterisation using AFM has been done to check the thickness and morphology of 2D flakes. The electrical and optical properties of the 2D flake are thickness dependent; therefore, it is essential to depict the thickness of the 2D flake. AFM is a sensitive technique to measure the surface non-uniformity, thickness of 2D fake, morphological shape and particle distribution over an area. Topography images can be mapped in two modes one is tapping mode, and the other one is contact mode. In tapping mode, the AFM cantilever vibrates near resonant frequency and oscillates up and down. This mode is suitable for delicate samples because the tip is not in contact with the sample. However, this mode compromises resolution for thinner samples, typically less than 10 nm. On the other hand, in contact mode, where the tip is in contact with the sample, we got higher resolved images but can damage the soft samples. Therefore, a cantilever with a low spring constant minimises the damage generated by the tip in contact mode. Figure 2.8 shows the schematic diagram for the AFM system. The main components of the AFM system include a cantilever with a fine probe (~10nm to 20nm). This laser beam is reflected from the back side of the cantilever at a particular angle and a photodiode at which the reflected laser is collected. AFM tip passages in response to tip-sample surface short-range van der Waals interactions. This response is sensed by focusing a laser beam on the cantilever, and the photodetector detects the reflected laser beam.

2.4 Kelvin Probe Force Microscopy (KPFM)

KPFM is a widely used and sensitive technique for surface potential detection. It is a dual-mode scanning method in which the first scan is taken for a topography image, and the second scan is taken at a particular lift height following the same path to detect surface potential. Contact potential difference (CPD), which is measured by the system, is defined as 10

$$CPD = \frac{(\phi_t - \phi_S)}{-e}$$

Where ϕ_t denotes the work function of the tip, ϕ_s indicates the work function of the sample, and e is the electronic charge. KPFM measures a material's work function, i.e., the energy required to remove an electron from the fermi level to the vacuum level. When an exterior electrical contact joins two conductors, electrons will move from higher Fermi level material to lower fermi level material to equalise the fermi energy of the combined system. Due to electron transfer between two materials, a potential difference arises at the materials' interface, known as contact potential difference (CPD). A similar kind of process between the AFM conductive tip and sample is shown in the schematic diagram.



Figure 2.9. Schematic representation for principle of KPFM.

To measure the CPD external potential applied to the sample or tip until the developed charges creating potential difference disappears. The system measures the applied potential required to obliterate charges, which is equal to the CPD. Different KPFM methods were developed based on the way to disappear these charges. Two modes to detect CPD are Amplitude mode KPFM (AM-KPFM) based on electric force detection and Frequency mode KPFM (FM-KPFM) based on electric force gradient detection. We have used AM-KPFM mode to detect the surface potential for which the schematic is shown. The AFM conductive tip and the sample acts as parallel plate capacitor having energy given by

$$U = \frac{1}{2}C(\Delta V)^2$$

Where *U* is the energy the capacitor stores, *C* is the capacitance between the tip and the sample, and ΔV is the voltage difference between the conductive probe and the sample. ΔV is further given as

$$\Delta V = (V_{\rm DC} - CPD) + V_{\rm AC} \sin \omega_e t$$

Where V_{DC} is the externally applied potential between probe and sample, V_{AC} is the externally applied AC single between tip and sample, and ω_e denotes the angular frequency of the applied AC voltage, which is very close to the cantilever's resonance frequency—the electrostatic force between the conductive tip and the sample change in energy with the separation distance.

$$E_{el} = -\frac{\partial U}{\partial z} = -\frac{1}{2}\frac{\partial C}{\partial z}(\Delta V)^2$$

Where E_{el} represents the electrostatic force between the probe and the sample.

Using the above two equations, we got



The oscillating electric field at ω_e acts as the sinusoidal driving force to the cantilever, which can cause motion in the cantilever. The cantilever only responds to the frequency near the resonant frequency; therefore, the 'DC term' and the ' $2\omega_e$ term' doesn't cause significant oscillation in the cantilever. The response of the cantilever is directly proportional to the amplitude of the ' ω_e ' term. The feedback loop aims to adjust the V_{DC} until it equals the CPD such that the oscillation of electrostatic force stops.



Figure 2.10. Schematic diagram showing the AM-KPFM system.

2.5 Optical maskless Lithography

We have used maskless optical lithography to pattern the desired shape and size of the electrodes on the 2D flake. Compared to e-beam lithography, it takes less time and is simpler to execute. It is a low-cost method due to its maskless advantage. An overview of the process is shown in the schematic diagram as shown in the fig. 2.11. Two types of optical lithography systems we have used to pattern the substrates.



Figure 2.11. Schematic diagram of maskless optical lithography with positive photoresist (left side) and negative photoresist (right side).

2.5.1 Projection Lithography

In this method, the exposure pattern is projected using the projector to the collimatorconnected microscope and then onto the substrate via an optical system. To fabricate the desired shape of contacts on the 2D material, we employed Laben BM-3000 Microscope associated with a projector. The contact electrode was made using the positive AZ5214E photoresist and its developer, Tetra methyl ammonium hydroxide (TMAH). The photoresist AZ5214E coated on the substrate (300nm SiO2/Si) having 2D materials with 4500 revolutions per minute for 30 seconds. The substrate was then placed on the hotplate for 1 minute of soft baking at 90 degrees Celsius. The soft-bake substrate was placed on the microscope's stage to locate the appropriate flake. The exposure pattern for the contact was created in a PowerPoint presentation and imported into the projector. The focus of the designs with the desired flake is required for the projection exposure of the pattern on the flake. The sample is first developed by dipping it in photoresist developer solution (TMAH) for 40 seconds after being exposed for 20 seconds (the optimal exposure period). This method allows substrate exposure with a 1 mm x 1 mm surface area and a 1 μ m resolution.

2.5.2 Micro writer

In addition to projection lithography, the laser writer is used to increase the lateral resolution of the electrode pattern. Our technology, the Durham Magneto Optics ML3, has a 0.6 µm resolution limit. In contrast to traditional lithography, the software mask can be graphically designed, adjusted in less time, and free of charge. This technique irradiates the AZ5214E photoresist-coated sample using a UV laser at 385 nm. The photoresist-coated wafer is retained on the system's wafer chuck. The software programme is used for other processes. The autofocus mechanism precisely focuses the sample once the optical system has focused on it using the user's estimated sample thickness. The pattern file is uploaded to the software to be exposed after autofocus. The optimised dose is set in the software to expose the photoresist. The exposed substrate is then developed with the developer (TMAH) for 40 seconds.

2.6 Electron Beam deposition

We have used the Electron beam deposition system of Excel Instruments to deposit Au/Cr on the patterned electrodes. E-beam deposition is a physical vapour deposition technique in which source material is evaporated using a high-energy E-beam. The patterned samples are fixed on the substrate holder, and the materials to be deposited are kept in separate slots of the graphite crucible holder. The tungsten filament is heated to emit thermionic electrons that are accelerated to have enough energy to evaporate any substance after the chamber has reached a high vacuum (10^{-6} torr). The magnetic field is used to direct the E-beam towards the surface of the evaporating material, and the E-beam is accelerated with 100 kV DC voltage. The total force F acting on the electron is Lorentz force given by¹¹

$$F = F_E + F_B = q_e E + q_e (v \times B)$$

Where q_e is the charge on electrons, E is the electric field experienced by electrons, v is the velocity of the electrons in the electromagnetic field, and B is the magnetic field applied on electrons. The first term in the above expression, i.e., $q_e E$ is the electric

force used to accelerate the E-beam, and the second term, $q_e(v \times B)$, is the magnetic force used to pull the E-beam towards the sample surface. Once the target material is heated with a high-energy E-beam, the materials start to evaporate towards the surface of the substrate and a uniform film of the target material is deposited on the substrate. The thickness of the depositing film can be detected with a quartz crystal monitor (QCM).



Figure.2.12 Scheme representing the Electron-beam deposition system.

2.7 Transport characterisation

The device's electronic performance has been tested using transport measurements. We have used the Keithley source metres model number 2635B and Aplab DC power supply to monitor current vs voltage characteristics. The electrical connections to the electrodes are made by copper wire using a silver paste, as shown in the schematics.



Figure 2.13. Scheme of Electrical connection of the device with source meter.

The conductivity of a 2D material can be determined from a current versus voltage measurement. These measurements also reveal if the contact between the 2D channel and the metal in contact is ohmic or Schottky. With current vs voltage characteristics, we may determine the sensitivity and response time of the device in sensing applications.

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Chapter 3

Tracking electronic band alignment across 2D bridge-channel MoS₂ during charge transport





3.1 Introduction

As discussed in chapter 1, the contact metal/semiconductor interface is an important parameter for charge injection in the field effect transistor devices. This chapter focuses on the detailed analysis of surface potential at contact metal and semiconductor interface during current conduction.

Probing of electronic band alignment along a semiconducting channel by noncontact means is one of the utmost needs for modern micro-electro-mechanical (MEMS) devices, where the complex architecture of hetero-structures, interconnects, and multiple contacts are engineered to manipulate the charge carriers¹⁻⁴. The band bending along the junctions or contacts occurs due to the change in the surface potential landscape of the channel, primarily introduced by the electrostatic semiclassical model of charge transport, which is also capable to explain the shortfalls of the classical transport model⁵.

Kelvin Probe Force Microscopy (KPFM), being capable of probing the spatial electrostatics charge distribution at the microscopic level, could be used to understand the surface potential distribution during the transport of the charge carriers^{6, 7}. KPFM has been widely explored to probe the work function, defect states at the surface, and interfaces $^{8-10}$. It can accurately probe the electrostatics of charge accumulation around defect centers and at the junctions by mapping the local contact potential difference (CPD) at the charge equilibrium state¹¹. Traditionally, the KPFM technique has been employed on various two-dimensional (2D) layered materials to investigate the electrostatic properties of the interfaces and defects. Recently, the modulation and control over surface potential by varying the layer number and through substrate effect have been established on MoS_2 flakes¹²⁻¹⁵. Kim *et al.* have deployed the KPFM technique to demonstrate the effect of gas and water molecule adsorption on the surface potential of MoS_2^{16} . D. J. Ellison et. al. have been instrumented engineering of electrostatic properties on various homo- and heterojunctions of 2D layered materials¹⁷⁻²⁰. To the best of our knowledge, three experimental publications on KPFM studies of 2D materials under biassing have been identified in the literature. The effect of gate voltage on the fermi level of graphene and the contact resistance of the Graphene-Metal contact under biassing was demonstrated in these reports^{21, 22}. In another case, Vakni et. al. were able to probe the accurate pinch-off voltage of a MoS_2 field-effect transistor⁷. However, it would be of vital importance to probe the detailed dynamics of the surface potential at non-equilibrium conditions, i.e., during the flow of charge in the channel.

In this chapter, the non-contact KPFM technique has been employed on a 2D MoS_2 flake, laid on two gold electrodes. The measurements were done to probe the surface potential and visualize the dynamics of the charge carriers within the channel and at the MoS_2/Au junction in an electronically non-equilibrium condition, during the charge carrier transport between source and drain electrodes. MoS_2 is a stable 2D semiconductor with high carrier mobility, is a suitable candidate for such nanoscopic measurements to probe the spatial distribution of surface potential^{23, 24}. Prefabricated Au electrodes were used to explore the charge injection via bottom electrodes and to avoid the MoS_2/Au interface contamination during the lithography process. In this chapter, we have demonstrated that the KPFM technique can pave a way to visualize the evolution of potential gradient at the junctions during charge transport and can directly track the potential gradient formation throughout the device.

3.2 Experimental Details

3.2.1 Fabrication of electrodes

The pattern of channel length of 20 μ m for electrodes on SiO₂/Si (p-type) wafer with SiO₂ thickness of 300 nm was made using optical maskless Durham Magneto Optics ML3 lithography system. The details of lithography procedure are discussed in the section 2.5.2 of chapter 2. The deposition of Au/Cr (60 nm/5 nm) on the patterned substrate were done using Electron beam deposition system. After the deposition, the liftoff process of photoresist was carried out using Acetone.

3.2.2 Synthesis of MoS₂

 MoS_2 flakes were micromechanically exfoliated from bulk crystal using scotch tape and then transferred on PDMS thin film.

3.2.3 Dry transfer of MoS₂

We have designed an indigenous set-up using an optical microscope and micromanipulator for precise transfer of MoS_2 flake on a pre-defined substrate's area, which is pre-fabricated Au/Cr electrodes. The schematic representation of the complete stepwise protocol of dry transfer technique is shown in **fig. 3.1(a)**. Initially, multilayer MoS_2 flake is micro mechanically exfoliated by using standard scotch tape technique followed bytwo pre-fabricated Au/Cr electrodes by using the optical microscope and micro-manipulator of the dry-transfer setup [**fig. 3.1(b**)].

The target substrate having Au/Cr electrodes is slightly heated to enhance the adhesiveness between the MoS_2 flake and the substrate, which is done only after the MoS_2 flake is in contact with the substrate at desired location²⁵.



