

. . .

To the Graduate Council:

I am submitting herewith a dissertation written by Olugbenga Adeyemi Olunloyo entitled “Atomically thin 2D Materials and Heterostructures: Preparation, Characterization, and Applications.” I have examined the final paper copy of this dissertation for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Physics.

Dr. Gong Gu, Major Professor

We have read this dissertation
and recommend its acceptance:

Dr. Norman Mannella

Dr. Haidong Zhou

Dr. Joon Sue Lee

Accepted for the Council:

Dixie L. Thompson

Vice Provost and Dean of the Graduate School

To the Graduate Council:

I am submitting herewith a dissertation written by Olugbenga Adeyemi Olunloyo entitled “Atomically thin 2D Materials and Heterostructures: Preparation, Characterization, and Applications.” I have examined the final electronic copy of this dissertation for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Physics.

Dr. Gong Gu, Major Professor

We have read this dissertation
and recommend its acceptance:

Dr. Norman Mannella

Dr. Haidong Zhou

Dr. Joon Sue Lee

Accepted for the Council:

Dixie L. Thompson

Vice Provost and Dean of the Graduate School

(Original signatures are on file with official student records.)

Atomically thin 2D Materials and Heterostructures: Preparation, Characterization, and Applications

A Dissertation Presented for the
Doctor of Philosophy
Degree
The University of Tennessee, Knoxville

Olugbenga Adeyemi Olunloyo

December 2024

© by Olugbenga Adeyemi Olunloyo, 2024
All Rights Reserved.

I dedicate this work to the invisible creator, the keeper of my soul, the giver of strength, grace, wisdom and mercy.

To my loving and supportive wife, Bukola Esther Olunloyo.

To my two wonderful sons, Ayomikun Samuel Olunloyo and Iyin Isaac Olunloyo.

To my parents, Samuel Bankole Olunloyo and Funke Abiodun Olunloyo.

Finally, to my siblings, Segun Olunloyo, Funmilayo Olusa, Bukola Daramola, sola olunloyo (late), Peju Olunloyo, gbenga olunloyo (late) and Femi Olunloyo.

Acknowledgements

First and foremost, I would like to give my heartfelt gratitude to Invisible God Almighty on whose Word I draw my essence. My ever-present help!

I would like to express my deepest gratitude to my advisors, Dr.Kai Xiao and Dr Gong Gu for their unwavering support, guidance, and encouragement throughout my research journey. Their insightful feedback and expertise have been invaluable in shaping this dissertation. I am truly grateful for the time and effort they invested in helping me achieve my academic goals.

I would also like to extend my heartfelt thanks to the members of my dissertation committee, Dr. Norman Mannella, Dr. Joon Sue Lee and Dr. Haidong Zhou, for their constructive and valuable suggestions, which greatly enhanced the quality of this work. Their diverse perspectives and expertise provided me with a well-rounded understanding of my research topic.

I am immensely grateful to my family for their unconditional love, patience, and support throughout this challenging journey. To my spouse, Bukola Esther Olunloyo (Bukolami), thank you for your constant encouragement, understanding, and for being a good help mate during the toughest times. To my parents: Mr and Mrs Samuel Bankole Olunloyo thank you for instilling in me the importance of education and for always believing in my abilities. To my second parents: Mr and Mrs Rufus Oluwafemi Ajayi for your support and encouragement all through these years. My Siblings whose calls has being a source of support especially my brother Femi Olunloyo

I would like to acknowledge CNMS staff in Oak Ridge National Laboratory where I did most of my research for the support and I would like to acknowledge my colleagues and friends Jerome, Namilla and Amaar especially for their support, camaraderie, and for providing a much-needed balance of work and life. Your friendship and encouragement have been instrumental in keeping me motivated and focused. I would like to acknowledge to thank my people in Knoxville, Dr Omitaomu and Family, Dr Akin Oyedele, Dr Femi Oyedeji and family, Dr Sunday and family, Dr Stephen Fatokun and Family, Dr Damilola and family, Mr Paul and family, Mr Victor Ale and Mr Idris.

Finally, I am grateful for the financial support provided by University of Knoxville, Tennessee and Center for Nanophase Material Science at Oak Ridge national Laboratory which enabled me to pursue and complete this research. Their generosity and belief in my work have been crucial in bringing this project to fruition. Thank you all for being a part of this journey and for contributing to the successful completion of my dissertation.

'..so that what is seen was not made out of things that are visible"

Abstract

Atomically thin two-dimensional (2D) materials and heterostructures have emerged as a frontier in materials science, offering unique physical properties and unprecedented potential for technological applications. These materials, such as graphene, transition metal dichalcogenides (TMDs), and hexagonal boron nitride (hBN), exhibit exceptional electronic, optical, and mechanical characteristics due to their reduced dimensionality and strong quantum confinement effects. As research progresses, the disassembling and reassembling the 2D materials to realize these heterostructures is still a hot and ongoing research. Ensuring clean interfaces and high-quality materials is crucial to access these novel properties.

After a brief introduction and literature review, Chapter 3 introduces different novel approaches to the stacking of different 2D materials and the fabrication of heterostructures with tailored properties, enabling the exploration of novel phenomena such as phase change investigation of PdSe_2 and the memcapacitive and memresistive effects of stacked nanosheets of PdSe_2 . These heterostructures are pivotal for advancing nanoelectronics, photonics, and phase transition devices. A simple polymer-free graphene transfer technique is introduced that improves the quality of transferred graphene.

Chapter 4 of the dissertation investigates the behaviour of various excitons such as free exciton, bound exciton along with defect states in a partially encapsulated GaSe by varying the GaSe thickness and temperature (4 to 295 K). This further expands our understanding of excitons and deep defects in 2D GaSe. This knowledge

is crucial for the future use of GaSe in nano-optoelectronics, particularly when it comes to manipulating its optical properties.

Finally, chapter 5 investigates the structural evolution and correlated optical properties of the various alloys between PdSe₂ and PdTe₂ with different Te fractions. we have observed several phase transitions using Raman spectroscopy, and transitions from PdSe₂ ambipolar transport characteristics to n-type in PdSe_{1.8}Te_{0.2}, and subsequently to p-type in PdSe_{1.5}Te_{0.5} as Te doping increases.

Table of Contents

1	Introduction	1
1.1	Objectives of this dissertation	2
1.2	The organization of this dissertation	2
2	Literature Review	4
2.1	Transitional metal dichalcogenide	6
2.2	Top-Down Methods forming 2D materials	6
2.2.1	Mechanical Exfoliation	6
2.2.2	Gold-Assisted Method of Exfoliation	8
2.3	Bottom-Up Methods:	9
2.3.1	Chemical Vapor Deposition (CVD)	9
2.4	Stacking and Transfer Methods of 2D Materials	11
2.4.1	Dry Transfer	13
2.4.2	Wet Transfer	16
2.5	Contamination control in heterostructures	20
2.6	The role of interlayer interaction on the structure and functionality of 2D materials	22
3	Novel approaches in van der Waals heterostructure fabrication	24
3.1	The role of van der Waals in electrical memory effects in stacked PdSe ₂	24
3.1.1	Introduction	24
3.1.2	Methods	26

3.1.3	Results and discussion	26
3.1.4	Summary and Conclusion	29
3.2	Polymer-Free Method of transfer of graphene	30
3.2.1	Introduction	30
3.2.2	Methods	31
3.2.3	Result and Discussion	31
3.3	PdSe ₂ encapsulation with graphene	31
3.3.1	Introduction	31
3.3.2	Methods and Approaches	32
3.3.3	Results and Discussion	36
3.3.4	Summary and Conclusion	36
3.4	Preparation of 2D moiré	42
4	The effect of encapsulation on excitons in GaSe	46
4.1	Introduction	46
4.2	Methods	47
4.3	Results and Discussion	48
4.3.1	Temperature dependent photoluminescence of GaSe	48
4.3.2	Defect-related excitonic emission in GaSe	50
4.3.3	The effect of encapsulation on excitons in GaSe	54
4.4	Conclusion and Summary	58
5	Understanding the effect of composition on the structure and electrical property of PdSe_{2-x}Te_x	60
5.1	Introduction	60
5.2	Methods and Approaches	62
5.3	Results and Discussion	62
5.3.1	Optical characterization of different alloys – Raman and simulation	62
5.3.2	Structural transition in alloys by STEM	63

5.3.3	Composition-dependent electrical properties of the alloys . . .	71
5.4	Conclusion and summary	78
6	Conclusion	79
6.1	Contributions of thesis	79
	Appendix	94
A	Appendix	94
A.1	A List of Publications	94
	Vita	96

List of Figures

2.1	Top-down and bottom-up approaches to build heterostructure (1) . . .	5
2.2	An optical image of monolayer and few layer PdSe ₂ crystals exfoliated on a SiO ₂ /Si substrate using a gold-assisted method	10
2.3	A 2D materials transfer system from HQ Graphene Inc (i) temperature control and vacuum substrate holder, (ii) control system in x-y-z direction, (iii) monitor	14
2.4	schematics show the procedure for dry transfer method	17
2.5	schematic procedure showing each step in Wet transfer process . . .	19
3.1	Dry transfer of PdSe ₂ on a 50 nm gold substrate	27
3.2	Height and deflection images showing the sample topography. The white, dashed lines in the height image indicate the area where two NSs are stacked. SMIM-C and SMIM-R images corresponding to the local capacitance and resistivity. dC/dV amplitude and phase data shows the concentration and polarity of charge carriers and dR/dV amplitude and phase indicates how the resistivity changes in magnitude and direction as a function of an applied AC voltage	28
3.3	Procedure for polymer-free transfer of graphene	33
3.4	Polymer-free transferred graphene on TEM grid	34
3.5	Raman measurement of suspended graphene after transfer	35
3.6	schematic diagram showing the procedure for the heterostructure graphene-PdSe ₂ -graphene fabrication	37

3.7	(a) Optical image of PdSe ₂ on CVD grown Graphene on copper substrate using the dry transfer method (b) Optical image of PPC/graphene transferred on PdSe ₂ /Graphene after etching Cu substrate (c) Optical image of graphene/PdSe ₂ /graphene on TEM grid after dissolving PPC	38
3.8	SEM image graphene-PdSe ₂ -graphene	39
3.9	STEM images of PdSe ₂ and graphene before laser irradiation	40
3.10	STEM images of Pd ₂ Se ₃ and Pd ₁₇ Se ₁₅ after laser irradiation of PdSe ₂ sandwiched graphene	41
3.11	procedure for fabricating MoS ₂ moiré using gold	44
3.12	MoS ₂ moiré on grid	45
4.1	Optical Image of exfoliated few-layer GaSe encapsulated with hBN on SiO ₂ substrate	49
4.2	Temperature-dependent -PL spectra of the 2L GaSe flake excited at 532 nm and fitted by six Lorentzian functions related to the free Exciton, Bound exciton and defect state	51
4.3	Comparison of temperature-dependent photoluminescence of encapsulated and unencapsulated few layer GaSe	52
4.4	Comparison of temperature-dependent photoluminescence of encapsulated and unencapsulated Bulk GaSe	53
4.5	Peak position of the different Number of layers of GaSe	56
4.6	(Left side): A plot of PL spectra of different excitons at various temperatures in GaSe (Right side): Peaks of different PL spectra at various temperatures of GaSe	57
4.7	(a) Different behaviours of excitons at different excitation power (b) intensity response at 601 nm wavelength (c) intensity response at 620 nm wavelength	59
5.1	Flakes of PdSe ₂ -PdTe ₂	64
5.2	Raman spectra of different composition between bulk PdSe ₂ -PdTe ₂ .	65

5.3	Raman spectra of different composition between few-layer PdSe ₂ and PdSeTe	66
5.4	Optical images of PdSe _{1.5} Te _{0.5} flakes transferred on TEM grid	67
5.5	Atomic resolution structure of few-layer PdSe _{1.5} Te _{0.5}	68
5.6	Atomic resolution structure of few-layer PdSe _{1.8} Te _{0.2}	69
5.7	Atomic resolution structure of few-layer PdSeTe	70
5.8	Right side- Raman plot of PdSe ₂ and Left side- top view of the atomic structure of PdSe ₂	72
5.9	Right side- Raman plot of both experimental and theory of thin PdSeTe and Left side- top view of the atomic structure of PdSeTe	73
5.10	Right side- Raman plot of both experimental and theory PdTe ₂ and Left side- top view of the atomic structure of PdTe ₂	74
5.11	Device design for PdSe _{2-x} Te ₂ flakes	75
5.12	Transfer curve of a typical few-layer PdSe _{1.8} Te _{0.2} device	76
5.13	Transfer curve of a typical few-layer PdSe _{1.5} Te _{0.5} device	77

Nomenclature

1T	charge density wave
CDW	charge density wave
CNMS	Center for Nanophase Materials Science
CVD	Chemical vapor deposition
DI	Deionized
EDX	energy-dispersive x-ray spectroscopy
GaSe	gallium selenide
hBN	hexagonal Boron Nitride
I_{ds}	Drain-source Current
IPA	Isopropanol
KOH	potassium hydroxide
MoS ₂	Molybdenum disulfide
NSs	Nanosheet
PC	Poly(Bisphenol A carbonate)
PDMS	polydimethylsiloxane

PdSe ₂	Palladium Diselenide
PdTe ₂	Palladium Ditelluride
PMMA	poly (methylmethacrylate)
PPC	poly(propylene) carbonate
PPMS	Physical Property Measurement System
SEM	Scanning Electron Microscopy
SMIM	scanning microwave impedance microscopy
STEM	scanning transmission electron Microscopy
T _c	Transition temperature
TEM	transmission electron microscope
XRD	x-ray diffraction
2D	two-dimensional
TMDs	transition metal dichacogenides
vdW	van der Waals

Chapter 1

Introduction

The pivotal moment in the history of 2D materials can be attributed to the efforts of Novoselov and Geim et al.(2) who achieved the successful exfoliation of graphene using scotch tape. This notable work was intended to present graphene as a new viable alternative material for silicon-based technologies whose properties can be controlled by external application of the electric field. Since then, there has been research on graphene showing extraordinary properties like high mechanical strength, conductivity (both electrical and thermal), and high flexibility. Graphene was shown to have a high electron mobility $200,000 \text{ cm}^2/\text{Vs}$ at room temperature (3) and a high thermal conductivity of $5 \times 10^3 \text{ W/m-K}$ (4). It also has an exceptional ability to carry ultra-high current densities of $1 \times 10^9 \text{ A/cm}^2$ (5). These extraordinary properties of graphene and many others have generated considerable interest. These properties have consequently necessitated diverse applications in the field of nanotechnology and science, such as high-speed electronic and optical devices, energy generation and storage, hybrid materials, chemical sensors, RF transistors, interconnects, ultra-capacitors, biosensors, stretchable electronics, thermo-electrics, photo voltaic.