Figure 3.1. Dry-transfer technique of MoS_2 flake on pre-fabricated Au/Cr electrodes. (a) Schematic representation of the followed dry transfer protocol used to transfer the MoS_2 flake. (b) Photograph of the indigenously build dry transfer stage using standard optical microscope and micro-manipulator.

3.2.4 Raman and AFM characterization



Figure 3.2 Characterization of MoS_2 flake. (a) Optical image of MoS_2 channel on Au electrodes. (b) Raman spectra of MoS_2 flake, showing the characteristics E^{1}_{2g} and A_{1g} modes and the peak difference of 25.55 cm⁻¹ between two modes represent the multilayer nature of the flake. (c) AFM topography image of MoS_2 flake, where the thickness profile along the (d) red and (e) blue dashed lines, as marked in **fig. 3.2(c)**.

To characterize the fabricated MoS₂ channel, Raman spectroscopy and PL measurements have been performed using WITEC alpha 300R Raman spectrometer with a 532 nm Nd-YAG laser with ~1 μ m spot size. The AFM and KPFM measurement have been done with BRUKER Multimode 8 AFM using Cr/Pt conductive coating probe. The biasing of the MoS₂ channel is done by using the Aplab DC power supply. **Fig. 3.2(a)** shows the optical image of the as-fabricated MoS₂, where micro mechanically exfoliated multilayer MoS₂ flake is transferred on pre-fabricated Au electrodes on SiO₂/Si (p-type) wafer. The channel length and the flake area have been found to be ~20 μ m and ~160 μ m² respectively. **Fig. 3.2(b)** is showing the Raman spectra of MoS₂ flake where two Raman active modes E¹_{2g} (inplane optical vibration of Mo and Sulphur atoms) at 380.24 cm⁻¹ and A_{1g} (out of plane optical vibration of Sulphur atoms) at 405.79 cm⁻¹ has been observed. The frequency difference between the two characteristics of Raman modes is found to be ~25.55 cm⁻¹, which confirms the multilayer nature of MoS₂ flake²⁶. To confirm the thickness and

surface morphology of the MoS_2 flake, the AFM measurement has been performed in tapping mode configuration [**fig. 3.2(d**)]. The thickness of multilayer MoS_2 has been found ~132 nm along the red dotted line [**fig. 3.2(d**)] and ~142 nm along blue dotted line [**fig. 3.2(e**)], where the surface roughness is ~5.12 nm.

3.2.4 PL characterization



Figure 3.3 Photoluminescence of MoS_2 . a) PL spectra for multilayer MoS_2 flake fitted with Lorentzian function to obtain the band gap at ~695.9 nm (~1.78 eV). b) The PL spectra of the MoS_2 flake at the different marked positions, which confirms that slight variation in peak position is originated due to the suspension of the sample.

In order to study the electronic band structure of the MoS_2 flake, photoluminescence (PL) measurement has been performed with 532 nm laser, as shown in **fig. 3.3(a)**. The Lorentzian fitting of the PL spectra suggests that strong PL peak is observed at ~695.9 nm, indicating a optical bandgap of 1.78 eV. The uniformity of the bandgap properties of the MoS_2 flake has been confirmed by recording the PL spectra at different points of the MoS_2 flake as shown in the inset of **fig. 3.3(b)** and corresponding PL spectra are shown in **fig. 3.3(b)**. A slight redshift in PL peak position along the MoS_2 flake near Au electrode edges²⁷.





Figure 3.4 Schematic diagram of electronic circuit of AM-KPFM system with multilayer MoS_2 flake. Top part shows the AM-KPFM system for CPD measurement and the bottom part is for AFM topographical imaging.

KPFM simultaneously measures the topography image and the surface potential mapping by two consecutive scans, where in the first scan, the conductive AFM probe measures the topography of the sample followed by a second scan, where the tip measures the CPD (Contact Potential Difference) following the same scan path with a constant lift height. In order to measure the CPD between the tip and the sample, a tip bias V_{DC} is applied to the conductive tip. Depending upon the electrostatic interaction

between probe and the sample, the conducting probe nullifies its oscillation when the applied bias equals to CPD of opposite polarity. The detailed electronics of applied bias voltage and feedback circuit are schematically represented in **fig. 3.4**. By using the obtained CPD through KPFM measurement, corresponding work function of a sample can be determined from the equation, $CPD = \frac{(\phi_t - \phi_s)}{-e}$, where ϕ_t and ϕ_s represents the work function of tip and sample, respectively and e represents the electronic charge²⁸.

3.3 Results and discussion

Amplitude Mode-Kelvin Probe Force Microscopy (AM-KPFM) was conducted on the MoS_2 channel to probe the nature of charge carrier diffusion locally during the charge injection at the MoS_2/Au interface. The instrumental error in measuring surface potential was ± 5.08 mV. KPFM measurements were carried out at thermally non-equilibrium condition i.e., with sample bias (V_d) varying from -2 V to 2 V, as shown in **fig. 3.5(a)** and **3.5(b)** where the tip lift height is kept constant at 30 nm.



Figure 3.5 Surface potential mapping of MoS_2 flake with varying applied bias. Contact Potential Difference (CPD) image of MoS_2 flake at (a) $V_d = 0 V$ and (b) with varying applied bias ranging from -2 V to +2 V along the channel. The contrast variation (dark to bright) depicts the increase in CPD along the channel, where each applied bias is mentioned on top.

At charge equilibrium condition i.e., $V_d = 0$ V, both the drain (D) and source (S) electrodes are at the same potential and the spatial distribution of surface potential (contrast) on MoS₂ flake seems pretty much uniform [**fig. 3.5(a**)], depicting the uniformity of the MoS₂ flake.

The surface potentials within MoS_2 flake close to S and D are invariable which is confirmatory of the fact that current is not flowing when $V_d=0$ V. A slight random variation in surface potential for some areas of MoS_2 flake originates due to the local defect sites, surface adsorbates, and thickness variation¹⁶. Keeping the S grounded [**fig. 3.4**], the V_d is varied from -2 V to +2 V and the corresponding surface potential mapping of the MoS₂ channel is recorded, shown in **fig. 3.5(b)**.



Figure 3.6 Evolution of band alignment and surface electric field along the semiconducting channel with varying applied bias (V_d) ranging from -2 V to +2 V. Variation of (a) surface potential and (b) surface electric field along the channel, marked with blue dotted line in **fig. 3.5**, for different applied bias. (c) The evolution of electric field at MoS₂/Drain and MoS₂/Source interfaces are plotted with varying applied bias.

When $V_d = +0.5$ V, a spatial gradient in contrast to surface potential is visible from S (darker) to D (brighter), which indicates a flow of current between S and D. As V_d is gradually increased from +0.5 V to 2 V, with an interval of 0.5 V, the contrast gradient between S and D is also increased due to increase in the potential difference between S and D indicating the increase in flow of current through MoS₂ channel. Similarly, when the drain is negatively biased, varying from -0.5 V to -2 V, it shows opposite effect in contrast as the corresponding S is at a higher potential than D, resulting in flow of current in opposite direction.

The CPD plots for different bias voltages are shown in fig. 3.6(a) along with the same blue dotted line of fig. 3.5(a) and 3.5(b). At $V_d = 0 V$, the CPD values for D and S are identical, and also there is no potential drop across MoS₂ channel, indicating current is not flowing through MoS_2 channel. When V_d =+0.5 V bias is applied at D, the difference between the CPD values of S and D is ~ 500 mV, which leads to creating a gradient of surface potential at the junction barrier region, resulting in a potential drop of ~ 44 mV along the MoS₂ channel, indicating initiation of current flow within the MoS₂ channel. It is quite evident from fig. 3.6(a) that the net applied potential between S & D majorly drops in two sections of the MoS₂ channel i.e., at the junction barrier and across the MoS₂ flake where maximum voltage drop is observed at the junction barrier due to high contact resistance of MoS_2/Au interface. As we increase the V_d from 0.5 V to 2 V with each step of 0.5 V, the potential drop within MoS_2 channel increases from ~44 mV to ~177 mV [potential drop in MoS_2 is taken along with the black dotted arrows in **fig. 3.6(a)**], leading to increase in current. Similar effect can be observed with negative bias of V_d as well where the potential drop within MoS_2 flake sweeps from ~ -77 mV to ~ -155 mV. Fig. 3.6(b) compares the variation in surface electric field with the change in V_d for different bias voltages where surface electric field is the first-order derivative of surface potential following the equation⁷, $E = -\frac{dV}{dx}$. When D is positively biased, the quasi-fermi level drops at D, creating a continuous gradient of electron occupancy up to S, initiating the diffusion of electrons from S to D. A similar reverse effect can be observed with negative bias. Hence in the case of non-zero V_d , the surface electric field will be unidirectional for both the contacts, as is evident in fig. 3.6(b), which is unlike the case for $V_d = 0 V$. With increasing the bias, the field strength i.e., peak value of electric field curve from fig. 3.6(b), increases gradually for both the polarities of V_d , as depicted in fig. 3.6(c).

The strength of the electric field of the depletion region at D gets boosted from $0.08 \times 10^6 \text{ Vm}^{-1}$ ($\mathbf{V_d} = -0.5 \text{ V}$) to $0.49 \times 10^6 \text{ Vm}^{-1}$ ($\mathbf{V_d} = -2 \text{ V}$) for negatively biased $\mathbf{V_d}$ and remains nearly constant (~ $0.10 \times 10^6 \text{ Vm}^{-1}$) for positively biased $\mathbf{V_d}$ [fig. 3.6(c)]. It is the consequence of the fact that the MoS₂/Au junction is forward biased for positive $\mathbf{V_d}$ and junction is reverse biased when $\mathbf{V_d}$ is negative, certifying the n-type nature of MoS₂ forming Schottky barrier at the junction. Similarly for the depletion region at S, the electric field increases from ~ $0.05 \times 10^6 \text{ Vm}^{-1}$ to ~ $0.31 \times 10^6 \text{ Vm}^{-1}$ with positive $\mathbf{V_d} = +0.5 \text{ V}$ to +2 V (MoS₂/S junction is forward biased) and saturates at ~ $0.17 \times 10^6 \text{ Vm}^{-1}$ for negative $\mathbf{V_d}$ (MoS₂/S junction is reverse biased). The value of $\mathbf{V_d}$, at which the surface electric field of D contact gets saturated is the pinch-off voltage⁷ and is found to be 0.3 V as shown in fig. 3.6(c). The pinch-off voltage is determined by the intersection of two extrapolated straight dotted lines [blue and red line in fig. 3.6(c)].



The band bending due to charge diffusion in the D-MoS₂-S (Au-MoS₂-Au)

Figure 3.7 Schematic of the band alignment along the MoS_2 flake (Au-MoS₂-Au structure) for (a) before and (b) after the contact formation. Band alignment for non-equilibrium condition for (c) Surface potential and (d) corresponding surface electric field profiles along the channel in thermally equilibrium condition, where depletion widths and built-in potentials for MoS_2/D and MoS_2/S interface are identified.

system can be understood easily from the schematics as shown in figs. 3.7(a) and (b) [The band diagram schematics during the biasing is plotted in fig. 3.8]. Fig. 3.7(a) represents the band alignment before MoS_2/Au contact formation whereas fig. 3.7(c) depicts the CPD profile of the suspended MoS_2 at $V_d = 0$ V along the blue dotted line as shown in fig. 3.5(a) and using the CPD profile in absence of applied channel bias work function has been calculated. To calculate the work function of the MoS₂ flake, initially ϕ_t is calibrated on a standard sample (gold electrode in our case) of known work function ($\phi_S = \phi_{Au} = 5.1$ eV), where the CPD for gold electrode is obtained as ~65.30 mV [fig. 3.7(c)] and lead to $\phi_t = 5.03$ eV. In second step, ϕ_{MoS2} is determined from the CPD equation by considering the obtained value of ϕ_t (= 5.03 eV) and calculating the average CPD for MoS₂ flake (i.e., -57 mV) from **fig. 3.7(c)**. The measured ϕ_{MoS2} of the flake is found to be ~ 4.97 eV, which matches well with the previously reported results for multilayer $MoS_2^{29, 30}$. The work function of MoS_2 is found to be ~ 4.97 eV, which is determined through CPD measurements concerning work function of Au (~ 5.1 eV)³¹ [as discussed in section 3.2.5]. The electronic band gap for multilayer MoS_2 is reported as ~ 1.3 eV 32 . Hence, considering the standard value of the electron affinity of MoS₂ i.e., ~ 4.3 eV³³, it can be concluded that the subjected multilayer MoS_2 is n-type in nature and the contact form at MoS₂/Au junctions shows Schottky behavior [fig. 3.7(a)] with barrier height (ϕ_B) ~ 0.80 eV, as per the Schottky-Mott rule ²⁷[Fig. 3.7(b)]. The depletion widths and built-in potential, in equilibrium condition, are experimentally determined, which are found to be $W_D \sim 3.5 \ \mu m$, $\Psi_{bi(D)} \sim 0.116 \ eV$ at MoS₂/D junction and $W_S \sim 1.6$ μ m, $\Psi_{bi(S)}$ ~ 0.104 eV at the MoS₂/S junction, respectively as shown in fig. 3.7(c) [detailed discussion in section 3.4]. In the ideal condition it is theoretically assumed that both the junction have identical barrier configurations, as so far, no standard route was there to locally visualize the band bending. However, in a real scenario, due to various anisotropic conditions of the semiconducting channel and the contact, variations in barrier parameters i.e., depletion width, built-in-potential are inhabitable in separate junctions. Variations in surface potential along the channel and at the junctions in a real device may be attributed due to the thickness (layer number) non-uniformity, presence of adsorbates, surface charges, impurities at the interface, and morphological variation along with the MoS₂ flake, which is not accounted in hypothetical ideal conditions.