However, the lack of bandgap of graphene has posed a limit on graphene applications, which has led to the emergence of other layered materials such as transition metal dichalcogenide with tunable bandgap from bulk to monolayer, Black

phosphorus, and other equally important materials like hexagonal Boron nitride(hBN) which acts as an insulator due to its large bandgap. The newly enriched properties of these layered materials have further widened the scope of applications of the 2D material. For instance, the Transition metal dichalcogenides exhibit diverse electronic characteristics due to their partially filled d orbitals. These range from insulating or semiconducting (e.g. Mo, Ti, and W dichalcogenides) to metallic or semi-metallic properties (V, Nb, and Ta dichalcogenides). Even more intriguingly, several research studies have emerged on the unique ways to stack various layer materials, forming novel heterostructures endowed with remarkable properties. The disassembling and reassembling the 2D materials to realize these heterostructures is still a hot and ongoing research. Ensuring clean interfaces and high-quality materials is crucial to accessing these novel properties. The work in the field intends to introduce novel approaches to address the critical issue of achieving a clean interface and to advance the transfer method for accessing these important properties.

1.1 Objectives of this dissertation

The Objectives of this dissertation are

1. To advance the methods of exfoliation, transfer, and stacking of 2D materials.
2. To address the challenges and limitations in the precise manipulation of 2D materials.
3. To investigate the several applications of different heterostructures fabricated using novel transfer and stacking techniques.

1.2 The organization of this dissertation

The Structure of this Dissertation is as follows:

- Chapter 2 presents a literature review describing the various major methods of synthesis of 2D materials with emphasis on mechanical exfoliation and chemical vapour deposition and several transfer and stacking techniques.
- Chapter 3 introduces a new method of transferring graphene without using polymers. It also introduces a hybrid of wet and dry transfer to fabricate a heterostructure of PdSe₂ sandwiched with graphene to investigate the phase transition of PdSe₂ under irradiation. A new technique of fabricating moiré using gold assisted method, discusses nanoscale probing of electrical memory effects in van der Waals heterostructure of PdSe₂.
- Chapter 4 Discusses exciton photoluminescence of encapsulated few-layer GaSe.
- Chapter 5 explores the optical , structural, and transport properties of the various alloys of PdSe_{2-x}Te_x.
- Chapter 6 Summary and conclusion.

Chapter 2

Literature Review

Synthesis of two-dimensional materials has garnered a lot of attention in recent years due to the fact that these materials possess distinctive features and have the potential to be utilized in a variety of fields, including electronics, optoelectronics, energy storage, and catalysis (6). The atomic thickness and vast lateral dimensions of two-dimensional materials are what distinguish them from three-dimensional materials. These characteristics give rise to unique electrical, mechanical, and thermal capabilities (7). Figure 2.1 shows the Particular attention is paid to techniques such as chemical synthesis, liquid-phase exfoliation, chemical vapor deposition (CVD), and mechanical exfoliation, respectively (8).

The synthesis of 2D materials is a rapidly advancing field with a variety of techniques available, each with its own advantages and limitations. Mechanical exfoliation, chemical vapor deposition, liquid-phase exfoliation, and chemical synthesis are among the most commonly used methods [(9), (10), (11)]. Emerging techniques like molecular beam epitaxy, electrochemical exfoliation, and laser ablation offer new possibilities for creating high-quality 2D materials[(12), (13)]. Continued research and development in this area are expected to lead to new materials with unprecedented properties and applications across various fields.

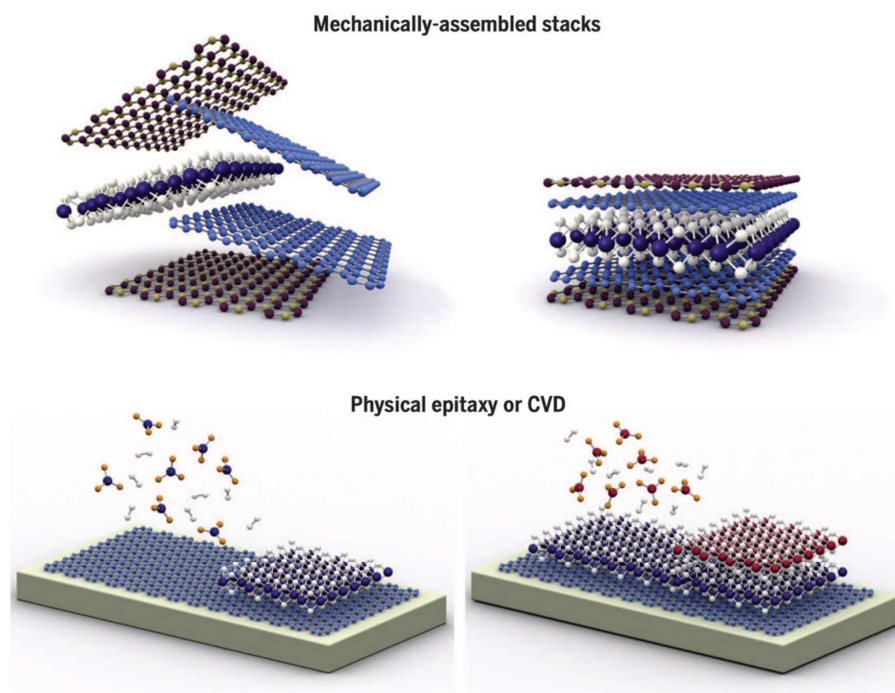


Figure 2.1: Top-down and bottom-up approaches to build heterostructure (1)

2.1 Transitional metal dichalcogenide

Transition metal dichalcogenides (TMDs) are a group of layered materials characterized by the structural formula MX_2 , where M denotes the transition metal (such as Mo, W, etc.) and X represents the chalcogen (such as S, Se, etc.). All TMDCs possess a hexagonal structure, where each monolayer consists of three layers stacked on top of each other in an X-M-X arrangement. The two predominant polytypes of monolayers are trigonal prismatic and octahedral. They possess distinct electrical and optical characteristics that result from the quantum confinement and surface effects that occur when bulk materials are reduced to monolayers, leading to a transition from an indirect bandgap to a direct bandgap. The variable bandgap in transition metal dichalcogenides (TMDs) is accompanied by a robust photoluminescence (PL) and significant exciton binding energy. This makes TMDs highly attractive for optoelectronic devices, such as solar cells, photo-detectors, light-emitting diodes, and photo-transistors.

2.2 Top-Down Methods forming 2D materials

2.2.1 Mechanical Exfoliation

This method, which was initially implemented in 2004 to produce monolayer graphene from graphite, has since been applied to most two-dimensional layered substances. This straightforward technique allows the separation of extremely crystalline 2D flakes. Mechanical exfoliation of Van der Waals crystals is one method that has been used to make very good monolayers or few-layer structures of transition metal dichalcogenides. However, exfoliating monolayers from tape depends on the likelihood of a crystal cleavage that results in the retention of (N-1) layers on the tape and the transfer of a single monolayer onto the SiO_2 substrate. The weak interaction between TMDCs and the SiO_2 substrate leads to a low probability of the event, as mentioned earlier, occurring and, as a result, provides limited control over the size of the

flake (14). This approach is limited by its very low yield and usually produces modest lateral dimensions, typically less than 5 μm . However, minor adjustments, such as applying exfoliation to the flakes by applying heat, lead to a marginal enlargement of the flakes.

The process of cleaving thin layers of two-dimensional materials involves overcoming interlayer bonding, which is a complicated balance of forces that is dependent on a number of parameters at the same time (15). In most kinds of layered materials, weak van der Waals bonds serve as the mechanism for holding the layers together in the (001) direction. On the other hand, covalent bonds are responsible for holding the layers together in the (100) and (010) directions (16). Their structures consisting of only one or a few layers of atoms result in a low bending stiffness, D , in the out-of-plane direction, which is approximately 1 electronvolt (eV) and high in-plane tensile stiffness (17). The interfaces between 2D materials and the substrate are typically influenced by many interactions, including chemical bonds, van der Waals forces, and electrostatic interactions (18).

These interactions can be altered by manipulating the chemistry of the interfaces. Van der Waals bonds possess a lower bond strength (0.4–4 kJ/mol) and a greater bond length (0.3–0.6 nm), while covalent bonds have a higher bond strength (e.g. 345 kJ/mol for C–C bonds) and a much shorter bond length (0.154 nm for C–C). Hence, the weak van der Waals forces can be overcome using mechanical, chemical, or electrochemical means, allowing for the straightforward separation of these layers along the (001) plane (19). Therefore, separating these layers in the (001) plane by mechanical, chemical, or electrochemical techniques is easy by overcoming the weak van der Waals forces.

Applying a peeling force to the ultra-thin sheets, which are formed of single or a few layers of atoms and are bonded to materials like a scotch tape, allows for the separation of the sheet from a substrate. When examined, the morphology of the samples that have been exfoliated typically reveals that the sheets have been partially torn during the peeling process (20). Cracks have begun to form and spread along

the interface between the sheet and the substrate to enable successful exfoliation. A further factor that contributes to the sheet splitting into smaller pieces is the presence of fractures located within the material. When subjected to peeling, the 2D sheets can be delicate due to their extremely thin nature, which consists of only a single or a few atomic layers. This presents a technical challenge in terms of controlling the geometry of exfoliation due to the intricate interaction between the characteristics of the material and the configuration of the peeling process.

2.2.2 Gold-Assisted Method of Exfoliation

The first major breakthrough in mechanical exfoliation of 2D materials that proved difficult due to stronger interlayer bonding was reported by Desai et al (21). Consequently, several previous reports on mechanical exfoliation have employed gold to improve yield, with gold deposited on the top surface of bulk crystals, followed by exfoliation, and then transferred to a clean new substrate before the gold is etched. Exfoliation of TMDC bulk crystals on gold substrates has also been reported to yield monolayers up to the centimeter scale (21). The gold-assisted method of exfoliation has proven to be effective in producing monolayers and few layers of TMDCs with stronger interlayer bonding. Example is PdSe₂ exfoliated using the gold-assisted method shown in Figure 2.2.

Gold atoms form a bond with chalcogen atoms, comprising the uppermost layer of MX₂ (21). The strength of the interaction between the evaporated gold and the uppermost layer is greater than the vdW interactions between that layer and the lowermost layers of MX₂ (22). This process facilitates the careful removal of the uppermost layer by means of a thermal release membrane, which is subsequently adhered to the intended target substrate, which may be SiO₂/Si or quartz (23). Following the release of the thermal tape onto a hot plate (130 °C), a gentle O₂ plasma is applied to the substrate in order to eliminate any remaining tape from its surface (24). Low O₂ plasma power and etching time are utilized to prevent the

etching away of the gold, which would expose the MX_2 monolayer beneath. Following this, the gold film is wet-etched with potassium iodide and iodine (KI/I_2) using a Transene Gold Etch-type TFA for four minutes. It is important to note that this etching method does not affect the TMDC flakes. Following this, isopropyl alcohol (IPA) and acetone are used to rinse for ten minutes in order to eliminate any remaining residues and acquire the large-area monolayers.

2.3 Bottom-Up Methods:

2.3.1 Chemical Vapor Deposition (CVD)

Chemical Vapor Deposition (CVD) is a method that involves the deposition of thin films or coatings onto a substrate surface by causing a chemical reaction between gaseous precursors [(25), (26)]. During CVD, reactive gases are injected into a chamber containing the substrate, initiating a chemical reaction that results in the deposition of a solid substance onto the substrate (27). This technique is extensively employed in the semiconductor sector, fabrication of coatings, and creation of diverse materials with distinct features (28). Chemical vapor deposition (CVD) has been extensively employed for the efficient manufacturing of high-grade, expansive two-dimensional (2D) materials (24). Contrary to the limited effectiveness of mechanical exfoliation and the subpar results of chemical synthesis in solution, CVD provides a well-coordinated approach that ensures high quality, efficiency, uniformity, and control throughout the process (24).