The evolution of band bending is also probed in non-equilibrium conditions, i.e., during charge injection (applied bias -2 V to +2 V), and the variation in built-in potential

 (Ψ_{bi}) at both the drain and source junctions are examined [detailed discussion in **fig. 3.9**], demonstrating Schottky behavior of the junctions. **Fig. 3.7(d)** demonstrates the surface electric field for both (source and drain) the interfaces at $V_d = 0 V$, which is obtained by calculating the first-order derivative of the surface potential plot [**fig. 3.7(c)**]. At the MoS₂/Au interfaces, the electrons from the fermi level of MoS₂ will diffuse towards the fermi level of gold to achieve thermal equilibrium [**fig. 3.7(b**)]. Hence, at both the junctions (D and S), the electrons will diffuse from semiconductor (MoS₂) to metal (Au) direction, resulting in the opposite direction of charge flow from the MoS₂ channel to Au, demonstrating opposite polarity in the electric field at D and S junctions [**fig. 3.7(d)**].



Figure 3.8 Evolution band diagrams with the biasing. (a),(b),(c) and (d) represents the energy band alignment when drain is positively biased where (e),(f),(g) and(h) represents the energy band alignment for negatively biased drain.

Schematics of energy band diagrams at different biasing are shown in **fig. 3.8**. As S is kept at ground for all the time, its fermi level of S remains unchanged while the fermi level of D is changing when biasing is applied to D. Fermi level of D drops as positive voltage is applied to D while its fermi level rises as negative voltage is applied to D. Au-MoS₂-Au system has quasi fermi level in non-equilibrium condition. There is spatial

gradient in energy bands of MoS_2 channel which arises due to current flow in the channel and the polarity of the slope of energy band gradient changes as the direction of current flow changes.



Figure 3.9 Variation of potential drop and built-in potential with the applied bias. Evolution of (a) potential drop within MoS_2 channel and (b) built-in-potential at the junctions with the variation in applied bias V_d , confirming the n-type Schottky behavior of the MoS_2 flake.

The evolution of potential drop (magnitude only) with the variation in applied bias along the suspended MoS₂ channel is plotted in **fig. 3.9(a)**, which shows a symmetric linear response with respect to the origin. Such symmetric response of the potential drop confirms that the current is increasing with increasing V_d for both the polarities of V_d. In order to understand the effect of charge carrier injection on the built-in potential (Ψ_{bi}) at MoS₂/Au junctions, the variation of Ψ_{bi} is plotted as a function of V_d [**fig. 3.9(b**)], where the magnitude of Ψ_{bi} is considered. For an instant, due to forward biasing at drain/MoS₂ junction, at V_d = 2 V the Ψ_{bi} increases to ~482 meV as compared to the equilibrium Ψ_{bi} of ~116 meV. Whereas, for reverse bias condition (V_d =-2 V), the Ψ_{bi} at drain/MoS₂ junction increases up to ~1198 meV, which shows nearly four times increment as compared to the forward bias. Such significant enhancement of Ψ_{bi} with varying V_d is observed for both the junctions in reverse bias condition, which confirms that both the Au/MoS₂ junctions behaves as Schottky barrier.

Furthermore, MoS_2/Au interface can be considered as a classical 2D abrupt junction, where the surface electric field can be defined as ^{34, 35,36}

$$\xi(x) \approx \frac{q N_D(x-W)}{\epsilon_{M_0 S_2} \epsilon_0 \rho_{M_0 S_2}} \tag{1}$$

where *q* is unit electronic charge, *W* is the depletion width, N_D is intrinsic doping concentration in n-type MoS₂, $\epsilon_{MoS2} \sim 7.6$ is dielectric constant for multilayer MoS₂ ^[27], ϵ_0 is the permittivity of free space and $\rho_{MoS2} \sim 40$ Å is screening length for MoS₂³⁷. Comparing the slope of experimentally calculated electric field curve at the MoS₂/D interface [**fig. 3.7(d**)] with the slope of electric field in equation (1), we can obtain the doping concentration $N_D \sim 1.32 \times 10^7 cm^{-218}$. The depletion width of MoS₂/Au interface could be analytically derived from the equation (1) as $W \sim \frac{\xi_{max} \epsilon_{MoS2} \epsilon_0 \rho_{MoS2}}{qN_D}$. However, experimentally the depletion width could be accurately measured directly from the CPD profile [**fig. 3.7(d**)].

Table 3.1 compares the key barrier parameters (depletion width and built-in potential), tabulated analytically²⁹, with the experimentally measured values from CPD profile [**fig. 3.7(d**)].

Table 3.1. Comparison between experimental values and analytically calculated values of parameters at MoS_2 /Au interface in thermal equilibrium, where $W_D, \Psi_{bi(D)}, W_S$ and $\Psi_{bi(S)}$ are depletion width and built-in potential for MoS_2/D interface and MoS_2/S interface respectively

Interface	Parameter	Experimentally calculated (EC)	Analytically calculated (AC)	Expression used for analytic calculation	Correction Factor (CF) $CF = \frac{AC}{EC}$
MoS ₂ /D	W _D	$\sim 1.9 \pm 0.9 \ \mu m$	~ 0.69 μm	$W \sim \frac{\xi_{max} \epsilon_{MoS2} \epsilon_{O} \rho_{MoS2}}{q N_D}$	~ 0.4
	$\Psi_{bi(D)}$	~ 0.116± 0.020 eV	~ 0.13 eV	$\Psi_{bi} = \phi_{MoS2} - \phi_{Au}$	~1.1
MoS ₂ /S	W _S	$\sim 1.5 \pm 0.4 \ \mu m$	~ 0.71 μm	$W \sim \frac{\xi_{max} \epsilon_{MoS2} \epsilon_O \rho_{MoS2}}{q N_D}$	~ 0.5
	$\Psi_{bi(S)}$	$\sim 0.106 \pm 0.004$ eV	~ 0.13 eV	$\Psi_{bi} = \phi_{MoS2} - \phi_{Au}$	~1.2

For MoS₂/D side, the depletion width and built-in potential are taken as the average value along different CPD profiles which is discussed in detail in section 3.4 of the chapter. Because of the irragular thickness of MoS₂ flake on Drain side, average values for depletion width and built in potential has been calculated. Ideally, MoS₂ should have identical contact formation at D & S, having uniform material properties throughout the semiconducting channel and the metal contacts. However, in real scenario, contacts are not identical and could have dissimilarities due to multiple reasons such as variation in local defects, contact area, film thickness, etc., and leading to non-uniform charge diffusion. Moreover, non-uniformity in geometry, as well as material properties (thickness, crystallinity, doping, defect states, adsorbates, etc.) of the channel lead to a distinguishable difference between ideal and real device configuration. Interestingly it has been found that for the built-in potential ($\Psi_{bi(D)}$ and $\Psi_{bi(S)}$) for both the experimental and calculated values matches well for MoS₂/S and MoS₂/D interface, while a difference is observed for the depletion width. Unlike depletion width, the built-in potential does not depend on multiple factors rather than the difference in work function of the two materials in contact, and hence demonstrates a very close match in experimental and analytical values. **Table 3.1** introduces correction factors for the analytically calculated depletion width to match with the experimentally measured values, eventually predicting scope for modification of the existing band approximation model.

3.4 Calculation of depletion width

We have repeated the depletion width and built-in potential calculations for a new device. To avoid the misperception, we have labeled the device discussed previous section of the chapter as Device 1 and the new device as Device 2. For Device 1, as D/MoS₂ interface is not homogeneous topographically due to thickness variation [**fig. 3.10(a)**], there is variation of depletion width along different profile lines at the same interface. We have taken potential profile along dotted lines 1,3,4 and 5 [**fig. 3.10(b**)] which are plotted in **fig. 3.10(c)**, (e), (f) and (g) respectively. Considering the surface potential of Drain andMoS₂ uniform, we have calculated the depletion width and average built-in potential for D/MoS₂ interface has been calculated and shown in *Table 3.2*. The standard deviation for depletion width is ~ 0.9 μ m, while the standard deviation for built-in potential is ~ 17 meV.



Figure 3.10 (a) Height image of bridge channel MoS_2 (Device 1). (b) KPFM image bridge channel MoS_2 on Au electrodes at 30 nm lift height. (c), (d), (e), (f), (g), (h) and (i) show the CPD profile along dotted lines marked as 1,2,3,4, 5,6 and 7 respectively in (b).

Table 3.2. Calculation of depletion width and built-in potential at D/MoS_2 interface for Device 1.

Parameter	Point 1	Point 3	Point 4	Point 5	Average	Standard
(D/MoS ₂						Deviation
interface)						
Depletion	~3.5 µm,	~1.7	~1.3 µm	~1.2 µm	~1.9 µm	~ 0.9 µm
width		μm				
Duilt in	145	102	104 moV	116	1167	17 meV
Duiit-iii	~143	~102	$\sim 104 \text{ meV}$	~110	~ 110.7	~ 17 meV
potential	meV	meV		meV	meV	

Parameter	Point 2	Point 6	Point 7	Average	Standard
(S/MoS ₂					Deviation
interface)					
Depletion	~1.6 µm,	~1 µm	~1.9 µm	~1.5 µm	~ 0.37 µm
width					
Built-in	~ 104 meV	~102 meV	~ 111 meV	~105.6 meV	~ 3.8 meV
potential					

Table 3.3. Calculation of depletion width and built-in potential at S/MoS_2 interface for Device 1.

In section 3.3 of the chapter, we have shown the point 1 of D/MoS₂ interface and point 2 of S/MoS₂ interface. While for S/MoS₂ interface topography of MoS₂ flake is uniform therefore we considered the surface potential of Source and MoS₂ uniform and calculated interface parameters i.e., depletion width and built-in potential are ~1.6 μ m and ~104 meV respectively. Similar calculations were carried out for the source side, as shown in **fig.3.10(d), (h), and (i)** where the potential profiles along dotted lines 2, 6, and 7.

3.5 Repetition of experiment with device 2

We have also performed the experiment on another new device (Device 2) to check the interface parameters showing height image and potential image in **fig. 3.11** (a) and **fig 3.11** (b) respectively. The interface parameters depletion width and built-in potential at the D/MoS₂ interface are ~1.6 μ m and 142 meV respectively which are quite close to the parameters of the device we discussed in the section 3.3 of the chapter. Similarly, for the S/MoS₂ interface calculated depletion width and built-in potential is 0.6 μ m and 114 meV respectively. But on source side due to variation in potential (might be due to defect sites) we are getting lower depletion width.



Figure 3.11 (a) Height image of bridge channel MoS_2 (Device 2). (b) KPFM image bridge channel MoS_2 on Au electrodes at 30 nm lift height. (c) and (d) showing the CPD profile along blue dotted lines marked at S and D respectively in the figure. 3.11(b).

3.6 Surface potential of MoS2 with biasing and determination of space charge density

Moreover, the first-order derivative of the built-in electric field [derived from **fig. 3.6(b**) and Equation (1)] provides the information about the space charge density ($\sigma \approx qN_D$ for an abrupt junction)²⁹ at the depletion regions of both the junctions, which is plotted in **fig. 3.12(a)**. In reverse bias condition, at the Schottky barriers, formed at D or S junctions, the metal-semiconductor junction gets widened and the associated barrier electric field i.e., built-in electric field elevates the space charge, which is reflected in the plot; as an increase in σ from ~ -0.14 x10⁻³ Ccm⁻² (V_d = 0 V) to ~ 0.44 x10⁻³ Ccm⁻² (V_d = +2 V) and ~ -0.21 x10⁻³ Ccm⁻² (V_d = 0V) to ~ 0.66 x10⁻³ Ccm⁻² (V_d = -2 V) is noticed at the

depletion region of S (for positive V_d) and D (for negative V_d), respectively. Apart from the MoS₂/Au contact region, a notable variation in surface potential is visible along the MoS₂ channel itself event if with zero applied voltage [**fig. 3.5(a)**], which was further plotted along with the lateral distance in **fig. 3.6(a)**. To investigate the effect of applied bias on the surface potential of MoS₂ channel itself, the evolution of CPD near the center point of the flake [pointed by red dotted line in **fig. 3.6(a)**] are plotted in **fig. 3.12(b)**. The change in surface potential of MoS₂ is not symmetric for both the polarities of V_d, depicting the asymmetric contacts of MoS₂ with S and D.



Figure 3.12 Applied bias dependent evolution of (a) average CPD along the marked red dashed line of MoS_2 channel, shown in Fig. 3.6 (a) and (b). space charge density (σ) at both the drain and source interfaces. The asymmetric nature of the space charge density and CPD plot with respect to the origin confirms the unipolar behavior of the MoS_2 flake.

3.7 Conclusion

Here, the core understanding of charge transport in semiconducting channel, via bottom Au electrodes, is achieved by experimentally probing the band alignment at the interface and within the channel in non-contact mode. Comprehensive analysis of surface potential during the charge transport reveals asymmetric contacts of MoS₂ with S and D and Schottky behavior of the MoS₂/Au interface. From the evolution of surface potential profiles of the MoS₂ for different bias voltage, we have experimentally demonstrated the variations in crucial parameters of MoS₂/Au junction that includes lateral built-in electric field (ξ), lateral built-in potential (Ψ_{bi}), and the space charge density (σ) which are the basic controlling factors of charge diffusion in semiconducting devices. The ability of

probing of electric field, built-in potential, space charge density at the junctions, and its evolution during charge conduction paves a path of benchmarking and optimizing the performance of real devices with ideal ones.

Note

 ✓ Authors and the paper's corresponding author gave their approval for inclusion of this work in present thesis. The corresponding publication is:

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Chapter 4

Nanoscale probing of surface potential landscape at MoS₂/BP van der Waals p-n heterojunction



4.1 Introduction

As per discussion in chapter 1, apart from the contact metal/semiconductor interface, the 2D van der Waals heterostructure interface is another influencing factor in transport properties of van der Waals heterostructure-based devices. In this chapter, we have conducted a detailed analysis of surface potential mapping of the p-n van der Waals heterostructure.

Progress in nanoelectronics demands absolute control over charge transport which can be achieved only by precise measurement of charge diffusion parameters of the conduction channels and junctions. In practice, the junction parameters are tabulated analytically following traditional semi-classical electrostatic theory assuming ideal conditions of the junction where material diffusion, defects, non-uniformity, and local electrostatic interferences are ignored [36]. However, in real conditions, the above-mentioned factors will have a significant influence to perturb the band alignment at the junction which can lead to measurable change in the nature of electron diffusion. Such perturbations in junction parameters will be more prominent for nanoscale junctions where the depletion width is comparable to the channel length, which will have a significant contribution in modulating the charge transport, especially for low-power nanoelectronics devices. Experimental probing of junction parameters has traditionally retained remarkably uncharted territory so far and has been dependent indirectly on charge transport measurements. For macroscale junctions the number of unaccountable variables is larger, however, thanks to the progress in 2D van der Waals heterostructure, a comparatively uniform and less complex junction could be fabricated and could be proven to be an excellent candidate to probe and understand the junction parameters in real conditions. Unlike conventional heterostructures, the lattice match is not a constraint in the case of van der Waals heterostructures thus opening the possibility of heterostructures of any twodimensional materials irrespective of their chemical composition¹. Van der Waal heterostructures with lateral or vertical stacking² and Type I, Type II, and Type III heterostructures based on the band alignments³ are being explored for optoelectronic, valleytronic and photonic applications ⁴⁻⁶. Layered molybdenum sulfide (MoS₂) and black phosphorus (BP) are perhaps the most popular 2D nanomaterials being explored by researchers for electronic applications ^{7, 8}. MoS₂ is n-type semiconductor having high electron mobility and layer number-dependent band gap which varies from 1.2 eV to 1.8 eV as thickness decrease from bulk to monolayer ⁹. Few layers black phosphorene with high carrier mobility is p-type semiconductor having band gap which varies from 0.3 eV for bulk to 2 eV for monolayer ¹⁰. The p-n junction, a basic building component of semiconducting devices, is thus obtained by combining n-type MoS_2 with p-type BP. The formation of p-n junction in 2D MoS_2/BP heterostructure is possible due to weak interlayer Vander Waals forces and the dangling bond free lattice^{11, 12}. The rectifying behavior and lateral built-in potential of van der Waals heterostructures with n-type and p-type constituents have been demonstrated by various researchers ¹³⁻¹⁸. For a heterostructure-based device, the quality of the p-n junction formed at interface of component materials significantly influences its electrical characteristics and performance. Thus, qualitative indepth analysis of the junction at the interface of Vander Waals heterostructure is of paramount importance.

In this chapter, we discussed the depletion region formed at interface of vertically stacked MoS_2/BP junction van der Waals heterostructure. The electrostatic potential distribution across the MoS_2/BP p-n junction was mapped with KPFM at different lift scan heights.

4.2 Experimental details

4.2.1 Synthesis

The optical contrast of two D flakes on PDMS thin film can be used to estimate the thickness of two D flakes $^{19, 20}$. We can control the thickness of the MoS₂/BP heterojunction by selecting



Figure 4.1 Optical images of MoS_2 on PDMS thin film. The less bright region in red square boxes shows the thinner MoS_2 as compared to brighter thick MoS_2 .

the desired thickness of MoS_2 flake on PDMS thin film as shown in **fig. 4.1**. The reason for the different optical contrast of different flakes on a particular substrate is the thickness-dependent refractive index of 2D flakes. Mechanically exfoliated flakes of BP and MoS_2 were transferred onto two different Polydimethylsiloxane (PDMS) thin films. BP flake on PDMS was then transferred onto Au (100 nm thick) coated substrate by applying the mechanical pressure. Using a homemade setup comprising of an optical microscope and linear stage, MoS_2 flake on PDMS was aligned and transferred over BP flake via dry transfer technique as discussed in section 2.1.3 of chapter 2.

4.2.2 Characterization

Preservation of structural integrity of lattice and clean interface is critical to formation of heterojunction/heterostructure by two dissimilar materials and Raman spectroscopy measurements (WITec Alpha 300R confocal Raman microscope, 532 laser line) at MoS₂/BP junctions were carried out to verify the same [**fig. 4.2(b**)]. The Raman spectra of individual MoS₂, BP flakes, and the MoS₂/BP heterostructure are shown in **fig. 4.2(b**).



Figure 4.2 (a) Optical microscopic image of MoS_2/BP heterostructure on Au substrate. (b) Raman modes of vibration of MoS_2 , BP, and MoS_2/BP heterostructure corresponding to red, green and blue spot in optical image. (c) Photoluminescence measurements of pristine MoS_2 (data taken from blue color circle marked in optical image) and MoS_2/BP heterostructure (data taken from red color circle marked in optical image) with 532 nm laser line. (d) AFM topographical image of MoS_2/BP heterostructure. (e) Height profile of MoS_2/BP heterostructure along the pink solid line shown in figure 1(d).

Peaks at 381.4 cm⁻¹ and 406.7 cm⁻¹ represent E_{2g}^{1} (in-plane optical vibration of molybdenum and sulfur atoms) and A_{1g} (out of plane optical vibration of sulfur atoms) Raman active vibrational modes of MoS₂. The frequency difference between these two characteristic Raman modes of MoS_2 is ~25.3 cm⁻¹, which depicts the multilayer nature of MoS_2 flake ²¹. The peaks at A_g^1 at 361.5 cm⁻¹, B_{2g} at 437.7 cm⁻¹, and A_g^2 at 465.4 cm⁻¹ correspond to A_{g}^{1} (out of plane), B_{2g} (in-plane vibration along zigzag direction), and A²_g (in-plane vibration along armchair direction) vibrational modes in black phosphorene, respectively. For black phosphorus, the Raman characteristics peaks are not affected by thickness of flake. Raman fingerprints of MoS₂ and BP at their junction thus confirm the formation of heterostructure [fig. 4.2(b)]. There is also no discernible shift in Raman peaks of MoS₂ and BP at the MoS₂/BP junction, indicating a strain-free heterojunction with fine van der Waals interaction. Further, photoluminescence (PL) spectra show [fig. 4.2(c)] the emission peaks at 685.5 nm and 675.7 nm for MoS₂ and MoS₂/BP heterostructure, respectively. The intensity of photoluminescence from MoS₂/BP heterojunction is lower than intensity of emission from region comprising of MoS₂ alone. The quenching of photoluminescence at the junction interface of MoS₂/BP heterojunction is due to the formation of the built-in field at the interface 22 . The blue shift (~ 25 meV) in PL spectra of MoS₂/BP interface may be attributed to reduced defect states arising due to oxidation, disturbing the electronic band structure ²³. The thickness of van der Waals nanomaterials plays an important role in determining their electronic properties and thus the topography of the MoS₂-BP junction as well as individual flakes was mapped using atomic force microscopy (AFM) of Bruker's multimode 8-HR. AFM tapping mode measurements were conducted in ambient conditions [fig. 4.2(d)] and show largely planar surfaces of BP and MoS₂ and their junction. The thickness profile of BP and MoS₂ is shown in fig. 4.2(e) which is taken along the solid pink line marked in fig. 4.2 (d). The thickness of BP flake is found to be ~60 nm and the thickness of MoS₂ is found to be ~30 nm along the marked line XPS spectra of MoS₂ doesn't show any significant shift in peaks corresponding to Mo $(3d_{3/2})$, Mo $(3d_{5/2})$, and S (2s) after formation of the heterojunction which indicates that Mo and S sites of MoS₂ flake do not form chemical bond with BP and the interaction between MoS₂ and BP in heterostructure is purely van der Waals interaction [fig. 4.3].



Figure 4.3 XPS spectra of MoS₂ and MoS₂/BP van der Waals heterostructures.

4.3 Degradation study of BP



Figure 4.4 (a) AFM topography image of MoS₂/BP heterostructure showing a planar MoS₂-BP heterojunction, (b) Time dependent Raman study of black phosphorene in ambient environment from 0 hour to 24 hours.

Oxidation effects had been thoroughly analysed using AFM and Raman spectroscopy. The AFM topography image, shown in **fig. 4.4** (**a**), was acquired during the KPFM measurements of the MoS₂/BP heterostructure. We observed a smooth image over BP region depicting non-degraded BP flake since the AFM image of degraded BP shows bubble shape droplets. In addition, the time-dependent Raman spectra are also studied which is shown in **fig. 4.4** (**b**). The oxidized layers (if present) will not contribute to the Raman signal and thus a significant decrease in Raman peak intensities would be observed for oxidized BP ²⁴. It is observed that the intensity of Raman modes of BP remains almost constant up to 8 hours of exfoliation.

However, a significant decrease in the peak intensity of Raman modes of BP after 24 hours indicates that the BP flake degrades in the ambient environment. The relative intensity of A_g^1 mode and A_g^2 modes can also be used to gauge the degradation of BP ²⁵. In our case, the relative intensity of A_g^2 mode vs. A_g^1 mode remains the same for up to 8 hours (**fig. 4.4**), demonstrating that the BP flake does not degrade. After 24 hours, a slight decrease in the relative intensity of A_g^2 vs. A_g^1 depicts the degradation of black phosphorene.

4.4 Standard deviation in measuring surface potential



Figure 4.5 (a) Height image and (b-f) Surface potential map of exfoliated HOPG on Au surface. (g) CPD profile along the solid line marked in *fig. 4.5* (b-f) for repetitive measurement.

We have done prior calibration of the AFM conducting probe with the standard *Highly oriented pyrolytic graphite* (HOPG) sample. In order to find the instrument error, we have measured the KPFM on standard HOPG sample exfoliated on Au surface. The **fig. 4.5** depict the height and surface potential map of the HOPG sample on Au surface. The area on HOPG sample where surface potential scans were repetitively taken has been marked in **fig. 4.5**(b-f) with solid line. We conducted five different measurements on the same HOPG sample [**Fig. 4.5** (b-f)] and plotted the CPD profile in **fig. 4.5**(g).

Position in	CPD 1	CPD 2	CPD 3	CPD 4	CPD 5	Standard
Fig.4.5(g)						Deviation
А	~ 98 mV	~ 97 mV	~106 mV	~109 mV	~107 mV	~4.9 mV
В	~89 mV	~90 mV	~ 99mV	~104 mV	~96 mV	~5.6 mV
С	~ 103 mV	~101 mV	~107 mV	~112 mV	~110 mV	~4.2 mV
D	~102 mV	~100 mV	~108 mV	~111 mV	~110 mV	~4.4 mV
Е	~105 mV	~100 mV	~112 mV	~118 mV	~113 mV	~6.3 mV
Average Standard Deviation						~5.08 mV

Table 4.1. Calculation of average standard deviation of CPD for HOPG sample

The CPD values for five different positions on solid line, marked as dashed line in **fig. 4.5(g)**, are used to calculate the instrument error. The CPD values correspond to different positions and measurements as mentioned in **Table 4.1**. We have calculated the standard deviation for each position as mentioned in the **Table 4.1** and the average standard deviation is found to be $\sim 5.08 \text{ mV}$. This value ($\sim 5.08 \text{ mV}$) also falls well within the maximum tolerance value mentioned in the instrument's manual ($\sim 10 \text{ mV}$), which confirms the reproducibility of the KPFM data in our system.