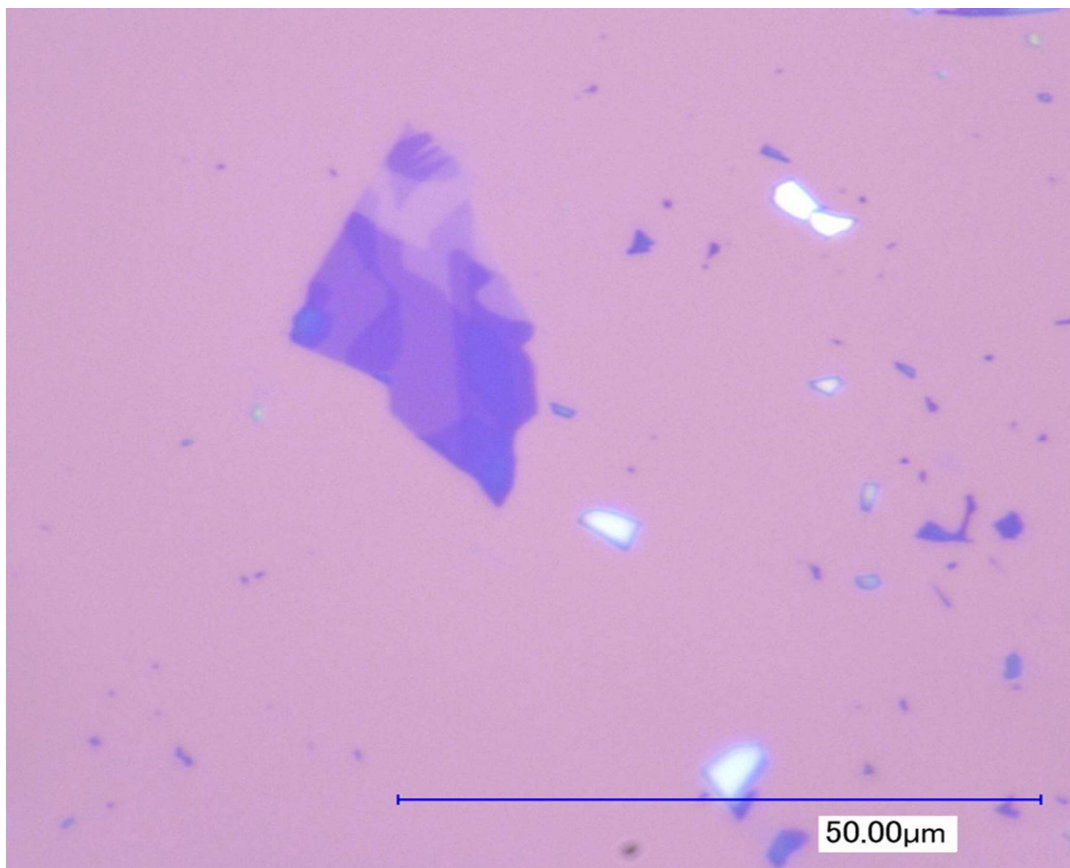


Figure 2.2: An optical image of monolayer and few layer PdSe₂ crystals exfoliated on a SiO₂/Si substrate using a gold-assisted method

2.4 Stacking and Transfer Methods of 2D Materials

In recent years, there has been significant interest in 2D-layered materials from a fundamental physics and applied science standpoint. Remarkably, a wide range of unique stacked structures with diverse properties and applications can be intentionally constructed. Examples of such structures include vertical van der Waals (vdW) heterostructures, twisted multilayer 2D materials, and hybrid-dimensional structures (29). The stacking technique is a potent approach to building precise and high-quality structures of 2D materials with atomic accuracy, in contrast to the conventional synthesis process (30). Mechanical stacking is the method most commonly used for assembling two-dimensional heterostructures. Stacking strategies for two-dimensional materials are the subject of many articles. Due to the rapid progress of vdW heterostructures and twistrionics, new and effective strategies for transferring and stacking materials with different twists have been developed (31). Direct growth of two-dimensional materials on substrates of interest for commercial applications is sometimes hampered by limitations such as the utilization of high growth temperatures, the utilization of chemically active growth precursors and promoters, and the requirement of epitaxy.

This has resulted in the creation of a vast number of ways for the layer transfer of two-dimensional materials from the growing substrate to the target application substrate. These methods have varied degrees of cleanliness, homogeneity, and damage associated to the transfer process (32). Chemical vapour deposition and other vapour-related growth methods have been shown to perform very well in terms of both quality and scalability, among the many techniques that may be used to manufacture two-dimensional materials (29). However, in order to create two-dimensional semiconductors with a reasonable carrier mobility, temperatures that are higher than 700 degrees Celsius are required. The growth conditions such as high temperature, has the potential to have adverse impacts on the substrate that is being

grown on, which can compromise the dependability and performance of the devices that are being created (33). While there have been recent advancements in methods that utilize precursors like salt to lower growth temperature and enhance growth quality, it is important to note that these precursors can also introduce undesirable effects such as doping and contamination to the substrate. As a result, the ability for high-quality 2D materials to be grown on a (growth) substrate and cleanly transferred to another (target) substrate for device fabrication is crucial (30).

When it comes to CVD samples, the growth of materials is closely affected by the substrates that they are grown on. If it is not possible to develop the appropriate materials directly on the substrate that is being targeted, then the heterostructure assembly should stack all of the 2D components in the order that they were built (31). After the substrate and the bottom material have been created, another piece of material, known as the top material, needs to be prepared or moved onto a carrier that is capable of providing essential structural support. As soon as the top material is separated from its substrate, it is able to immediately fit exactly on the carrier without developing any creases or breaking (34). There are at least three categories that can be used to classify common carriers. These include viscoelastic stamps, which include polydimethylsiloxane (PDMS), deposited metal films, such as gold films, and amorphous polymer membranes, which include polymethyl methacrylate (PMMA), polycarbonate (PC), and poly-propylene carbonate (PPC).

The primary objective of transfer is to separate the upper material and place it onto the lower material without causing any damage. In order to fully realize the promise of large-area two-dimensional (2D) materials in a variety of applications, such as electronics, optoelectronics, catalysis, energy harvesting, and so on, it is essential to ensure that the transfer of these materials is damage-free. On the other hand, because the majority of atoms are located on the surface, two-dimensional materials are susceptible to etchants and water, which are invariably utilized throughout the typical wet transfer processes. This is due to the fact that all or the majority of their atoms are directly exposed.

It is therefore essential to build appropriate assessment methods in order to promptly and precisely describe two-dimensional materials both before and after the transfer process. This is done in order to guarantee that quality control is managed effectively. The post-transfer film cleanliness, defectivity, and uniformity, as well as the electronic and optoelectronic transport properties of nanoscale devices fabricated from the transferred films, can be used as benchmarking metrics to determine the strengths and weaknesses of various layer transfer methods. This is in addition to the transfer speed and complexity, which are also important factors to consider. A 2D transfer system used for various stacking is shown in Figure 2.3.

2.4.1 Dry Transfer

Van der Waals (vdW) heterostructures composed of several 2D materials have exhibited numerous unconventional phenomena in the field of nanoscale science and technology. 2D materials possess the unique ability to be stacked together, thanks to the presence of van der Waals forces that hold the layers together. Heterostructures can be created using techniques that enable the removal of lattice mismatch limitations and interface reactions. The formation of such van der Waals (vdW) heterostructures has been accomplished using a technique known as the transfer method. There have been a number of different transfer methods for two-dimensional materials investigated in order to produce these heterostructures. There have been a number of different transfer methods for two-dimensional materials investigated in order to produce these heterostructures. These transfer methods include the wet release transfer, the dry release transfer, and the stamping methods. When it comes to the techniques that may be used to investigate different forms of heterostructures, the dry release transfer method has been acknowledged as the most adaptable and flexible technique by researchers.

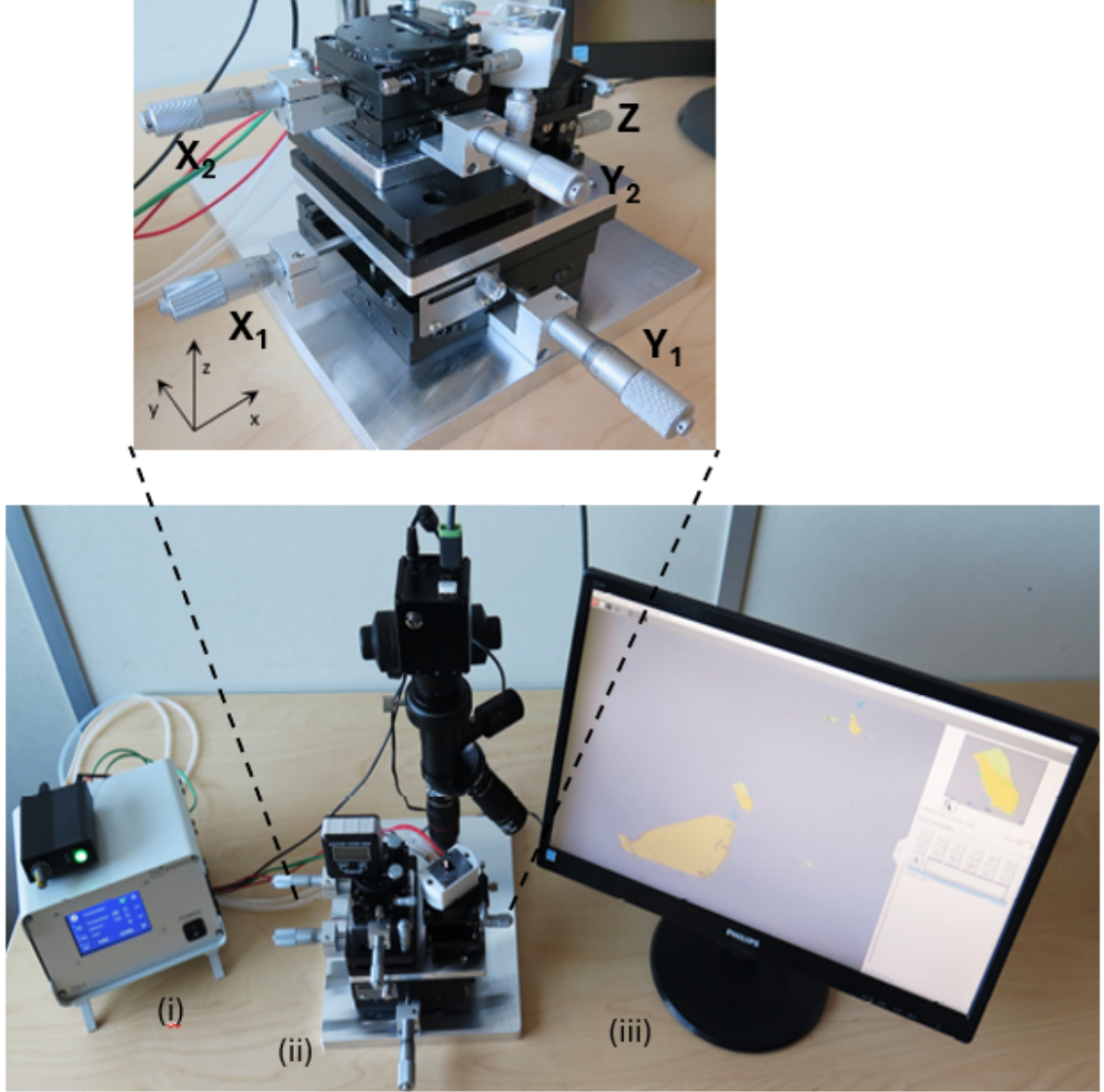


Figure 2.3: A 2D materials transfer system from HQ Graphene Inc (i) temperature control and vacuum substrate holder, (ii) control system in x-y-z direction, (iii) monitor

Using this technique, flakes of the two-dimensional material are initially exfoliated on a sheet of polymer, and then they are transferred onto another material without the polymer sheets being dissolved by organic solvents. The dry transfer technique enables the manipulation of two-dimensional flakes with great precision. The flakes that mechanical exfoliation produces become less or less directly exposed to water as the process continues. Instead, a polymer layer serves as the transfer medium to prevent the flakes from becoming wet. Using this approach, it is also possible to put CVD flakes in the desired locations. To accomplish this, an additional step involves turning the carrying layer over. Detailed explanations of each technique are included in this part, including illustrations of the equipment used to carry out dry transfer. Some polymers, like polypropylene carbonate (PPC) and PC, are used in this process. The procedure of dry transfer using polymers is described in Figure 2.4.

Van der Waals-based heterostructures

This Method employs hBN as the mediator in picking of other 2D materials. It is suitable for stable 2D materials and especially air sensitive materials (35). A PPC membrane (the carrier) is initially spin-coated onto a Si substrate. Following the exfoliation of some h-BN flakes onto the PPC membrane, the desired flake material is chosen. By mechanically detaching the PPC membrane from the Si substrate, it is firmly adhered to a PDMS stamp. At this instant, a mounting platform brings a graphene flake (the lower material) on a Si/SiO₂ substrate into complete contact with the h-BN flake. The target flake is captured when the h-BN flake is raised due to the robust vdW interaction between the two substances. An additional desired h-BN flake is captured using the identical method, forming an encapsulated h-BN/TMDCs/h-BN heterostructure. This method, on the one hand, facilitates an effective transfer process between diverse two-dimensional materials via vdW forces. In contrast, h-BN is methodically inert and electrically insulating, making it a viable candidate for substrates of other 2D materials seeking to improve their carrier transport capabilities. A highly desirable feature of heterostructures assembled

via vdW pick-up is that the interfaces are atomically pristine and devoid of carrier residues, owing to the mechanism of self-cleansing.

Polymer-based heterostructures

The isolation of 2D materials and their assembly into van der Waals heterostructures has attracted much attention because of their diverse functionalities when fabricated into devices and their wide-ranging applications in electronics, optoelectronics, and sensing. However, the performance of these devices depends on the method and the interface quality between the layers. A clean interface ensures high performance and maximizes their functionalities. Contaminants introduced during exfoliation and transfer usually gather as blisters between layers, severely affecting the transport properties and compromising the perfect vdWs interlayer adhesion between the layers (36). There are many ways to avoid these contaminants, such as Pre-treatment using oxygen plasma, which improves yield and size of flakes but also increases the interaction of the oxidized silicon substrate with the desired flaked, which results in a reduced Raman intensity of the 2D material. The wet transfer process typically begins with the growth of 2D materials on a substrate, often using chemical vapor deposition (CVD). A polymer support layer, such as poly(methyl methacrylate) (PMMA), Poly(Bisphenol A carbonate) (PC), poly(propylene) carbonate (PPC) or polydimethylsiloxane (PDMS),

2.4.2 Wet Transfer

Wet transfer is a widely used technique for transferring two-dimensional (2D) materials, such as graphene, hexagonal boron nitride (h-BN), and transition metal dichalcogenides (TMDs), from their growth substrates to target substrates (37). This process is crucial for integrating 2D materials into various electronic, photonic, and optoelectronic devices ((38), (39)).

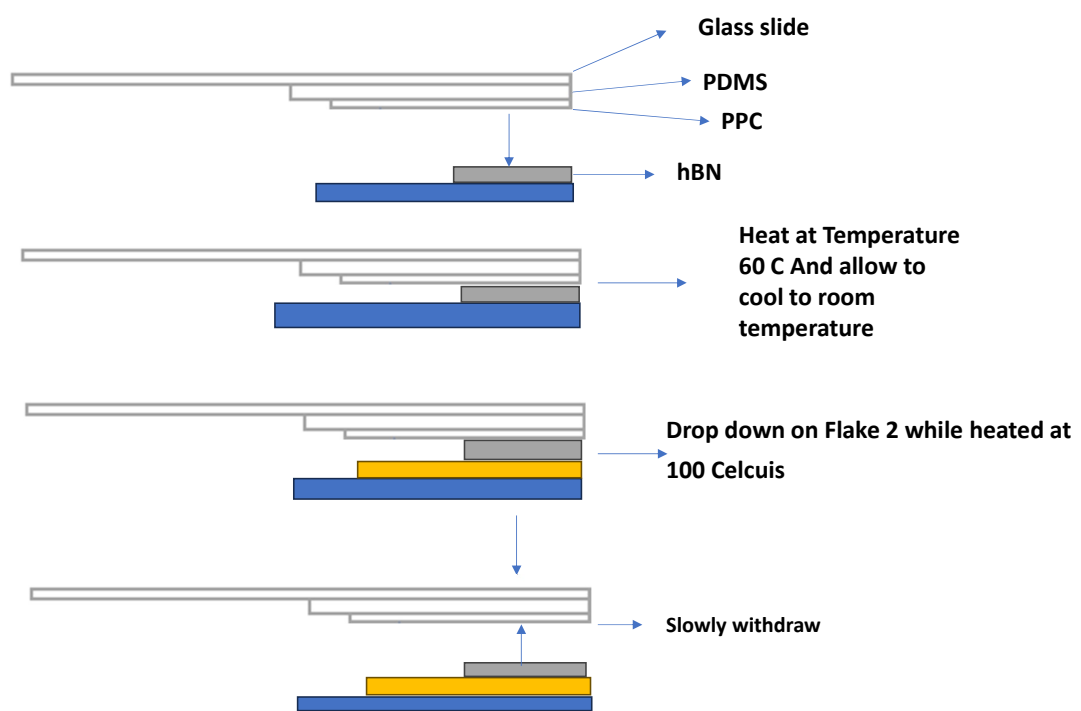


Figure 2.4: schematics show the procedure for dry transfer method

is then spin-coated onto the 2D material Figure 2.5 (a). This support layer provides mechanical stability and protection during the transfer process. Next, the underlying substrate is etched away using a suitable chemical etchant Figure 2.5 (b). For example, SiO_2 layer on Silicon is etched using potassium hydroxide (KOH), copper substrates used for graphene growth can be etched using ammonium per sulfate or ferric chloride solutions. The polymer with 2D material underneath is rinsed in DI water 2-3 times once the substrate is removed Figure 2.5 (d). Wet transfer offers several advantages, including the ability to transfer large-area films and preserve the material's intrinsic properties. However, challenges such as the introduction of defects possibly through etching, residues contamination from the polymer layer, and alignment issues remain. Optimizing the wet transfer process is essential for achieving high-quality 2D material integration, which is crucial for developing advanced applications in nanoelectronics, flexible devices, and other cutting-edge technologies. Wet transfer methods involve the use of solvents by any mean (40). The solvents could be etchant such as potassium hydroxide (KOH), Gold etchant, Iron Chloride (FeCl_3), Acetone, IPA, Chloroform, etc. The wet transfer is always very effective, especially for stable CVD-grown 2D materials in which the adhesion of 2D materials with growth substrate is high because of the growth conditions. However, it is unsuitable for sensitive 2D materials since it involves the use of solvent in the transfer process. The 2D material, now supported by the polymer layer, is carefully transferred to the target substrate, which can be silicon, TEM grid, glass, or any other desired material Figure 2.5(e). Finally, after positioning the 2D material on the target substrate, the assembly is dried and heat gently at 80-90 C, Figure 2.5 (f) and the polymer support layer is removed using solvents like acetone or chloroform depending on the polymer used Figure 2.5 (g). The Schematic diagram is shown in Figure 2.5.

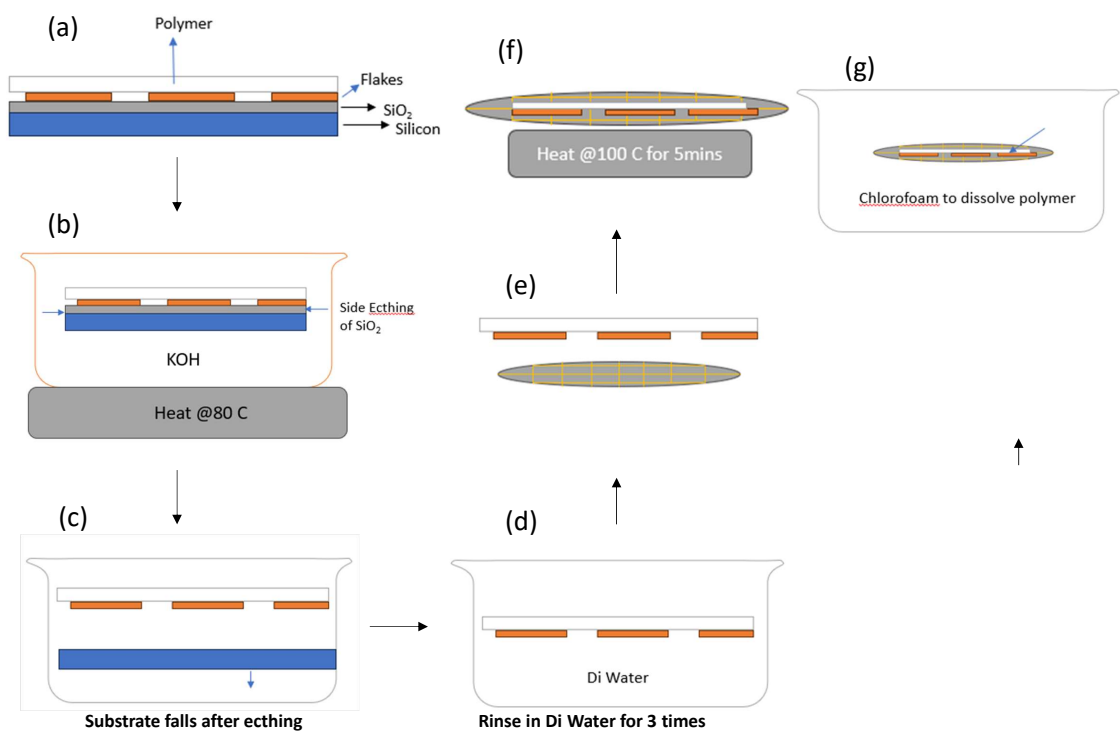


Figure 2.5: schematic procedure showing each step in Wet transfer process

2.5 Contamination control in heterostructures

During the fabrication of heterostructure, the presence of contamination on the surfaces of two-dimensional (2D) crystals presents significant challenges to the fundamental research and practical uses of 2D crystals(41). Surface residues are responsible for the uncontrolled doping and charge carrier scattering that occurs in two-dimensional crystals. Furthermore, trapped residues in two-dimensional vertical heterostructures that are mechanically formed frequently impede the coupling between stacked layers(42). During the process of transfer, the surface of two-dimensional materials has the ability to spontaneously adsorb and react with molecules discovered in the surrounding environment.

The interlayer contaminants pose a significant challenge. This issue can potentially diminish the performance of the two-dimensional materials stack and impose limitations on achieving a realistically sized and homogeneous device. Contaminants trapped within the layers tend to segregate into isolated regions, adversely impacting device functionality and optical response (36).Several Methods have been employed for cleaning transferred 2D materials. Thermal annealing is the predominant method employed to clean the surface of 2D materials. The existence of interlayer impurities is a key challenge that must be overcome in order to successfully fabricate van der Waals heterostructures(43). This is due to the fact that it has the potential to either decrease the performance of the two-dimensional materials stack or constrain the size of the practicable homogeneous device. When contamination is trapped, it has a tendency to split into isolated bubbles that are typically between tens and hundreds of nanometers in size(44). This phenomena is brought about by a balance between the expense of elastic energy to produce such bubbles and the gain in surface van der Waals energy that occurs from the production of clean interface regions(45).

During fabrication of heterostructure, Of the many polymer used in this process, PMMA, which stands for poly(methylmethacrylate), has been utilized extensively as a supporting layer in order to prevent the transfer process from causing harm to

two-dimensional materials(46). The removal of the Gr and h-BN layers from the copper foil and the assembly of these layers into van der Waals heterostructures on the substrate of choice have both been accomplished by the use of polymer sacrificial layers, such as poly(methyl methacrylate) (PMMA)(47). The latter are commonly annealed at temperatures that are higher than 500 degrees Celsius in order to remove the PMMA; nonetheless, the complete removal of the PMMA residue is still a difficult challenge to solve.

Following the transfer of two-dimensional materials onto the target substrate, the polymer layer ought to be eliminated in order to get a surface that is free of contaminants(48). When the polymer residue is left behind on the surface, it produces a number of issues, such as an increase in the contact electrical or thermal resistance between the two-dimensional material and the electrode in the device, as well as unwanted doping on the two-dimensional materials. In addition, it is vital to have a clean surface when using two-dimensional materials as a growth template for the synthesis of heterostructure. It has been reported that there are numerous ways that may be used to remove the polymer layer during transfer of 2D materials. One of the most common methods for removing the polymer layer is to dissolve it in an organic solvent and then anneal it after thermal processing (49). In recent times, a method that utilizes ultraviolet (UV) light and annealing at high temperatures for an extended period of time have been devised in order to effectively remove the polymer layer. On the other hand, it is still difficult to totally eliminate the polymer residue. As an additional point of interest, the removal of the polymer layer from other two-dimensional materials has not yet been thoroughly investigated.

2.6 The role of interlayer interaction on the structure and functionality of 2D materials

Another important factor to be considered during creation of heterostructure is the role of interlayer bonding. Interlayer bonding in two-dimensional (2D) materials plays a critical role in determining their mechanical, electronic, and thermal properties(50). Unlike bulk materials, 2D materials are composed of atomic layers held together by van der Waals forces rather than strong covalent bonds. This weak interlayer interaction allows for the easy exfoliation of individual layers, ((51),(52)). These interactions not only result in the formation of polymorphs with distinct stacking sequences, but also the facilitation of the exfoliation and interlayer stacking of various TMDs for the purpose of the development of TMD-based heterostructures(53)

One of the most significant impacts of interlayer bonding is observed in the mechanical properties of 2D materials. For instance, graphene, a single layer of carbon atoms arranged in a hexagonal lattice, exhibits extraordinary strength and flexibility due to its robust in-plane covalent bonding(32). However, the overall mechanical integrity of stacked graphene layers is influenced by the weaker interlayer van der Waals interactions, which can affect the material's response to external stresses and strains.

Interlayer bonding also influences the electronic properties of 2D materials. In multilayer graphene, for example, the interaction between layers can lead to changes in electronic band structure, resulting in phenomena such as bandgap opening or modulation(54). This effect is particularly notable in transition metal dichalcogenides (TMDs) like MoS, where the electronic band structure can vary significantly between monolayer and bulk forms(55). By controlling the stacking order and rotational alignment of layers, researchers can engineer novel electronic properties, such as the emergence of moiré patterns and flat bands, which are essential for studying correlated electron phenomena and superconductivity(56).

Interlayer bonding in 2D materials is a fundamental aspect that influences their mechanical strength, electronic characteristics, and thermal conductivity. Understanding and manipulating these interlayer interactions enable the design and optimization of advanced materials and devices with tailored properties, opening new avenues for applications in electronics, photonics, and beyond.

Chapter 3

Novel approaches in van der Waals heterostructure fabrication

3.1 The role of van der Waals in electrical memory effects in stacked PdSe₂

3.1.1 Introduction

Computer systems based on the von Neumann architecture have demonstrated unparalleled efficiency in solving intricate mathematical problems. Nevertheless, the rapid progress in big data, the Internet of Things (IoT), and artificial intelligence (AI) has brought to light substantial obstacles for conventional von Neumann computers (57), (58). These challenges encompass excessive energy consumption and sluggish processing rates, making them unsuitable for addressing progressively intricate problems. The physical separation of the central processing unit and the data memory component as characterized in the traditional von Neumann design, limits the possibility of achieving a high integration density of devices and the transfer of data between these components results in a significant energy consumption that accounts for up to sixty percent of the overall processing energy. In contrast to von

Neumann design, neuromorphic computing design which mimics the brain where both the central processing unit and the data memory component are in the same space, overcomes the limitation of von Neumann design(59).

Scanning microwave impedance microscopy (SMIM) is employed to examine the specific capacitive and resistive characteristics of orthorhombic PdSe₂ nanosheets (NSs) and NS stacks at the nanoscale. This mesoscale method serves as a connection between the behavior of individual atoms and the overall performance of larger devices (60). SMIM is a technique in atomic force microscopy where a tip at the nanoscale is used to scan a surface of a sample. SMIM not only gathers data on the topography, but also measures the local electrical properties. This is done by transmitting micro waves at around 3 GHz through a nanoscale tip that is in contact with the sample, generating a near-field electromagnetic wave. The microwave signal reflected by the probe is contingent upon the impedance of the tip-sample contact. Demodulation is used to extract data on the capacitive (SMIM-C) and resistive (SMIM-R) properties of materials at the nanoscale (61). When used in conjunction with the microwave signal, voltage spectroscopy (VS) allows for the precise measurement of capacitive and resistive properties at specific points in an area of interest, based on the applied DC voltages. The local electronic properties, such as the type and density of charge carriers, can be examined by demodulating the SMIM-C channel in relation to an extra AC voltage.

This work indicate that NSs demonstrate memcapacitive behavior and resistive switching, which may be altered by stacking NSs, and NSs can display either n-type or p-type behavior with different levels of inversion in vertical geometries. By stacking n- and p-type nanosheets (NSs), the inversion can be tailored, presenting another way of modulating the memcapacitance.

3.1.2 Methods

The bulk PdSe₂ single crystal was manufactured using a self-flux approach. Thin flakes of PdSe₂ were obtained by exfoliating a bulk PdSe₂ single crystal onto a 50 nm Au substrate shown in Figure 3.1. The exfoliation process involved the use of Nitto SPV blue tape. After exfoliation, the various thin flakes of PdSe₂ were stacked on other flakes with different thicknesses using the dry transfer method to ensure a clean interface. We avoided the use of gold etchant by exfoliating first directly on gold substrate before the dry transfer process.

3.1.3 Results and discussion

We examine multiple PdSe₂ nanosheets (NSs) with thicknesses ranging from 15 nm to 60 nm in Figure 3.2. Scanning microwave impedance microscopy (SMIM) signals, specifically SMIM-C and SMIM-R, display similar responses within these NSs and their stacked regions. However, dC/dV (differential capacitance-voltage) measurements reveal distinct local electronic properties between the NSs and the substrate (). The dC/dV amplitude peaks at NSs that are 15 nm, 20 nm, and 31 nm thick, indicating different charge carrier concentrations compared to the 45 nm thick NS and the overlap area of 15 nm and 45 nm sheets, highlighted by white dashed lines in Figure 3.2.