4.5 Result and discussion

Electrical characterization of a heterojunction is necessary if it is to be considered in any kind of electronic applications. The local variations of surface potential at and around heterojunction can be mapped using Kelvin probe force microscopy (KPFM) which is an AFM based advanced tool for surface potential measurements. Since electrostatic forces are known to be long-range forces, when probing electrostatic potential with KPFM, the conducting probe is kept at a specific distance from the sample surface, and this distance is known as lift height. In the KPFM technique, a conductive AFM probe scans the path, followed by a topographical at a specific scan lift height. Lift scan height is an important parameter to probe electrostatic potential distribution and the lateral resolution of the AM-KPFM (Amplitude modulated-KPFM) mode is decided by the lift scan height.



Figure 4.6 (a) Surface potential mapping for MoS_2/BP heterostructure for varying lift heights 15 nm, 20 nm, 40 nm, 80 nm and 100 nm. (b) CPD profile along the marked solid blue line [fig. 4.6(a)] for different lift heights. (c) Lateral electric field at MoS_2/BP junction interface for different lift heights along the solid blue line in fig.4.6(a).

For precise calibration, we performed the surface potential measurements for MoS_2/BP heterostructure for various lift heights of 15 nm, 20 nm, 40 nm, 80 nm, and 100 nm as shown in **fig. 4.6(a)**. AM-KPFM measurements were carried out in ambient conditions with Pt/Cr coated probe. It is clear from **fig. 4.6(a)**. that the potential image is sharpest and well resolved at 15 nm height while resolution decrease as lift height increases. At 100 nm lift scan height, the resolvability of surface potential variations over flakes is not good as for 15 nm lift height. The surface potential profiles at MoS_2/BP junction interface along the marked line for different lift scan height is plotted in **fig. 4.6(b**). The drop in the potential at MoS_2/BP junction is steeper in the case of 15 nm and the drop becomes broader as lift height increases from 20 nm to 100 nm. The transition lateral width in potential from BP to MoS_2 indicates the lateral depletion region

while vertical width depicts the lateral built-in potential at MoS_2/BP junction interface. For 15 nm lift height, depletion width is narrower and built-in potential is maximum while reverse is true for the case of 100 nm lift height. The lateral electric field distribution at MoS_2/BP junction interface can be extracted by taking the first-order derivative of surface potential profiles [**fig. 4.6(c)**]. The electric field plots for various lift heights show that the peak intensity of the electric field at MoS_2/BP junction interface is maximum for lift height of 15 nm and the value of peak electric field intensity decreases with increase in lift height. The area attributed to record surface potential decreases as the distance between tip and sample surface decreases, resulting in better lateral resolution ²⁶. Thus, a lift height of 15 nm is optimum for obtaining a well-resolved surface potential map of MoS_2/BP junction and the corresponding scans are most suitable for further physical analysis of heterostructure.



Figure 4.7 (a) Areal distribution of surface potential for 15 nm lift height. (b) CPD profile along the solid red line marked in fig. 4.6(b) for 15 nm lift height. (c) Schematic diagram of tip-sample electrical circuit in KPFM mode during without contact, with external electrical contact and with applied DC voltage (d) The electric field at MoS_2/BP junction interface along marked solid red line in fig. 4.6(b) for 15 nm lift height.

Fig. 4.7(a) shows the areal distribution of surface potential of MoS_2/BP heterostructure when surface potential is scanned at 15 nm lift height. The peak value of the surface potential distribution ~ 156 mV corresponds to MoS_2 flake on Au substrate while the peak value of ~ 190 mV corresponds to MoS₂/BP heterostructure. A significant peak at ~408 mV represents the surface potential of BP with 60 nm thickness and the peak value at ~462 mV is for ~ 79 nm thick BP. The surface potential values at BP/MoS₂ heterojunction are different from that of BP and MoS₂ which is a confirmatory fact of charge transfer at the interface of junction. The MoS₂ crystal we have used in MoS₂/BP heterostructure formation was n-type in nature while the crystal of BP was p-type in nature. It is quite interesting to inquire p-n junction formed at MoS₂/BP junction interface spatially with the electrostatic potential distribution. Further, the surface potential profile at MoS₂/BP junction interface along the solid line in fig. 4.2(a) (for 15 nm lift height) is plotted in fig. 4.7(b). To determine the exact values of interface parameters for the MoS₂/BP junction heterostructure, the potential profile is fitted with sigmoidal function. In fig. 4.7(b), the lateral distance in the transition of the surface potential of BP to MoS₂ is lateral depletion width at n-type MoS₂ and p-type BP which is found to be ~442 nm. The drop value of potential from BP to MoS_2 is lateral built-in potential which is found to be ~203 meV. The Contact potential difference (CPD) measured by KPFM is basically the difference in the work function of conducting probe and the sample [Fig. **4.7(c)**] and can be calculated using the following equation 27

$$CPD(MoS2) = \frac{(\phi_t - \phi_{MoS2})}{-e}$$
(1)

$$CPD(BP) = \frac{(\phi_{t} - \phi_{BP})}{-e}$$
(2)

Where ϕ_t is work function of tip, ϕ_{MoS2} is work function of MoS₂, ϕ_{BP} is work function of BP and e represents the electronic charge. The relative CPD at MoS₂/BP junction interface is given as

$$\Delta CPD = CPD(MoS2) - CPD(BP) = \frac{(\phi_{MoS2} - \phi_{BP})}{e}$$
(3)

The relative CPD of MoS_2/BP represents the difference in work functions of MoS_2 and BP and hence the difference in fermi level of MoS_2 and BP. The difference in Fermi energy levels of MoS_2 and BP is ~0.196 eV and fermi level equilibration which happens via charge transfer between BP and MoS_2 results in the formation of an in-built electric field. Experimentally, this built-in electric field is a first-order derivative of the surface potential, as shown in **fig. 4.7(d)**, and its magnitude at the MoS_2/BP junction interface is in the order of ~ 10^6 V/m. The slope of electric field distribution reveals the information of doping carrier concentration at MoS_2/BP junction interface. For a classic 2 D abrupt junction, the built-in electric field within depletion region can be defined as²⁸⁻³⁰

$$\xi_{MoS2}(x) \approx \frac{qN_D(x - W_n)}{\epsilon_{MoS2}\epsilon_{O}\rho_{MoS2}}$$
(4)

$$\xi_{BP}(x) \approx -\frac{qN_A(x-W_p)}{\epsilon_{BP}\epsilon_0\rho_{BP}}$$
(5)

where *q* is electronic charge, W_n is the depletion width along MoS₂ side, N_D is intrinsic doping concentration for n-type MoS₂, ϵ_{MoS_2} ~7.6 is dielectric constant for multilayer MoS₂³¹, ϵ_0 is permittivity of free space and ρ_{MoS_2} ~40 Å is screening length for MoS₂³². Similarly, W_p is depletion width along BP side, N_A is intrinsic doping concentration in p-type BP, $\epsilon_{BP} \sim 8.3$ is dielectric constant for multilayer BP ³³ and ρ_{BP} ~23.2 Å is screening length for BP ³⁴. Comparing the first order derivative of equation (4) with the fitted slope of electric field for MoS₂ side shown with solid blue line in **fig. 4.7(d**), the doping carrier concentration for MoS₂ is found to be ~ 7.2 x 10⁸ cm⁻². Similarly, comparing the slope of electric field for BP side shown with solid red line in **fig. 4.7(d**) with the equation (5), N_A is obtained as ~4.4 x 10⁸ cm⁻². Using equation (4) and (5), depletion width for peak value of electric field can be written as³⁵

$$W_{MoS2} \sim \frac{\xi_{max} \epsilon_{MoS2} \epsilon_{O} \rho_{MoS2}}{q N_D} \tag{6}$$

$$W_{BP} \sim \frac{\xi_{max} \epsilon_{BP} \epsilon_O \rho_{BP}}{q N_A} \tag{7}$$

where W_{MoS2} and W_{BP} are depletion widths on MoS₂ and BP sides, respectively. We analytically calculated $W_{MoS2} \sim 185.7$ nm and $W_{BP} \sim 192.5$ nm using equations (6) and (7) respectively. Analytical calculations obtain the total depletion width of $W_{D}=W_{MoS2} + W_{BP} \sim$ 378.2 nm, while experimental measurements obtain depletion width of $W_D \sim 422$ nm. We introduced a correction factor (CF) to match experimentally calculated (EC) depletion width with the analytically calculated (AC) depletion width which is defined as $CF = \frac{AC}{EC}$. The value of correction factor is determined as ~ 0.8. The difference between analytically calculated and experimentally calculated depletion widths is mainly owing to the environmental effects, defect states and van der Waals gap between the individual layers of MoS₂ and BP, as well as between MoS₂ and BP. These calculations were performed for the solid red line mark in **fig. 4.6(a)**, however the calculated parameters will differ slightly depending on the thickness of BP or MoS₂.



Figure 4.8 (a) Height profile of MoS_2 along pink dotted line in fig. 4.2(d) and (b) the corresponding potential profile along the same line from fig. 4.6(a) for 15 nm lift height. (c) Thickness profile for MoS_2 along wine dotted line in fig. 4.2(d) and (d) Built in potential for the same (e) Height profile for MoS_2 along red dotted line in fig. 4.2(d) and (f) corresponding potential profile. (g) Built in electric field at MoS_2/BP junction interface with varying MoS_2 thickness.

The thickness dependence of built-in potential at MoS₂/BP junction is examined by plotting the variation of CPD for various thickness profiles of MoS₂ on fixed thickness of BP [fig. 4.8 (a-f)]. It is observed that built in potential is 0.16 eV for 16 nm MoS₂ while for 35 nm MoS₂ it is 0.22 eV. For higher thickness, i.e., for 65 nm thick MoS₂ flake, the built-in potential is 0.23 eV confirming no significant variation in built in potential. Furthermore, the effect of MoS₂ flake thickness on built-in electric field is determined. The strength of built-in electric field at MoS₂/BP junction at the interface increases with the increase in thickness of MoS_2 as depicted in fig. 4.8(g). Fermi level of MoS_2 varies with the variation in the thickness while the fermi level of BP is same for 60 nm thickness. The difference in the fermi levels of MoS₂ and BP is increases as thickness of MoS₂ is increasing resulting in the greater charge transfer across the junction hence an increase in built-in electric field with the MoS₂ thickness. The work function of MoS₂ significantly depends on thickness of MoS_2 flake ³⁶ which attributes to the change in built-in potential and built-in electric field at MoS₂/BP p-n junction at the interface. While the work function of BP is almost constant for ~60 nm thickness. The difference in the fermi levels of MoS₂ and BP increases as thickness of MoS₂ increases resulting in the greater charge transfer across junction and hence an increase in built-in electric field with MoS₂ thickness. Study and quantification of the dependence of built-in potential and built-in electric field on layer number is essential for designing futuristic devices based on $2D MoS_2/BP$ heterostructures.

4.6 Reproducibility of the results

We also performed KPFM measurements on another MoS_2/BP heterostructure on a different AFM system (asylum research MFP3D), and the changes in built-in potential for MoS_2/BP heterostructures with the thickness of MoS_2 are reproducible [fig. 4.9].



Figure 4.9 (a) Height image and (b) Surface potential map of MoS2/BP heterostructure on Au substrate. (c) Thickness profile of BP along the solid red color line marked in fig.4.9 (a). (d) Thickness profile of MoS_2 along the solid green color line marked in fig.4.9 (a). (e) Thickness profile of MoS_2 along the solid green line marked in fig.4.9 (a). (f) CPD profile along the solid magenta color line marked in fig.4.9 (b). (g) CPD profile along the solid purple color line marked in fig.4.9 (b).

To validates our experimental findings, we have done DFT simulations for work function calculations at MoS_2/BP interface. The DFT calculations have been performed using the PAW potential³⁷ and PBE-GGA exchange correlation functional ³⁸, as implemented in VASP ^{39, 40}. The structures were fully relaxed and optimized using an 8 x 1 x 1 k-point grid in the Monkhorst pack sampling scheme. Charge density and potential calculations were performed using a denser 15 x 2 x 1 k-point mesh for higher accuracy. The energy cut off of 500 eV was used for the expansion of wavefunctions. The convergence criteria for electronic and ionic relaxations have been set to 10^{-6} eV and 10^{-2} eV, respectively, for differences in total energy between successive iterations in self-consistent field cycles. A vacuum thickness of >15 Å

was used to avoid interaction between periodic images. The DFT-D2 van der Waals (vdW) dispersion correction⁴¹ was used to consider vdW interactions between the layers.



4.7 DFT Calculations

Figure 4.10 (a) Top view of MoS_2 layers stacked over phosphorene; (b), (c) and (d) Side view of n MoS_2 layers stacked over phosphorene, n varies from 1 to 3, respectively.

Three structures consisting of n layers of MoS_2 stacked over a single layer of phosphorene have been considered chapter, where n=1-3, as shown in **fig. 4.10**. Supercells comprising of 1×4 rectangular unit cells of phosphorene stacked over 1×5 of rectangular unit cells of MoS_2 rotated by 90° were constructed in order to minimize the lattice mismatch between MoS_2 and BP. Such an approach has been adopted in an earlier study⁴². The optimized interlayer distance between MoS_2 and phosphorene layers is 3.3 Å, while that between MoS_2 layers is 3.7 Å. The optimized lattice constants and bond lengths are provided in Table 4.2 below.

vdW	Lattice	Lattice	Bond-	Bond-	Work	Band gap
heterostructure	constant	constant	length	length	Function	(eV)
	а	b	P-P	Mo-S	(eV)	
	(Å)	(Å)	(Å)	(Å)		
Phosphorene	3.30	23.12	2.22,	N.A.	4.75	0.90
single layer			2.26			
(BP)						
MoS ₂	3.18	22.06	N.A.	2.41	5.56	1.67
BP+1-layer	3.25	22.2	2.21,	2.41-	4.67	0.45
MoS_2			2.25	2.42		
BP+2-layer	3.23	22.15	2.20,	2.41-	4.60	0.50
MoS_2			2.25	2.42		
BP+3-layer	3.22	22.13	2.20,	2.41-	4.61	0.53
MoS_2			2.25	2.42		

Table 4.2. Different parameters tabulated for different thicknesses (N.A. stands for not applicable)

The work function is found to decrease with the increase in the number of MoS_2 layers and is almost constant as we go from two MoS_2 layers to three MoS_2 layers. This trend is consistent with and in agreement with the experimental results.



Figure 4.11 Planar average electrostatic potential with respect to absolute vacuum shown for the three studied systems.

Difference in electrostatic potential between MoS₂ and phosphorene induces dipoles and hence, polarization at the MoS₂/BP interface, which leads to an out-of-plane electric field, as shown in **fig. 4.11**. The out-of-plane electric field calculated from the negative gradient of the planar average electrostatic potential, $E_z \approx -\frac{\varphi_{top-layer}-\varphi_{bottom-layer}}{d_{top-layer}-d_{bottom-layer}} \approx -\frac{\delta\varphi}{\delta d}$, as depicted in **fig. 4.11**, is provided in **Table 4.3**. E_z drops with the number of MoS₂ layers.

Table 4.3. Theoretical Calculation of Out-of-plane Electric field at MoS₂/BP interface

vdW heterostructure	Out-of-plane Electric field		
	(V/Å)		
Phosphorene single layer	0		
(BP)			
MoS_2	0		
BP+1-layer MoS ₂	0.22		
BP+2-layer MoS ₂	0.11		
BP+3-layer MoS ₂	0.07		

The band gap of the three systems investigated is also listed in **Table 4.2**. The band structure of MoS_2 monolayer on top of a single layer of phosphorene is in accord with the previous report ⁴². The band gap of MoS_2/BP vdW heterostructures has been found to increase with the number of MoS_2 layers in the heterostructure. All the three studied vdW heterostructures show indirect band gap, as visible in the band structure plots provided in **Fig. 4.12**. The type II band alignment, as found in the band structure, indicates a n-MoS₂/p-BP junction, which arises at the interface of MoS_2 and BP.



Figure 4.12 (a), (b) and (c)Atom projected band structure of $n-MoS_2/p-BP$ heterostructure with the number of MoS_2 layers varying from 1 to 3, respectively.

4.8 Conclusion

We have given an experimental visualization of the potential landscape of the 2D p–n junction of MoS_2/BP van der Waals heterostructure at a real condition by using KPFM. The width of the depletion region formed at real condition is compared with the analytically calculated values generally assumed for ideal condition. The spatial accuracy of surface potential variations at junction is found to be lift scan height dependent and width of depletion region is best resolved with lift scan height of 15 nm. By deducing the parameters like lateral built-in potential and built-in electric field from surface potential maps, we have determined the depletion width of MoS_2/BP p-n junction with nanoscale precision. The magnitude of both of these parameters at junction is shown to be positively correlated with thickness of MoS_2 . The engineering and characterization of depletion region of van der Waals heterojunctions with nanoscale precision are important from perspective of designing 2D electronic devices with controlled charge transport.

Note

✓ Authors and the paper's corresponding author gave their approval for inclusion of this work in present thesis. The corresponding publication is:

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Chapter 5

Tuning the photoluminescence in twisted MoS₂



5.1 Introduction

Irrespective of contact metal/semiconductor interface and van der Waals heterostructure's interface, the electronic and optical band structure can be changed by twisting two flakes of the same 2D material (as conferred in chapter 1) which we have deliberated in this chapter.

Twistronics is a newly emerging discipline that allows 2D materials to modify their electronic band structure by twisting them at specific angle relative to each other. Twisting, which offers an impurity-free single-material platform and introduces a new degree of flexibility to the system (i.e., twist-angle), has irreplaceable advantages over other methods for altering the electrical band structure of 2D materials¹⁻³. Creation of Moiré superlattice and modified Moiré bands in two-dimensional systems including twisted bilayer graphene (TBG)⁴⁻⁷, twisted bilayer transition metal dichalcogenides (TBTMDs)⁸⁻¹⁰, and twisted bilayer phosphorene^{11, 12}, exhibit unique and tuneable features. In 2018, this field gained attention due to the discovery of superconductivity in the twisted bilayer graphene for the twist angle of 1.1 degree and the angle is known as magic angle¹³. When compared to TBGs with various twist angles, the magic-angle TBG (MATBG) stands out due to its distinctive flat bands and resistance to atomic and electronic reconstruction at 1.1°, which preserves its strongly correlated states¹⁴. Following this, twistronics has been extended to multilayer systems, starting with twist-angle disorder in twisted bilayer-twisted graphene (TBG)¹⁵, and moving on to superconductivity in twisted trilayer graphene (TBBG)¹⁶ and tunable correlated states in twisted bilayer-bilayer graphene (TBBG)¹⁷.

After twisted graphene, the electronic properties of twisted TBTMDs have also been explored¹⁸. Similar to TBG, correlated states and flat bands¹⁹ were also identified recently in the TBTMDs structures, that might result in topological insulator phases²⁰, Mott-like insulator states²¹, and superconductor states²², showing that the novel physical characteristics like magic angle TBG nearly recur in TBTMDs.

The various applications in electronic and optoelectronic devices, such as rectifying and optical response, have come under increasing scrutiny as research into modification in electronic structure, interlayer coupling, and excitonic properties in twisted 2D systems has advanced. The expression for optoelectrical characteristics and interlayer coupling strength controlled by twisting was demonstrated by Choi et al. in 2019²³. Additionally, they discovered that stacking MoSe₂ and WSe₂ vertically at twist angles of 15° and 30° would significantly affect the interlayer coupling in 2D semiconductors and subsequently make it more difficult for carriers to cross the heterostructure, suggesting the creation of an

equivalent transport potential barrier between two layers. However, the bandgap is widened as a result of the decreased interlayer coupling strength and the ensuring transport potential barrier, which increases spectrum responsiveness and external quantum efficiency. Although there was no natural interlayer work function difference in homojunctions like a 30° twisted MoS_2 bilayer, Liao et al. discovered that it had improved rectification properties with large on/off ratio of 10^8 an order of magnitude larger than the untwisted sample which they attributed to the higher on-current²⁴. In order to optimise the transport property of twisted TMDs, twist-angle driven interlayer coupling strength would therefore be a key access that needs more study.

In this chapter, we have utilized CVD technique to synthesized twisted MoS_2/MoS_2 interface. The surface KPFM and EFM studies have been conducted to inquire the effect of twist on surface electrostatic properties. Furthermore, optical characterization such as PL and reflectance spectroscopy performed at room temperature to investigate the impact of twist.

5.2 Experimental details

5.2.1 Synthesis

 MoO_3 and sulphur powder were used as precursors during the one-zone CVD process to create MoS_2 hexagons on a 300 nm SiO₂ substrate at 800 °C in an inert argon environment (as described in section 2.1.2 of chapter 2). For the CVD process, a MoO_3 to sulphur power ratio of 0.3: 3 was used. The gap between MoO_3 and sulphur power was maintained at 20 centimetres. The Ar gas flow was kept at 100 sccm.

5.2.2 Characterization

5.2.2.1 Optical microscope, Raman and FESEM characterization

The CVD grown hexagonal MoS_2/MoS_2 interface is primarily characterized by optical microscope. **Fig. 5.1(a)** is showing the optical image of the CVD-grown twisted MoS_2/MoS_2 interface taken at 100X resolution. To calculate the exact twist angle, the FESEM (Field Emission Scanning Electron Microscopy) measurements have been conducted on the MoS_2/MoS_2 homostructure which is shown in **fig. 5.1(b)**. The tilt angle between two hexagonal MoS_2 flakes is found to be ~6.7 degrees. Raman microscopy is then used to characterise the created homo-structure. The observations were performed using a WITEC alpha 300R Raman spectrometer outfitted with a 532 nm Nd-YAG laser with a 1 μ m spot size.

The Raman spectra of the three regions identified as 1, 2, and 3 in **Fig. 5.1(a)** are shown in **Fig. 5.1(c)**, and two Raman active modes have been identified: E_{2g}^1 (in-plane optical vibration of Mo and Sulfur atoms) at 380.07 cm⁻¹ and A_{1g} (out-of-plane optical vibration of Sulfur atoms) at 406.91 cm⁻¹. It is discovered that the two Raman mode characteristics have a frequency difference of 26.84 cm⁻¹, confirming the multilayer structure of MoS₂ hexagons. We didn't observe a significant shift in Raman modes at the twisted interface.



Figure 5.1 (a) Optical image of CVD grown twisted MoS_2 in a hexagonal shape. (b) FESEM image of twisted MoS_2 . (c)Raman characterization of twisted MoS_2 at three regions.

5.2.2.2 AFM characterization

To check the morphology at the nanoscale, the tapping mode AFM measurements have been done in ambient environment with BRUKER Multimode 8 AFM and Cr/Pt conductive coating probe which is shown in **fig. 5.2(a)**. The thickness profile along the hexagon MoS_2 and along the interface are shown in **fig. 5.2(b-d)** corresponding to blue, green and red line marked in **fig. 5.2(a)**. The thickness for individual hexagon is observed ~7.6 nm and 7 nm and the thickness at the interface is found to be ~ 14.5 nm. The thickness of the interface is approximately equal to the sum of thickness of individual hexagon flakes which confirm the formation of interface.



Figure 5.2 (*a*) *AFM image of CVD grown twisted MoS2 in hexagonal shape.* (*b*), (*c*) *and* (*d*) *representing thickness corresponding to three different regions marked in figure* 5.2(*a*).

5.3 Result and discussion

5.3.1 Surface potential and electrostatic forces exerted on surface charges

In order to study to electrostatic properties of twisted MoS_2 , the KPFM and EFM measurements has been conducted. **Fig. 5.3** (a) is showing the KPFM scan for twisted MoS_2 captured at 20 nm lift height with Cr/Pt conducting probe. The surface potential contrast is quit uniform depicting the uniform charge distribution over the MoS_2 flakes. The surface contrast between two hexagonal flakes is observed ~50 mV depicting the work function difference between two flakes which arises due to the little bit difference between the thickness of both the hexagons²⁵ [**fig. 5.2(b**) and **fig. 5.2(d**)].



Figure 5.3 (a) *KPFM image of twisted* MoS_2/MoS_2 *interface at 20 nm lift height. (b),* (c) and (d) representing EFM images at $V_t=0$ V, 1 V and -1 V respectively

We didn't observe the significant difference of surface potential between twisted region (region 2) and untwisted region (region 1). Electrostatic force Microscopy (EFM) is performed to investigate further electrostatic properties of MoS_2/MoS_2 twisted homostructure for lift height 20 nm. In EFM mode, the resonance frequency peak gets shifted according to the nature of force excreting on the sample by biased tip which can be clearly observed in the electrical phase image. Dark phase-contrast originates when the electrostatic force between tip and sample is attractive while bright phase-contrast depicts

the repulsive force between the conductive biased tip and the sample²⁶. The EFM phase scans at zero tip voltage is shown in **fig. 5.3(b)**. As expected, at zero tip biasing the phase contrast of MoS_2 flake and SiO_2 substrate is not distinguishable. However, the contrast of phase image at 1 V is clearly distinguish MoS_2/MoS_2 flakes from that of the substate [**fig. 5.3(c)**] and this contrast found to be flipped when -1 V is applied to the conducting probe [**fig. 5.3(d)**]. For 1 V tip voltage, the electrostatic charges in MoS_2/MoS_2 flakes are experiencing attractive forces (bright contrast of MoS_2 w.r.t. SiO_2 substrate) while for -1 V tip voltage, the electrostatic charges are repulsive forces (Dark contrast of MoS_2 w.r.t. SiO_2 substrate) depicting the dominant nature of coulombic interaction of the surface charges. However, the we didn't find the difference in electrostatic properties of MoS_2 flake's twisted and untwisted region.