Typically, a lower dC/dV signal corresponds to higher charge carrier concentrations, but the interpretation is complex due to the non-monotonic nature of dC/dV signals. Factors like shifts in flat band voltage and series resistance can influence the signal. Generally, both heavily doped and insulating materials show low dC/dV responses, with the signal peaking at certain concentrations (10^{17} - 10^{18} atoms/ cm³) and decreasing at higher or lower concentrations. Additionally, dC/dV amplitude signals vary for n-type and p-type carriers at the same concentration.

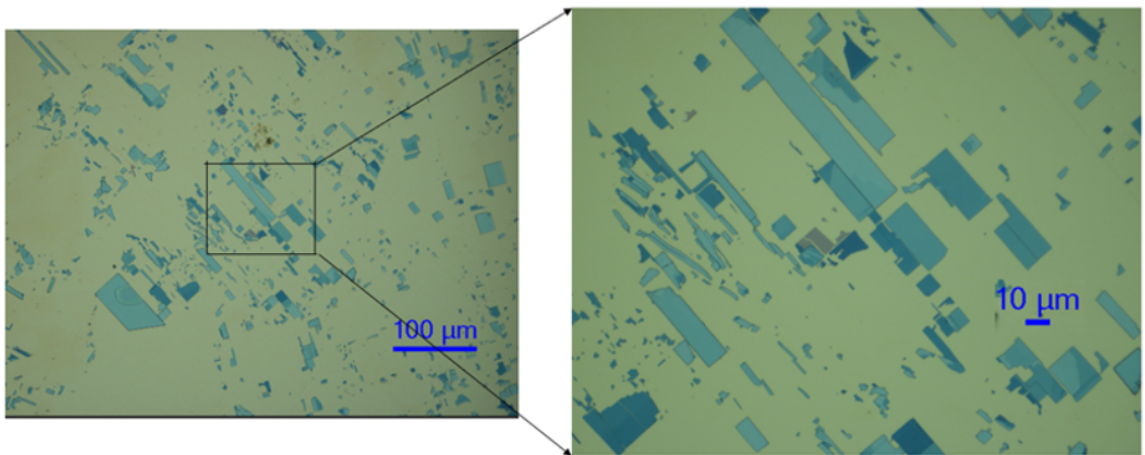


Figure 3.1: Dry transfer of PdSe₂ on a 50 nm gold substrate

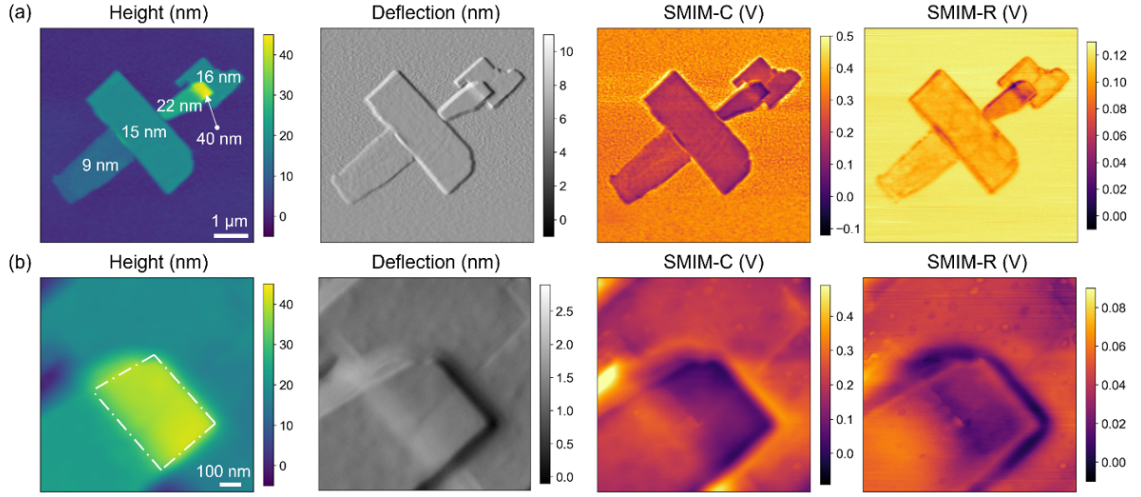


Figure 3.2: Height and deflection images showing the sample topography. The white, dashed lines in the height image indicate the area where two NSs are stacked. SMIM-C and SMIM-R images corresponding to the local capacitance and resistivity. dC/dV amplitude and phase data shows the concentration and polarity of charge carriers and dR/dV amplitude and phase indicates how the resistivity changes in magnitude and direction as a function of an applied AC voltage

Capacitance-voltage curve analysis confirms that higher dC/dV signals correlate with lower charge carrier concentrations, and vice versa. The dC/dV phase image shows opposite values for areas with high and low concentration NSs, indicating different types of active charge carriers, even without DC voltages.

Stacking alters the SMIM-R signals, resulting in distinct and separate remanent values for the stack. Single nanosheets (NSs) display hysteresis in the behavior of SMIM-R loops primarily when subjected to negative voltage. The resistivity decreases as the voltage approaches -2 V and returns to its starting condition before reaching 0 V. PdSe_2 that has been exposed to electron-beam irradiation exhibits resistive switching as a result of conductive filaments emerging specifically along the boundaries between its grains, which is not observed in non-irradiated PdSe_2 . No filaments are observed in nanoscale tests using thick non-irradiated PdSe_2 NSs, due to the utilization of a TiW top electrode and an Au bottom electrode. Scanning tunneling microscopy uncovers that the process of resistive switching is caused by the switching of defect states and the migration of Se vacancies. Nanoscale experiments indicate that p-type charge carriers exhibit a more pronounced accumulation, resulting in a dominant inversion branch in the capacitance-voltage curve and displaying p-type features.

3.1.4 Summary and Conclusion

We employed nanoscale Scanning Microwave Impedance Microscopy (SMIM) techniques to investigate the properties of PdSe_2 nanosheets (NSs) and their arrangements. Our findings indicate the presence of memcapacitive behavior and resistive switching, notably in NS stacks. Although the macroscopic data indicated the presence of both n-type and p-type properties, we observed p-type behavior at the nanoscale level. The stacking of n- and p-type NSs modifies the behavior of inversion and depletion, hence altering memcapacitance and memresistive effects. Identifying

local variations is essential for optimizing device performance, and the identified patterns can be applied in the design of neuromorphic hardware components.

3.2 Polymer-Free Method of transfer of graphene

3.2.1 Introduction

Chemical vapor deposition (CVD) manufacture of large-area graphene and other two-dimensional materials on typical growth substrates has been the subject of numerous attempts, which have ultimately led to a breakthrough in this field. Nevertheless, a significant obstacle has surfaced in the form of the absence of dependable after-growth transfer techniques for the layering of two-dimensional membranes onto arbitrary substrates for the purpose of large-scale technological applications. At the moment, the most significant problems that are related with the transfer of two-dimensional materials are caused by cracks, wrinkles, and interfacial contaminants that are formed during the transfer process. These characteristics limit the homogeneity and electronic performance of the material, such as carrier mobility.

In most cases, the removal of supporting polymer coatings, such as poly (methyl methacrylate) (PMMA), is insufficient and necessitates the application of severe chemical treatments. As a result, the removal process results in the production of organic waste solvents and leaves inevitable contamination on surfaces, in addition to metals and etchant residues in etching-based delamination, which leads to a decrease in the quality of graphene. Techniques that do not need the use of polymers are effective in preventing contamination; nevertheless, they are not suitable for applying to vast areas. For this reason, there is a significant demand for procedures that do not require the utilization of organic solvents and that are capable of ensuring contamination-free transfer.

3.2.2 Methods

A polymer-free technique was recently developed. It employs the use of polymer which is spin coated on clean silicon substrate and is heated at 100 °C for 5 minutes. The polymer is then peeled off from the substrate and perforated at the center with a diameter of 2-3 mm. The perforated polymer is placed on the graphene grown on copper and heated at 90 °C for 10 minutes for good adhesion. Finally, it is etched using FeCl_3 and rinsed in DI water. The schematic steps and results are shown in Figure 3.3.

3.2.3 Result and Discussion

The optical microscope, SEM as shown in Figure 3.4 and Raman spectroscopy as shown in Figure 3.5 are used to carefully examine the quality of the transferred materials. Comparing graphene transferred using PMMA assisted transfer and this new method, we confirmed that there are less residues as seen the SEM image. Numerous more 2D material systems grown on various substrate types can be developed using this technique.

3.3 PdSe_2 encapsulation with graphene

3.3.1 Introduction

Transition Metal Dichalcogenides (TMDs) exhibit a variety of phases and phase transitions, which can significantly alter their electronic, optical, and structural properties. Understanding these phase transitions is crucial for potential applications in electronics, optoelectronics, and other advanced technologies (62). For instance, MoS_2 can change from the semiconducting 2H phase to the metallic 1T phase through chemical doping, such as lithium intercalation. This transition significantly alters its electronic and catalytic properties. MoTe_2 is known for its reversible phase transition

between the 2H and 1T' phases upon thermal cycling (63). This makes it a candidate for phase-change memory applications while WS₂ and WSe₂ exhibit phase transitions under strain or doping, which can be utilized to engineer their electronic and optical properties for specific applications. Most TMDCs exist in 1T Phase is a metallic phase where the transition metal atoms are octahedrally coordinated by the chalcogen atoms. It is less stable and can transition to other phases under certain conditions. 2H Phase is a semiconducting phase where the transition metal atoms are trigonal prismatic coordinated by the chalcogen atoms. It is the most stable and commonly observed phase for many TMDs. 3R Phase is phase has a rhombohedral structure and is another semiconducting phase. It is less common but still significant in some TMDs. 1T' and 1T'' Phases are distorted 1T phases can exhibit topological and superconducting properties, adding to the functional diversity of TMDs (64). We investigate the phase transition of PdSe₂ under irradiation at the atomic scale. To achieve this It, therefore, required a graphene-PdSe₂-graphene system.

3.3.2 Methods and Approaches

Creating a heterostructure of PdSe₂ encapsulated with graphene at both the top and bottom involves a hybrid of the wet and dry transfer methods. The interface between the top graphene-PdSe₂ and PdSe₂- graphene was confirmed clean using the TEM analysis. This required a heterostructure of graphene-PdSe₂-graphene with a clean interface. The procedure involves the exfoliation of PdSe₂ using the gold-assisted method, and the PdSe₂ flakes were transferred to the CVD-grown graphene/copper. Afterward, a separate graphene/Cu was spin-coated with PPC at 3000 rpm, etched with FeCl₃, and rinsed in DI water a minimum of three times. The PPC-graphene film is placed on the PdSe₂/graphene/Cu and is gently heated first at 60 °C for 10 minutes and then at 90 °C for 15 minutes to enhance adhesion between the PPC-graphene and PdSe₂-graphene-Cu.

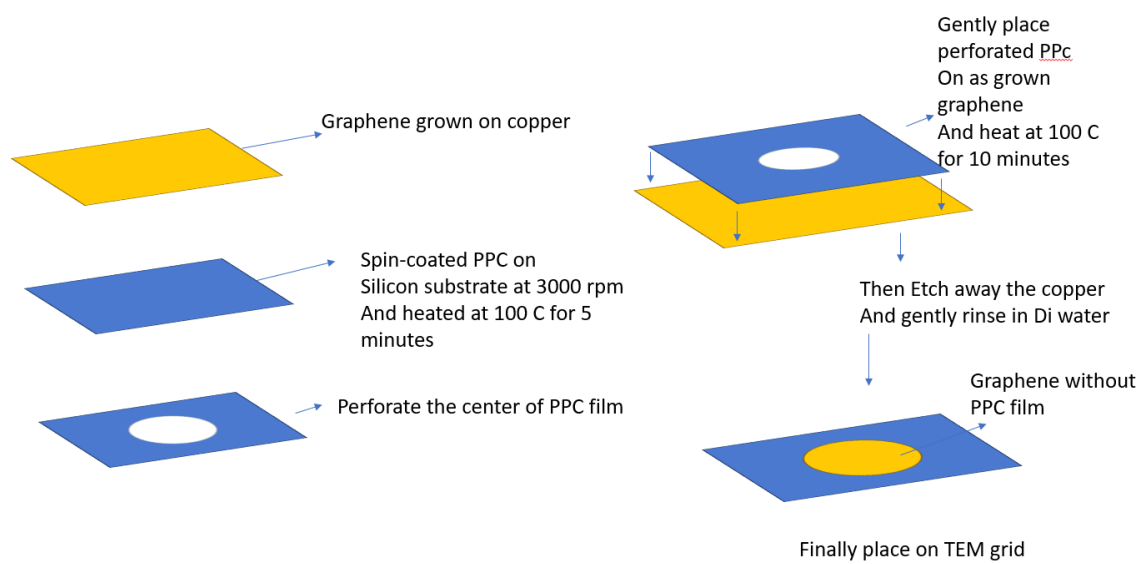


Figure 3.3: Procedure for polymer-free transfer of graphene

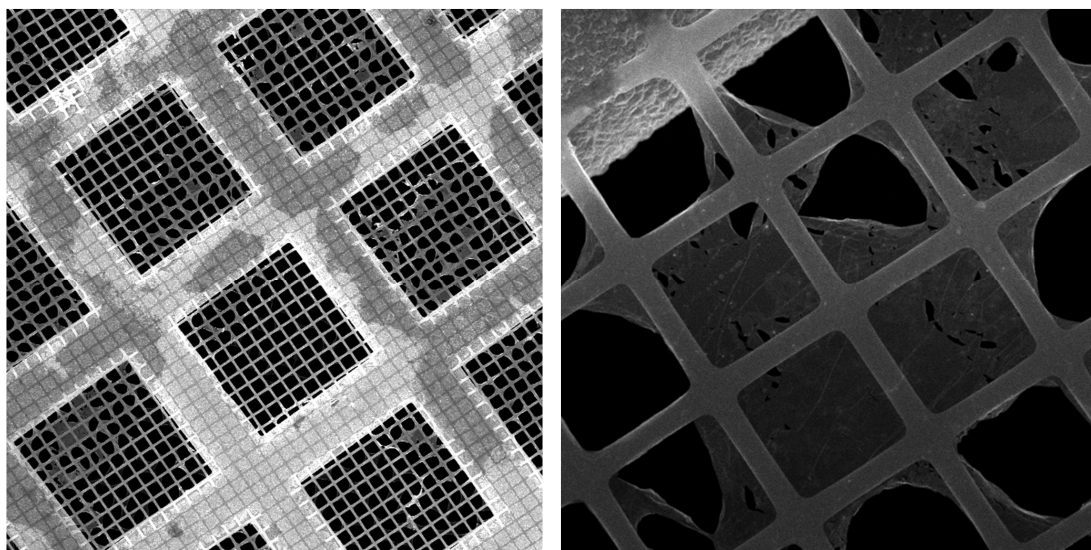


Figure 3.4: Polymer-free transferred graphene on TEM grid

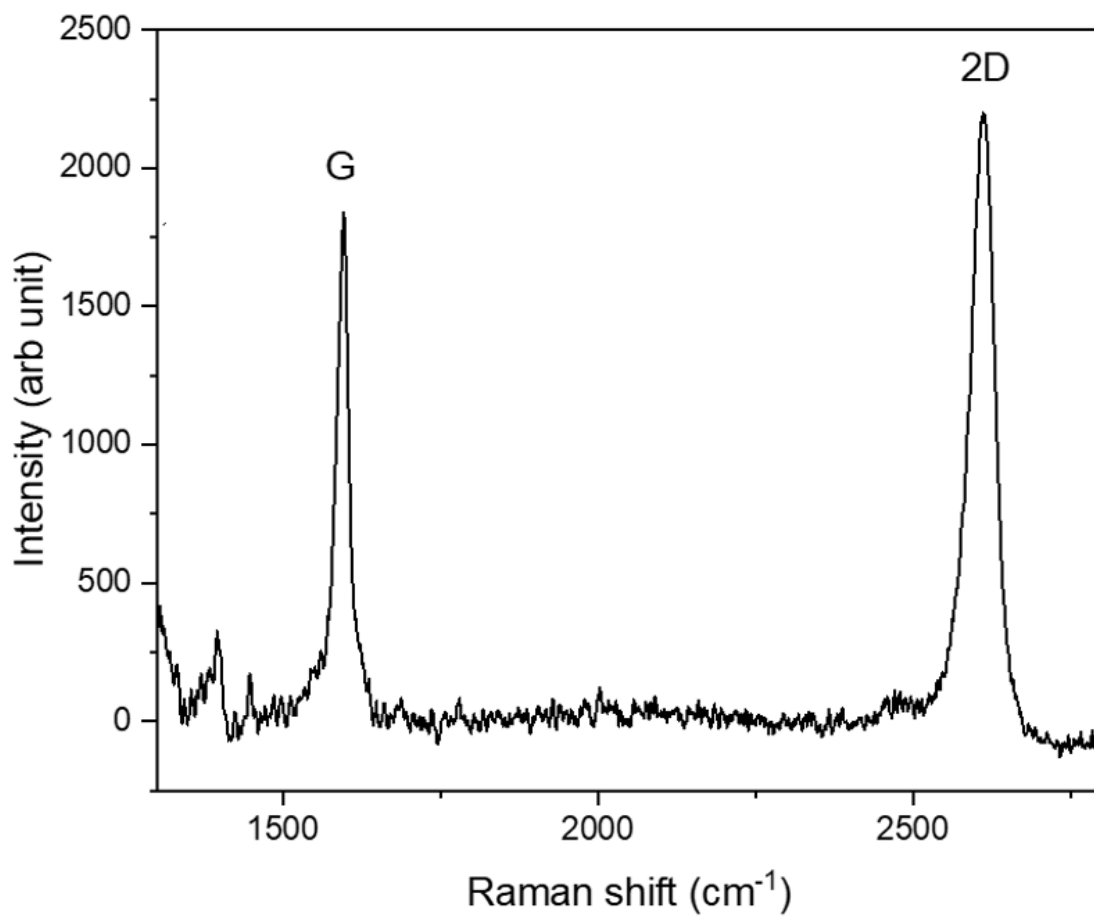


Figure 3.5: Raman measurement of suspended graphene after transfer

The PPC-graphene-PdSe₂-Cu is placed gently on FeCl₃ to etch away the bottom graphene, leaving PPC-graphene-PdSe₂-graphene. Place the PPC-graphene-PdSe₂-graphene on the TEM grid and heat it at 100 °C for 5 minutes to ensure good adhesion. The top PPC is removed by dissolving with chloroform for 2 hours. Figure 3.6 shows a schematic diagram of the procedure and Figure 3.7 shows the corresponding optical Images of each step in Figure 3.6.

3.3.3 Results and Discussion

We present a PdSe₂ flake that has undergone a gradual and incremental rise in laser power. Figure 3.8 shows the SEM image of the PdSe₂ sandwiched with graphene. Figure 3.9 shows the clean graphene and PdSe₂ flakes before laser irradiation. we manually controlled the laser by turning it on with a continuous power output of about 80 V and subsequently turning it off. By increasing the laser power, we successfully induced a phase transition in the PdSe₂ flake. Every image was obtained while the laser was not in operation and the sample was at the ambient temperature. By employing this method, we can systematically induce a slow transition in phase, effectively immobilizing the transformation for subsequent analysis. We observed a phase change from PdSe₂ to Pd₂Se₃ then to Pd₁₇Se₁₅ as shown in Figure 3.10.

3.3.4 Summary and Conclusion

In summary, we have successfully shown that layered PdSe₂ can undergo a phase change to metallic phases Pd₂Se₃ and Pd₁₇Se₁₅ when exposed to laser irradiation. Using STEM imaging, we observed the phase transformation of PdSe₂ sandwiched between layers of graphene following each pause in laser irradiation. This utilization of laser-induced phase transition is expected to facilitate the manufacture of devices as needed.

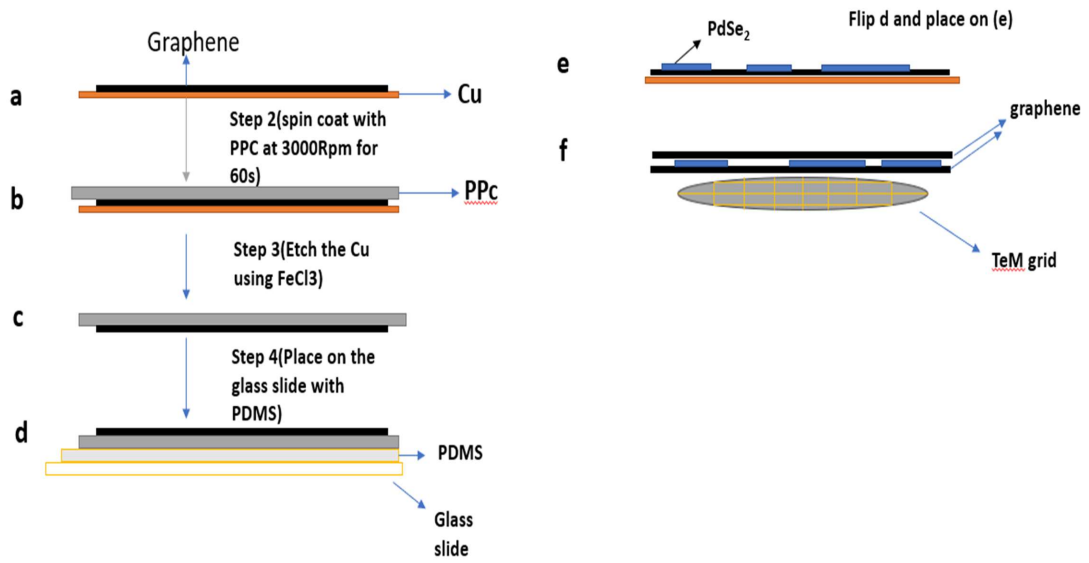


Figure 3.6: schematic diagram showing the procedure for the heterostructure graphene-PdSe₂-graphene fabrication

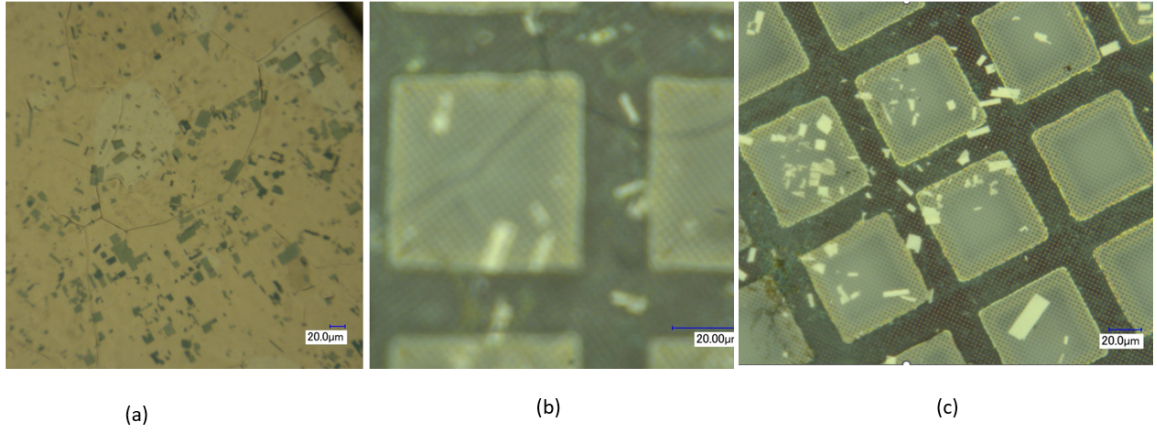


Figure 3.7: (a) Optical image of PdSe₂ on CVD grown Graphene on copper substrate using the dry transfer method (b) Optical image of PPC/graphene transferred on PdSe₂/Graphene after etching Cu substrate (c) Optical image of graphene/PdSe₂/graphene on TEM grid after dissolving PPC