5.3.2 Optical band gap shift and spin orbit coupling determination

Twistronics mainly effect the band structure of the material. To figure out the variation in the optical band gap the Photoluminescence (PL) measurements are carried out at the three different region 1, 2, and, 3 as marked in **fig. 5.1(a)**. **Fig. 5.4(a)** is showing the PL spectra for three regions and we observed blue shift in band gap at twisted interface.



Figure 5.4 (a) PL measurements for three different regions for MoS_2 . (b), (c) and (d) representing deconvoluted PL for corresponding to three different regions marked in fig. 5.1(a).

This shift cannot be due to the increase in the thickness at the interface, because in MoS_2 PL gets red shifted if thickness increases²⁷. In our case blue shift in PL spectra with increasing thickness is evident that the blue shift is due to twistronic property. For the core understanding of blue shift in optical band gap, we further deconvoluted the PL spectra for three region which are shown in **fig. 5.4(b-d)**. The deconvoluted PL spectra quantify the quasi particle associated with photo response of MoS_2 which are A exciton, B exciton, and T trion respectively. In **fig. 5.4(b-d)**, peak area filled with green color represents B exciton, the peak area filled with orange color is A exciton, and the peak area with blue color is trion T. The relative intensity of A exciton and trion T is almost similar in region 1 and region 3, while for region 2 the intensity of trion decreases and the intensity of A exciton increases. Possibly the trions are getting converted into A exciton at the interface due to the interlayer coupling between two hexagonal MoS_2 flakes. The schematic with twist angle is shown in **fig. 5.5.**



Figure 5.5 The schematic representation of crystal structure and morphological view of twisted MoS₂ flakes.

To determine the strength of interlayer coupling, we have calculated spin orbit coupling energy (i.e., the difference of energy of A exciton and B exciton) for different three regions as shown in **table 5.1**. The spin-orbit coupling energy for region 1, and region 3 is found to be ~0.126 eV, and ~0.124 eV respectively which are nearly comparable. The value of spin-orbit coupling energy for region 2 i.e., for the twisted interface is found to be 0.145 eV which is significantly larger than the same for region 1 and region 2 as shown in **table 5.1**. Enlarged spin-orbit coupling at the twisted interface depicts the strong interlayer coupling. Moreover, the PL energy shift from untwisted (3 and 1 region) to twisted region (2 region) for A exciton, B exciton and trion T is 8.9 meV, 28.4 meV, 9.7 meV respectively. We observed that B exciton is highly sensitive to the twistronic as compare to A exciton and Trion.

Regions	A (nm)	B (nm)	T (nm)	spin orbit coupling	
				energy [A-B] (eV)	
3	685.153	640.557	701.711	0.126	
1	684.759	641.032	701.172	0.124	
2	681.669	631.294	697.857	0.145	

Table 5.1 Shift in the A, B, and, T due to twistronic and spin-orbit coupling energy calculations.

5.3.3 Optical white light reflectance spectroscopy measurements

Fig. 5.5 (a) is depicting the reflectance mapping of the twisted MoS_2 . In mapping image, it is clearly visible that reflectance intensity at twisted interface is higher. The reflectance contrast is uniform for both the MoS_2 flakes for non-twisted region (shown in light blue color) and for twisted region the white color contrast is also even. The corresponding reflectance spectra for three regions are shown in **fig. 5.5(b)**. The peak for B exciton is obtained at ~ 629 nm for the untwisted region and for twisted region it is observed at ~678 nm for untwisted region and ~677 nm for twisted region. We observed the slight blue shift in reflectance spectra of B exciton at the twisted region.



Figure 5.5 (a) Reflectance mapping for the MoS_2/MoS_2 twisted sample at 626 nm. (b) reflectance spectra corresponding three different regions marked in *fig. 5.5 (a)*.

It is well known that Excitonic peaks for MoS_2 in reflectance spectra are thickness dependent. As thickness of MoS_2 flake increases the A excitonic peak gets red shifted. In case of B excitonic peak the peak doesn't show any significant shift in reflectance
spectra²⁸. However, in our case the, the thickness of interface is almost double the thickness of single hexagon but reflectance peak of B exciton and A exciton for thicker part i.e, twisted interface are blue shifted. The blue shift might be contributed due to twist at the interface.

5.4 Conclusion

Here, we have synthesized MoS_2/MoS_2 twisted homostructure with 6.7-degree twist angle in hexagon morphology using CVD method. The surface electrostatic properties are independent of twist angle while blue shift in PL is found at twisted interface might be due to increase in spin orbit coupling. The PL peak energy shift in B exciton is prominent as compare to A exciton and trion. The slight bule shift of B exciton and A exciton at twisted interface in case of reflectance spectra might attributes to the twistronic.

Note

✓ This manuscript is under preparation

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Chapter 6

Influence of hexagon morphological shape on excitonic properties of MoS₂



6.1 Introduction

Apart from the contact metal/ 2D semiconductor interface and 2D/2D van der Waals interface (as discussed in chapter 1), the morphological shape of 2D channel material also influences the electrical and optical properties of the FET devices which we have discussed in this chapter.

Morphological shape has a significant impact on the optoelectronics properties of twodimensional materials^{1, 2}. Mechanical exfoliation of the 2D material prevents the material from obtaining the desired morphological shape. However, we can control the morphological shape using Chemical Vapor Deposition (CVD) method^{3, 4}. The most favorable morphological shape of two-dimensional materials synthesized by CVD technique is a triangular shape due to the least energy vital for the creation. However, by altering the growth parameters of the CVD reaction or with the choice of substrate on which sample grows, the morphological geometries of two-dimensional materials other than triangular ones have been demonstrated⁵⁻⁷. The triangular and hexagonal shapes were found to be more stable due to minimum surface free energy following Wulf construction⁸⁻¹⁰. Theoretical studies show that by modifying the chemical potential through edge state control, a variety of catalytic activities as well as requisite electronic and magnetic properties are possible for 2D materials¹¹⁻¹³. By modulating the morphological shape, even the basal plane of CVD grown MoS₂ hexagon becomes activate for hydrogen evolution reaction¹⁴. Most findings yet have focused on the synthesis aspect, leaving plenty of room to investigate the electrical and optical properties of various morphological shapes of two-dimensional materials.

Due to the monolayer's 2D structure and the environment's poor dielectric screening, the Coulomb interaction is amplified significantly in 2D materials. This leads to the creation of bound electron-hole pairs, or excitons, which dominate the optical properties of semiconducting 2D materials¹⁵⁻¹⁸. Excitons further lower down their energies by capturing an electron (negative trion) or hole (positive trion) and forming another quasi particle called charged excitons or trion. These excitons play a crucial role in optically controlled valleytronic devices based on 2D materials¹⁹. MoS₂ has a high electron mobility and superior optical response, making it one of the most studied 2D materials²⁰⁻²⁴. In MoS₂, the valence band split due to strong spin orbit coupling, forming two excitons known as A exciton (lower energy) and B exciton (high energy)

whereas A exciton peak is associated with negatively charged trion. Experimentally, these excitons can be detected with PL emission spectroscopy. Due to high binding energy of these exciton in 2D MoS₂, these are observable at room temperature. While, the trion having low binding energy and are rarely observed at room temperature. To understand the dynamics of exciton in MoS₂ and other 2D materials, the temperature dependent PL studies has been done²⁵⁻²⁹. Recent studies showed that the temperature-dependent excitonic dynamics for MoS₂ is morphological shape-dependent¹. However, excitonic dynamics in the complete hexagonal shape of MoS₂ is not explored till now.

In this chapter, we synthesized a few-layer 2D hexagon MoS_2 flake utilizing the CVD technique. We further did the temperature-dependent photoluminescence measurements for hexagonal MoS_2 flake. The motive of our work is to inquire about morphological shape dependent excitonic dynamics for CVD-grown hexagonal MoS_2 flake.

6.2 Experimental details

6.2.1 Synthesis

 MoS_2 hexagons were synthesized in one-zone CVD system (as discussed in section 2.1.2 of chapter 2) on 300 nm SiO₂ substrate using the precursors MoO₃ and Sulphur powder at 800 °C in an inert argon environment. The ratio of MoO₃ to sulfur power was taken as 0.3: 3 for the CVD reaction. The distance between MoO₃ to sulfur power was kept 20 cm.

6.2.2 Characterization

MoS₂ hexagons were grown over large area with sharp and equilateral edges as depicted in the optical microscopic image in **fig. 6.1(a)**. To characterize the CVD synthesized MoS₂ hexagon, Raman spectroscopy measurements were carried out using a WITEC alpha 300R Raman spectrometer equipped with a 532 nm Nd-YAG laser with a 1 μ m spot size. **fig. 6.1(b)** depicts the Raman spectra of MoS₂ flake's basal plane, with two Raman active modes observed: E¹_{2g} (in-plane optical vibration of Mo and Sulphur atoms) at 380.07 cm⁻¹ and A_{1g} (out-of-plane optical vibration of Sulphur atoms) at 406.91 cm⁻¹. The frequency difference between the two Raman mode characteristics is found to be 26.84 cm⁻¹, confirming the multilayer nature of MoS₂ hexagons. The vibrational mode E¹_{2g} is found to be blue-shifted for the edges of MoS₂ hexagon. The MoS2 hexagon's uniform contrast in the Raman mapping image shows a uniform areal distribution of vibrational modes [**fig. 6.1(c)**].



Figure 6.1 (a) Optical image of CVD grown multilayer MoS_2 . (b) Raman vibrational modes for hexagonal MoS_2 . (c) Raman mapping image over whole hexagon MoS_2 flake. (d) PL mapping to check the optical band gap over whole area. (e) AFM topographical image of MoS_2 for morphological map.

The thickness and surface morphology of the MoS_2 flake were examined using tapping mode configuration with BRUKER Multimode 8 AFM and Cr/Pt conductive coating probe is used for AFM measurements. The thickness of multilayer MoS_2 has been determined to be ~6 nm indicating 9 layers of MoS_2 [**fig. 6.1(e)**]. All edges of MoS_2 were found to ~3 µm showing highly symmetric morphological shape. To check the distribution of the optical band gap the over the entire flake, the PL mapping of the hexagon was performed in the ambient condition which is shown in **Fig. 6.1(d)**. Optical band gap is almost uniform over the region of MoS_2 hexagon. The Raman and PL mapping were done at 100x objective with 3 mW laser power in ambient environment.

6.3 Results and Discussion



Figure 6.2. (a) *Temperature dependent PL mapping of CVD grown* MoS_2 . (b)-(g) *shows the deconvoluted PL spectra for* MoS_2 *hexagon at different temperatures where* A, B and T *represents the A exciton, B exciton and trion respectively.*

To examine the low temperature PL behaviour, the MoS_2 hexagon were kept in~10⁻³ mbar vacuum on a cryogenic stage. The low-temperature PL measurements were taken at 50x objective with 3 mW laser power. Fig. 6.2(a) is showing the red shift in PL spectra as temperature increased from 93 K to 293 K. The reason for red shift with increasing temperature is in-plane lattice constant's thermal expansion, phononphonon interaction, enhanced electron-phonon interaction, and slight distinction in the bond length³⁰. The overall decrease in PL intensity with increasing temperature is observed which attributes to the activation of non-radiative transitions due to increase in electron-phonon coupling³¹. To probe the dynamics of exciton and charged excitons, the temperature-dependent PL spectra is deconvoluted as shown in fig. 6.2(b-g). All peaks are Lorentzian fitted and normalized w.r.t B exciton because we didn't observe the significant change in intensity of B exciton with the temperature. The change in the shape of PL spectra has been observed as temperature decreases from 293 K to 93 K due to the increase in the population of trions. In deconvoluted PL spectra light green color line corresponds to the A exciton, the magenta color line corresponds to the B exciton and, the blue color line corresponds to the trions, T respectively. The binding energy of trions is much lower as compare to A and B exciton, making trions thermally less stable hence more thermal quenching at high temperatures.