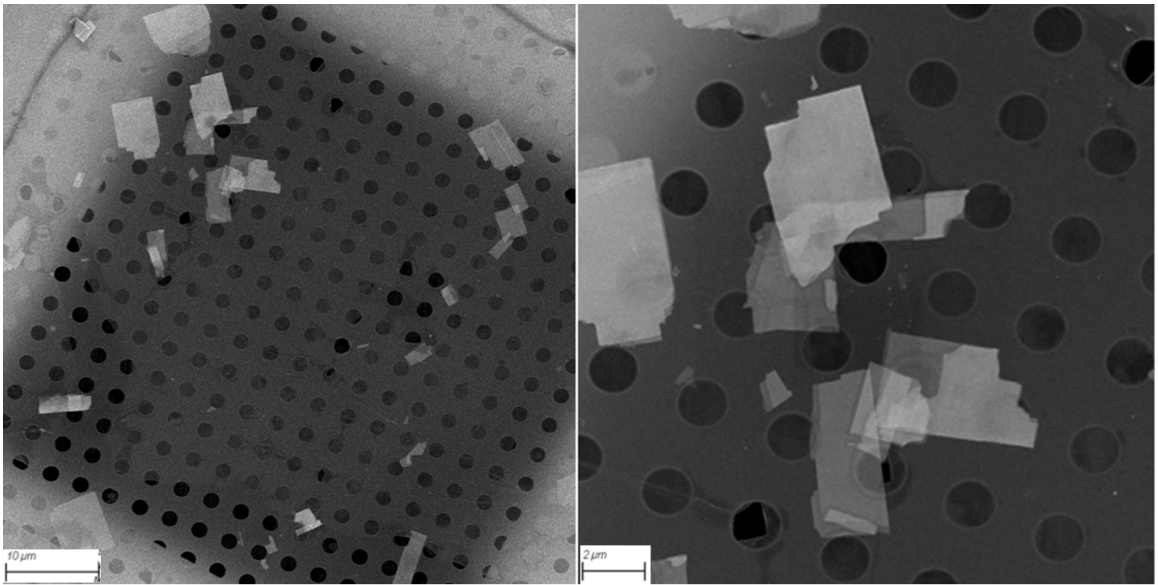


Figure 3.8: SEM image graphene-PdSe₂-graphene

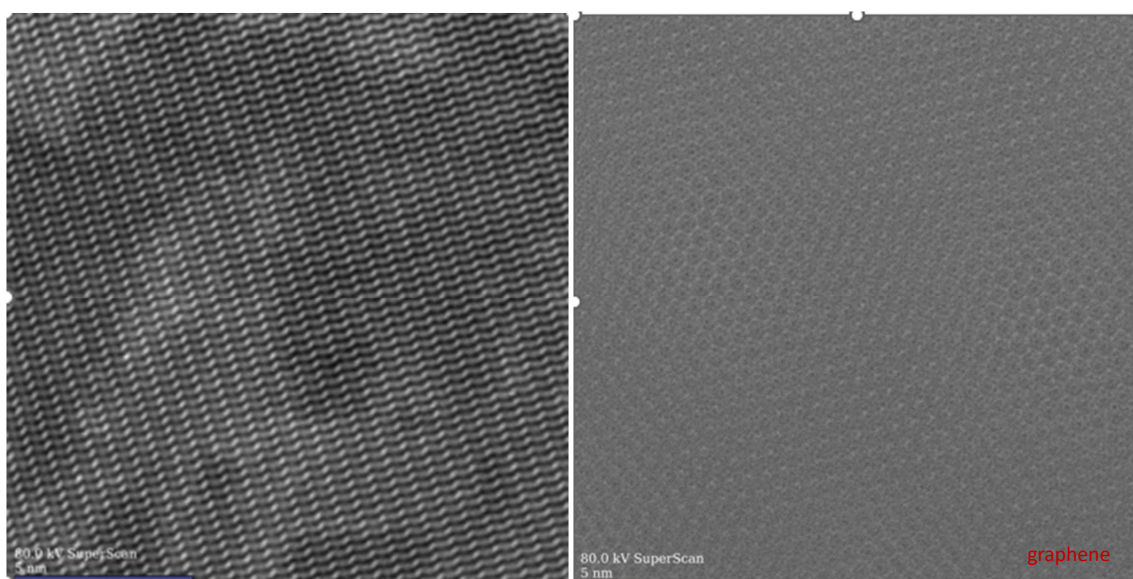


Figure 3.9: STEM images of PdSe₂ and graphene before laser irradiation

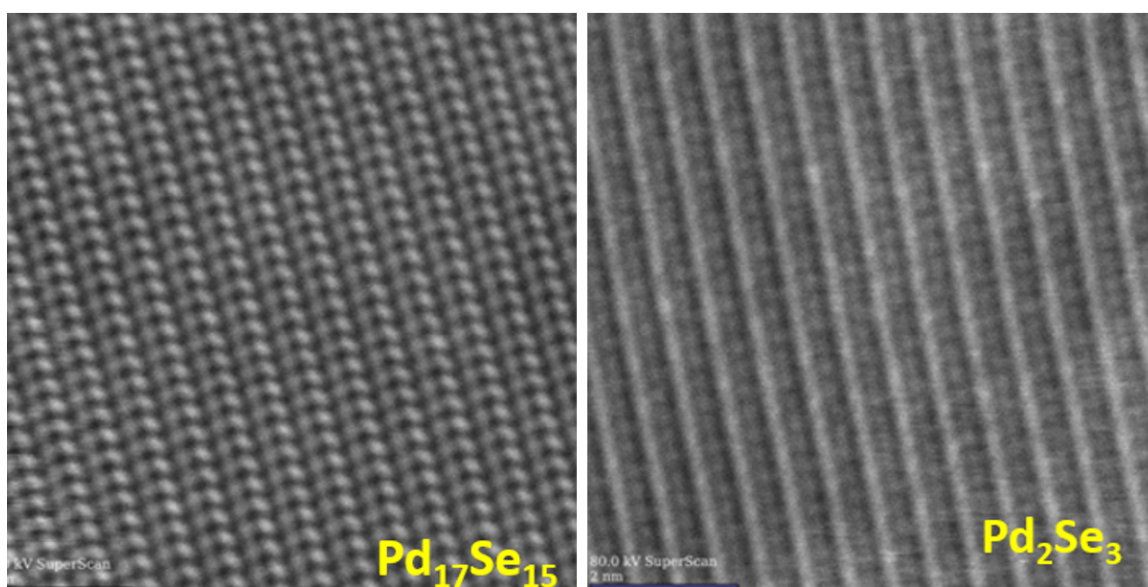


Figure 3.10: STEM images of Pd_2Se_3 and $\text{Pd}_{17}\text{Se}_{15}$ after laser irradiation of PdSe_2 sandwiched graphene

3.4 Preparation of 2D moiré

The emergence of two-dimensional (2D) materials has revolutionized materials science, offering unprecedented opportunities to explore new physical phenomena and develop innovative applications (65). Among these developments, 2D moiré superlattices have attracted significant attention due to their ability to host a variety of novel electronic, optical, and mechanical properties (66). Moiré patterns arise when two or more layers of 2D materials are stacked with a small twist angle or lattice mismatch, leading to a periodic superlattice that can significantly alter the material's properties.

The preparation of 2D moiré superlattices involves several key steps, including the selection of appropriate 2D materials, precise stacking and alignment, and careful characterization to ensure the desired moiré patterns are achieved (67). The most commonly used materials for creating moiré superlattices are graphene, transition metal dichalcogenides (TMDs) such as MoS_2 and WS_2 , and hexagonal boron nitride (h-BN).

The first step in preparing 2D moiré superlattices is the selection of high-quality monolayers of the desired 2D materials. These monolayers can be prepared using various methods such as mechanical exfoliation, chemical vapor deposition (CVD), or liquid-phase exfoliation. Mechanical exfoliation, while often yielding high-quality samples, is limited in scalability. CVD, on the other hand, allows for the growth of large-area monolayers, making it suitable for practical applications. Once the monolayers are prepared, the next step is to stack them with precise control over the twist angle or lattice alignment. This can be achieved using techniques such as dry transfer, where the monolayers are sequentially picked up and transferred onto each other using a polymer stamp or wet transfer where CVD grown materials which are difficult to pick up using dry transfer method, are randomly placed Controlling the twist angle to a desired value, often within a few tenths of a degree, is crucial

for achieving the desired moiré superlattice. Advanced techniques such as tear-and-stack, where a single monolayer is torn into two pieces and one piece is rotated before stacking, can provide fine control over the twist angle (68).

In addition to 2D materials and stacking order, the twist angle, a unique characteristic, is recognized as a new component of structural flexibility. This parameter has demonstrated its worth in fine-tuning band topologies and electrical characteristics, specifically in twisted bilayer graphene (69). Different angles of twisting result in moiré patterns with specific periods, giving rise to unique properties and new phenomena in twistrionics (70). One example is the discovery of unconventional superconductivity in the magic-angle graphene system, which has attracted considerable interest (71). This section discusses preparing the moiré using a newly developed method. This method involves the use of a very thin film of gold to transfer CVD-grown samples by avoiding the usual etching procedure, which introduces contamination. The CVD-grown samples are picked up using a freshly evaporated 10 nm gold film spin-coated with PPC. These flakes are placed on another CVD-grown flake and heated for 20 minutes. Finally, the PPC is peeled off leaving a high density of moiré. The procedure for the new approach is shown in Figure 3.11, and the result is shown in Figure 3.12.

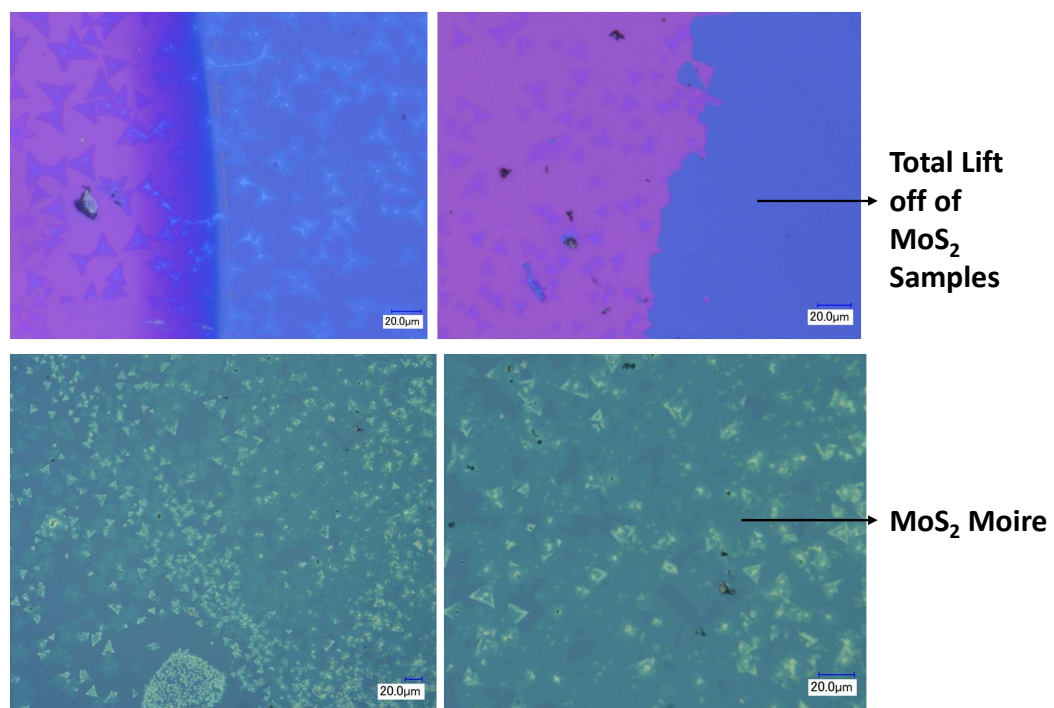


Figure 3.11: procedure for fabricating MoS₂ moiré using gold

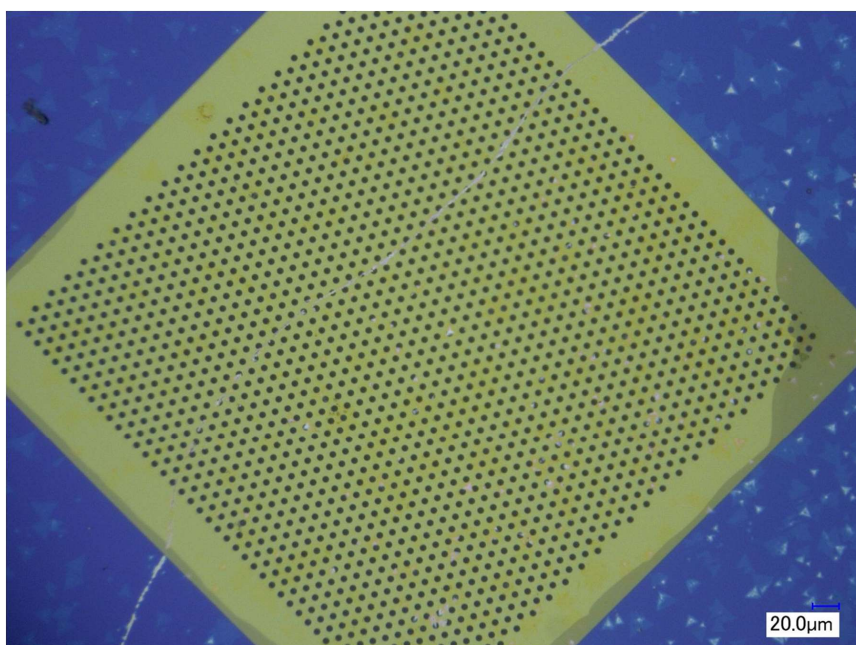


Figure 3.12: MoS₂ moiré on grid

Chapter 4

The effect of encapsulation on excitons in GaSe

4.1 Introduction

The atomically thin 2D TMDCs semiconductors have emerged over time as the ideal platform to investigate exciton due to their reduced dielectric screening and indirect-direct bandgap change from bulk to monolayers (72). Their exciton-dominated optical properties make them suitable for light-emitting and photonic devices (73).

GaSe, an inherently unstable two-dimensional material, exhibits semiconducting properties. The GaSe monolayer has a thickness of 0.98 nm and a lattice constant of 0.374 nm (74). It is composed of a sequence of four atoms arranged as Se-Ga-Ga-Se. Intralayer planes are held together by a strong covalent connection, while interlayer planes are held together by weak van der Waals (vdW) bonding (75).

Gallium Selenide (GaSe) is a layered semiconductor material that has garnered significant attention due to its unique electronic and optical properties. One of the key features of GaSe is the presence of band-gap excitons, which play a crucial role in its optoelectronic behavior. In GaSe, these excitons are particularly interesting because

of the material's direct band-gap nature and its layered structure, which influences the excitonic properties. (76)

The band-gap of GaSe is approximately 2.02 eV at room temperature, which places it in the visible range of the electromagnetic spectrum. This band-gap is direct, meaning that the maximum of the valence band and the minimum of the conduction band occur at the same momentum value. This property enhances the efficiency of light absorption and emission processes, making GaSe a promising candidate for optoelectronic applications such as photodetectors, light-emitting diodes, and solar cells (76). The formation of excitons in GaSe is facilitated by its relatively high dielectric constant and effective masses of electrons and holes, which result in strong Coulomb interaction between the charge carriers. The exciton binding energy in GaSe is significant, on the order of several tens of meV, which allows these excitons to exist even at room temperature. This is in contrast to many other semiconductors such as MoS₂, WS₂ and WSe₂ where thermal energy at room temperature is sufficient to ionize excitons. (74). The reduced dimensionality in GaSe also leads to an increase in the oscillator strength of excitonic transitions, making the excitonic effects more pronounced in optical spectra. Several experimental studies of GaSe have revealed sharp excitonic absorption peaks in the optical absorption spectrum. (77) (78) (72). While there are lots of investigation on the excitonic behaviour in GaSe ((79), (80)). There is a no study of the emission properties of encapsulated GaSe. This work presents an analysis of the behavior of excitons in GaSe encapsulated with hBN with regard to variations in temperature, intensity, and thickness. Additionally, it examines the impact of hBN encapsulation on these variations.

4.2 Methods

GaSe single crystals were produced employing the chemical vapor transport technique. The precursor materials utilized for the synthesis are Ga (99.96 percent purity) and

Se (99 percent purity). The molar ratio of Ga and Se was combined with iodine (I) as a transport agent in a stoichiometric ratio of 1:1. Once the components were thoroughly blended, the powder was enclosed in a quartz tube of 25 cm in length and 6 cm in diameter. The tube was then placed under a vacuum pressure of 5×10^4 Torr. The temperature for growth T was adjusted to 800 C in the growth zone and 850 °C in the reaction zone for a duration of 120 hours. Afterward, it was cooled down to room temperature in a continuous way. By adhering to a systematic approach to the crystallization technique, a superior-grade crystal formed in the low-temperature section of the quartz tube. Gase Bulk was exfoliated using the scotch tape in the glove box and was encapsulated with hBN partially as shown in Figure 4.1 using dry transfer method.

4.3 Results and Discussion

4.3.1 Temperature dependent photoluminescence of GaSe

In this section we discuss the effect of temperature on the exciton radiative recombination of few layer GaSe and the emission properties of strained GaSe. We identified three distinct peaks at X_1 565 nm (2.19 eV), X_2 575 nm(2.15 eV) and X_B 620 nm(1.99 eV) at room temperature. X_1 originates from the direct band gap, X_2 originates from the indirect band gap. When the temperature (T) is increased from 4 to 295 K, the X_1 peak undergoes a red-shift, moving from about 570 nm (2.17 eV) to 565 nm (2.19 eV). Similarly, the X_2 peak red-shifts from approximately 1.978 eV, and the X_B peak red-shifts from approximately 2.033 to 1.915 eV. The photoluminescence spectra of the free, bound, and defect states all exhibited redshifts, resulting from a band gap narrowing, which we observed throughout a broad temperature range ranging from 4k to 295K. The band gap narrows due to the expansion of the lattice in-plane constant and the rise in the interaction between electrons and phonons (81).