6.3.1 Determination of carrier concentration



Figure 6.3. (*a*) *Effect of temperature on the intensities of A, B, and T.* (*b*) *logarithm of ratio of trion to exciton intensity with the temperature inverse.*

Fig. 6.3 (a) is showing the temperature dependent intensities of A exciton and trions which are normalized w.r.t. intensity of B exciton. The measured intensity dynamics with temperature indicates the non-thermodynamical equilibrium of exciton and trions populations³². At low-temperature increase in PL intensity is mainly dominated by the trion populations due to low electron-phonon coupling. As trions are thermally less stable therefore dissociating into A excitons as temperature increases from 93 K to 293 K. The fact that there is no substantial change in the ratio of PL intensities of B exciton to A exciton indicates that the quality of MoS₂ is not affected by temperature. From Boltzmann distribution function, the expression for temperature dependent ratio of trion intensity to exciton intensity is given as¹

$$\ln\left[\frac{I_T}{I_A}T^{-1/2}\right] = \ln\left[Mk_B^{1/2}\right] + \frac{E_T(E_C - E_F)}{k_B T}$$
(1)

where $M = \frac{Y_T}{Y_A} \frac{m_T (2\pi m_e)^{1/2}}{4hm_A}$, Y_T and Y_A defines the radiative decay rates of trions and A exciton respectively, m_A and m_T are total masses of A exciton and trion while m_e representing the effective mass of electron. I_T is intensity of trion, I_A is intensity of A exciton, E_T is binding energy of trion at room temperature which we consider as 32 meV³³, $E_C - E_F$ is the fermi energy of electrons, k_B is the Boltzmann constant, M is constant, and T is temperature. We have plotted the experimental data of **fig. 6.3(b)** using equation (1). We determined the fermi energy from the fitting parameter as 31 meV. The expression for electron concentration is given as

$$n_e = N_C e^{-\left(\frac{E_C - E_F}{k_B T}\right)}$$

$$N_C = 2 \left(2\pi m_e \frac{k_B T}{h^2}\right)^{3/2}$$
(2)

where

 $m_e = 0.48 m_o^{34}$, m_o is rest mass of electron and h is plank's constant. Considering the fermi energy as 31 meV as we obtained from fitted data of **fig. 6.3(b)**, we have calculated the carrier concentration $n_e \sim 1.52 \times 10^{12}$ cm⁻² using equation (2), which is order of carrier concentration of monolayer MoS₂ found for other morphology.

6.3.2 Determination of electron -phonon strength



Figure 6.4. (a) *Temperature-dependent peak energy shift for PL emission of A, B, and T. (b) Temperature-dependent valance band splitting for MoS*₂ *hexagon. (c) Broadening of the line width of A, B, and T with the temperature.*

Fig. 6.4(a) is showing the peak position of PL energies of A, B, and T w.r.t temperature. We found that energies of A, B, and T are getting red-shifted with the temperature as expected. Furthermore, the expression for temperature-dependent band gap for excitons is given as

$$E_X(T) = E_X^0 - S < \hbar\omega > [\operatorname{coth}(<\hbar\omega > /2 k_B T) - 1]$$
(3)

Where $E_X(T)$ is the peak energy of exciton at temperature T, E_X^0 is the peak energy of exciton at 0 K temperature, S is the dimensionless electron/exciton coupling constant, $\langle \hbar \omega \rangle$ is average energy of the phonon contributing to the temperature change of exciton energy, and k_B is Boltzmann constant. The experimental data for peak energy shift for A, B and T are fitted using equation (3). The fitting parameters are shown in **Table 6.1**.

The red shift in A, B, and T energies attributes to the in-plane lattice constant's expansion with an increase in temperature, enhancement in electron-phonon interaction, and phonon-phonon interaction^{30, 35}. The energy at zero temperature for A, B and T is found to be 1.91 eV, 2.04 eV, and 1.88 eV respectively. These values are higher than the band gap values reported previously. Also, the electron phonon coupling constant is determined as 2.23, 2.10 and 2.55 for A, B and T respectively which indicates the strong electron-phonon coupling. The phonon energy contributing to the increase in temperature is 22.84 meV, 19.91 meV, and 31.84 meV for A, B and, T respectively. The temperature dependent splitting of valence band is shown in **fig. 6.4(b)**. The strong interlayer spin-orbit coupling of ~132 meV is observed which is in consistent with previous reports. We observed that for this range of temperature, there is no significant splitting in the valance band. Hence, the valence band splitting energy doesn't contribute to the energy shift of A and B exciton depicting the energy shift is purely due to electron phonon coupling.

Table 6.1 Exciton and trion parameters for hexagonal MoS_2 , calculated by fitting the energy dependence of the exciton and trion on temperature using equation (3).

Parameter	Α	В	Т
E_X^0 (eV)	1.91	2.04	1.88
S	2.23	2.10	2.55
ħω (meV)	22.84	16.91	31.84

Fig. 6.4(c) indicates the change in the Full width half maxima (FWHM) of Lorentz fitted PL of A, B and T with the changing temperature. The total line width includes three factors: an inhomogeneous broadening factor, homogeneous broadening due to interaction of acoustic phonon with exciton, and homogeneous broadening owning to the interaction of optical phonon with exciton³⁶. The expression for line width peak broadening of excitons with the increasing temperature is given as³⁷

$$\Gamma(T) = \Gamma_{inh} + A'T + B' \left[exp\left(\frac{E_{LO}}{k_B T}\right) - 1 \right]^{-1}$$
(4)

Where $\Gamma(T)$ is the line width of exciton at temperature T, Γ_{inh} represents the residual linewidth at T = 0K, A represents the exciton-phonon coupling constants for low frequency phonon mode and B is the exciton-phonon coupling constants for *high*-frequency phonon modes, E_{L0} is the energy of the high-frequency phonon mode, and k_B is Boltzmann's constant. The **fig. 6.4(c)** is fitted using equation (4) for A, B and T respectively and the fitting parameters are shown in Table 6.2. The inhomogeneous line width is associated with structural defects and the thickness of the flake which is determined as 13.66 meV, 25.52 meV, and 33.49 meV for A, B and T respectively. The second term in equation is neglected as these interactions are dominating below the 50-kelvin temperature. The exponential increase in the linewidth with increasing temperature depicts the broadening is due to interaction of optical phonon with exciton and the exciton-optical phonon coupling constant is found to be 34.29 meV, 36.35 meV, and 28.64 meV for A, B and T respectively.

Table 6.2 Exciton and trion parameters for hexagonal MoS_2 , calculated by fitting the temperature dependent broadening of excitonic emission PL using equation (4).

Parameter	A exciton	B exciton	T trion
$\Gamma_{inh} (meV)$	13.66	25.51	33.49
B'(meV)	34.29	36.35	28.64

6.4 Conclusion

Here, we synthesis the hexagonal morphological shape of multilayer MoS_2 with CVD technique. The temperature dependent PL measurements reveal the band gap at zero kelvin and high carrier concentration. Exciton-phonon coupling constant has been determined which is found to be little higher than other morphological shape. With the decreasing temperature, we didn't observe the splitting in the valence band. Prominent coupling of optical phonon with exciton is observed. The temperature dependent excitonic properties for MoS_2 in hexagonal morphological shape revealed which information is useful for futuristic excitonic and optoelectronic devices.

Note

 \checkmark This manuscript is under preparation

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Chapter 7

Summary and future prospects

7.1 Summary of the thesis

This thesis focuses on comprehending the details of electronic energy band alignment at the contacts and interfaces of 2D materials, van der Waals heterostructures, and excitonic dynamics in 2D materials, which are crucial to charge transport in 2D electronic devices. Band alignment at the contacts has previously been assessed indirectly from electronic response or analytically predicted by following different transport models. Thus far, no direct experimental technique has been created to determine the critical interface parameters at contact or the interface's real conditions and estimate their divergence from ideal conditions. We employed the KPFM technique to probe the band alignment at the interfaces and μ -PL studies to understand the excitonic dynamics. This thesis's findings will help advance the application of electronic devices based on 2D layered materials.

The first chapter of the thesis describes the literature studies on the surface and interfaces of 2D materials, different geometrical configurations used in fabricating contacts, engineering of contacts, metal/semiconductor band alignments, types of van der Waals heterostructures based on stacking as well as band alignment. Synthesis routes to van der Waals heterostructures and engineering band alignment at the van der Waals interfaces have been discussed. Moreover, the effect of the morphological shape of 2D material on its properties is also discussed.

The second chapter of the thesis includes the description of synthesis techniques and experimental set-up used to conduct the research work presented in the thesis. The Dry transfer and CVD methods synthesize the 2D materials and van der Waals heterostructure. The KPFM technique is used to measure surface potential of the sample, while μ -PL is used to study the band gap studies. The low-temperature μ -PL is used to probe the excitonic dynamics. This part also covers essential characterization tools like Raman and AFM. Discussions are also made about the experimental setup used for device manufacturing.

In the third chapter, we discussed a non-contact and direct way to accurately probe the energy band bending at nanoscale spatial precision on MoS_2 flake laid on gold electrodes by mapping the surface potential landscape at non-equilibrium conditions during carrier injection. With systematically varying the charge carrier injection, the contrast gradient in surface potential profiles is studied along the MoS_2 channel.

The highlights in the third chapter work are provided below:

- Experimentally found depletion widths and built-in potentials for Au-MoS₂ interface quietly match the analytically calculated one.
- Real-time mapping of band alignment in thermally non-equilibrium conditions and the interface parameters like the lateral electric field and space charge density during the charge transport have been determined.
- Au-MoS₂ interface is n-type Schottky contact
- > Drain/MoS₂ and Source/ MoS₂ contacts are asymmetric.

In the fourth chapter of the thesis, we showed the formation of the p-n junction at the MoS₂/Black phosphorene (BP) interface and conducted a nanoscale investigation to measure the band alignment under realistic conditions experimentally. Kelvin probe force microscopy (KPFM) technique measures the spatial distribution of built-in potential, built-in electric field, and depletion width.

The highlights in the fourth chapter work are provided below:

- The spatial distribution of built-in potential, built-in electric field, and depletion width at the p-n junction at the MoS₂/Black phosphorene (BP) interface and experimentally measure the band alignment under realistic circumstances.
- > The lift height of \sim 15 nm is optimised for the surface potential study.
- The increase in the lateral built-in potential and lateral built-in electric field at MoS₂/BP interface is observed with increasing the thickness of the MoS₂ flake.
- Calculations using the Density Functional Theory (DFT) were performed to validate the experimental findings, which matched those of the experiments.

In the fifth chapter of the thesis, we conferred the opening of the band gap in CVDgrown twisted multilayer MoS_2 .

The highlights in the fifth chapter work are provided below:

- Using the CVD technique, 6.7 degrees twisted MoS₂/MoS₂ interface with hexagon morphology is synthesized.
- Blue shift in PL is attributed to a twisted interface.
- Analysing the deconvoluted PL fitting, we observed enhancement of spin-orbit coupling energy at the interface.
- > The energy shift in B exciton at the MoS_2/MoS_2 interface is more prominent.
- > The twist angle interface doesn't influence the surface electrostatic properties.

It is possible that the twist at the interface is the cause of the blue shift in reflectance spectra that is seen.

In the sixth chapter of the thesis, we discussed the influence of morphological shape on the excitonic properties of MoS_2 . The uniform growth of MoS_2 hexagons is confirmed by Raman and photoluminescence (PL) spectroscopy. The temperaturedependent PL analysis determined the high carrier concentration, high optical band gap, and electron-phonon coupling constant.

The highlights in the sixth chapter work are provided below:

- ▶ Highly symmetric hexagon of multilayer MoS₂ synthesized with CVD technique.
- Red Shift in band gap with increasing temperature owing to thermal expansion of lattice parameter and increased electron-phonon coupling.
- > Temperature-dependent PL studies show higher carrier concentration of $n_e \sim 1.52 \times 10^{12} \text{ cm}^{-2}$.
- > Higher value of PL peak energy is found regardless of the multilayer nature of MoS_2 .
- > Coupling strength for exciton and optical phonon is determined.
- > Valence band splitting is independent of temperature.

7.2 Future prospects

In the future, I plan to investigate further fascinating 2D material phenomena, which are briefly detailed below as

- As discussed in chapter 6 of the thesis, the morphological shape of 2D material affects electronic and optical properties. CVD technique could be used to synthesize the van der Waals heterostructures with different morphological shapes for example triangular MoS₂ in hexagonal WS₂. The optoelectronic properties of these kinds of heterostructure could be explored.
- In chapter 4 of the thesis, we discussed the change in band alignment at MoS₂/BP heterostructures as the thickness of MoS₂ is increased. The tunning of band alignments for other 2D heterostructures, like MoS₂/WS₂ etc., could be explored by changing the thickness of one constituent 2D material.
- Chapter 3 of the thesis describes the contact metal/2D semiconductor interface during current conduction. Similar approach could be applied to 2D van der Waals heterostructure's interface in addition with gating effect.

- Many fundamental vital issues still need to be resolved as the investigation of practical applications of excitonic devices based on van der Waals heterostructures continues. For instance, we are still learning about an excitonic switch's energy or switching rate and the range of motion that excitons can experience in a van der Waals heterostructure.
- It is noteworthy that the twisted bilayer graphene system exhibits a so-called magic angle, where the Dirac cones surrounding the Fermi level are flattened, and the density of states of carriers is localized, leading to strongly correlated states and a variety of fascinating phenomena. This motivates later research on comparable twisted 2D superlattices, such as twisted bilayer TMDs that exhibit comparable flat bands and correlated states under particular circumstances, while the honeycomb structure in h-BN validates the potential for the realization of controllable ferroelectricity through rotational stacking. Moreover, twistronic further could be explored to the van der Waals heterostructures.