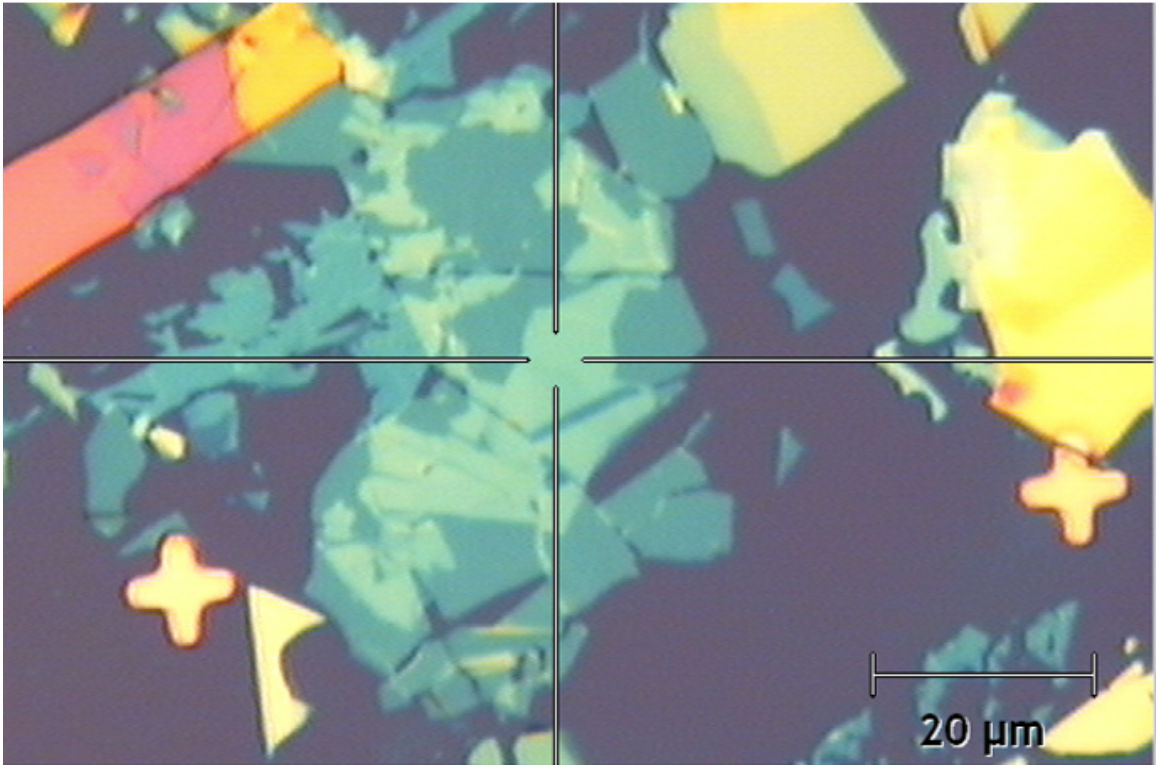


Figure 4.1: Optical Image of exfoliated few-layer GaSe encapsulated with hBN on SiO₂ substrate

When the spectra of open and encapsulated bulk GaSe were examined, we found that the encapsulated GaSe had distinct peaks, whereas the open GaSe had a broad spectrum. Both spectra were then deconvoluted using the Lorentz deconvolution technique. Bandgap redshift is due to the thermal expansion in-plane lattice constants, change in the bonding length, electron-phonon interactions, and phonon-phonon interactions (82). Redshifts were also observed in both free and bound exciton, with the redshift of defect states being more pronounced in certain instances, as shown in . The photoluminescence response in the bulk GaSe and thin layers are shown in Figure 4.2 and Figure 4.3.

4.3.2 Defect-related excitonic emission in GaSe

The optical properties of 2D materials are influenced by defects that arise due to diverse synthesis techniques, resulting in various forms and impacts (83). Multiple significant studies have demonstrated the influence of defects on the Photoluminescence of 2D materials (84). The presence of several inherent lattice defects, such as vacancies, substitutional impurities, adatoms, and grain boundaries, is common in transition metal dichalcogenides (TMDCs) (85). These defects are places where excitons, electrons, and holes can be trapped. Defects impact the carrier concentration, exciton dynamics, and band topologies (86), (87), (88). As a result, this has an impact on the processes of exciton-based radiative recombination and non-radiative recombination. We observe the presence of many defects arising from the increase in the photoluminescence (PL) intensity. Defect states in GaSe arise from strain effects caused by mechanical exfoliation and are particularly noticeable at low temperatures and the encapsulated region as shown in Figure 4.4

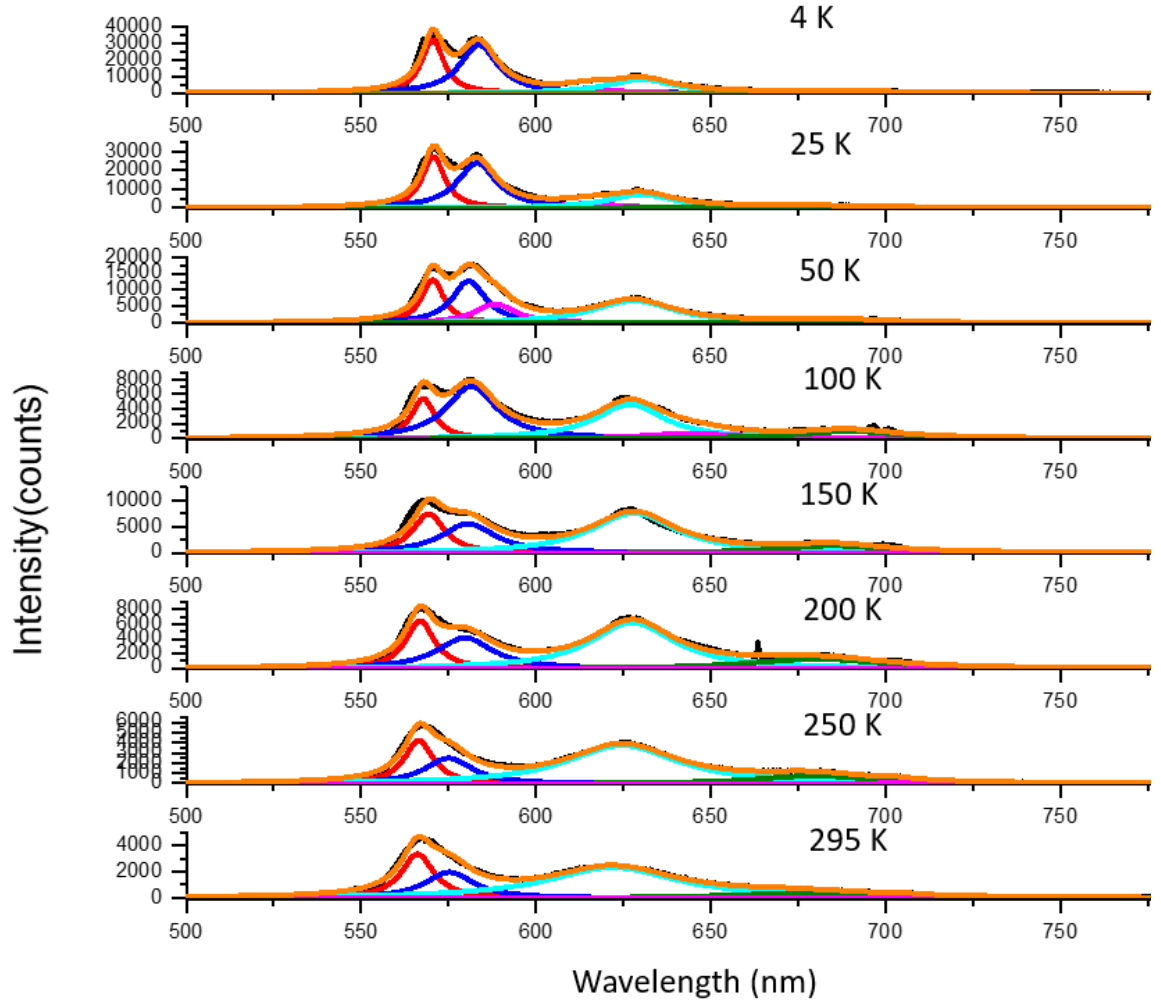


Figure 4.2: Temperature-dependent -PL spectra of the 2L GaSe flake excited at 532 nm and fitted by six Lorentzian functions related to the free Exciton, Bound exciton and defect state

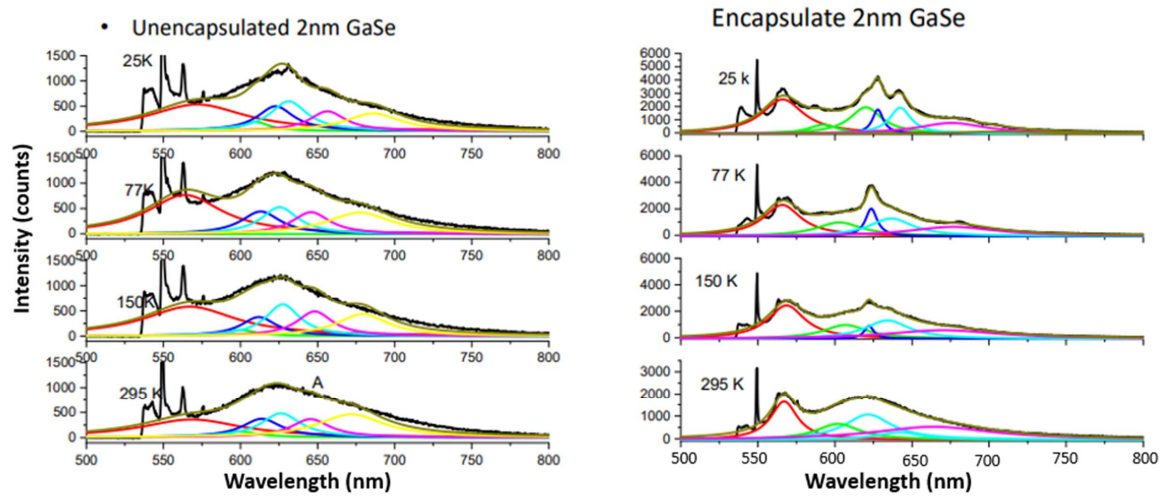


Figure 4.3: Comparison of temperature-dependent photoluminescence of encapsulated and unencapsulated few layer GaSe

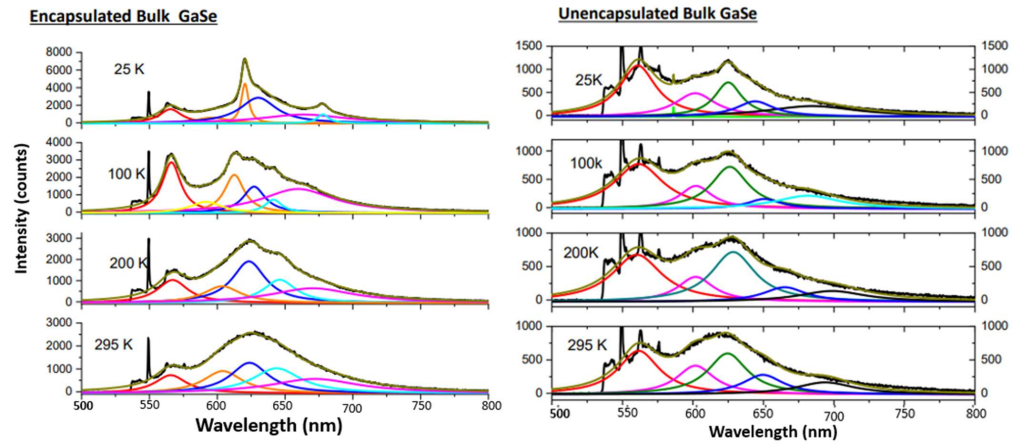


Figure 4.4: Comparison of temperature-dependent photoluminescence of encapsulated and unencapsulated Bulk GaSe

4.3.3 The effect of encapsulation on excitons in GaSe

Encapsulation of Gallium Selenide (GaSe) significantly impacts its excitonic properties, which are crucial for its performance in optoelectronic applications. Encapsulation refers to the process of covering GaSe with a protective layer, typically made from materials like hexagonal boron nitride (h-BN) or other two-dimensional (2D) materials as shown in Figure 4.1

One primary effect of encapsulation on GaSe is the reduction of surface oxidation and contamination. GaSe, being a layered semiconductor, has a large surface area that is prone to degradation when exposed to air. This degradation can introduce surface states that trap excitons, reducing their recombination efficiency and quenching photoluminescence (89). By encapsulating GaSe, the surface is protected from environmental degradation, preserving the intrinsic excitonic properties and enhancing the material's stability and optical performance. encapsulation can lead to strain effects due to lattice mismatches between GaSe and the encapsulating material (80). This strain can modify the band structure of GaSe, leading to shifts in the excitonic energy levels. For instance, tensile or compressive strain can alter the bandgap and exciton binding energy, thereby tuning the photoluminescence wavelength and intensity (90).

Furthermore, encapsulation can improve the thermal stability of GaSe. This is particularly important for applications where the material is subjected to varying temperatures. Enhanced thermal stability ensures consistent excitonic behavior, which is critical for reliable device performance ((91), (92)). The photoluminescence (PL) spectra of an ML-TMD on a silicon substrate exhibit a rather large peak that is caused by the recombination of excitons through radiation; Monolayer TMDCs exhibits a PL peak that has a full-width at halfmaximum (FWHM) that is typically between 45 and 50 or 75 meV when it is observed on a silicon substrate. As opposed to this, the PL spectrum of a hBN/MoS₂/hBN exhibits a similar PL peak that has a substantially smaller full width at half maximum (FWHM) of around

22 meV. This significant reduction in FWHM is mostly due to the suppression of inhomogeneous broadening that is caused by substrates. We also observed similar effect in hBN encapsulated GaSe with a substantial reduction in the full-width at half maximum (FWHM) in both few-layer and bulk as shown in Figure 4.3 and Figure 4.4 respectively.

Intensity dependent photoluminescence of GaSe

The decrease in exciton intensity with increasing temperature can be attributed to thermally stimulated non-radiative recombination, which is induced by an augmentation in the electron-phonon interaction . Photoluminescence intensity was observed to increase linearly with the number of layers. There is a clear link between linear behavior and the volume of the emitting layer. Thinner flakes have more nonradiative recombination because they have more surface defects caused by strain than the emitting volume (93). This is shown in Figure 4.5. Figure 4.6 shows the PL spectra of excitons and how their peak changes with temperature. At low excitation intensities, the photoluminescence is typically dominated by excitonic recombination, where an electron recombines with a hole to emit a photon. As the excitation intensity increases, the PL intensity generally increases as well (94). However, at higher excitation intensities, the PL intensity may start to saturate or even decrease due to several factors such as non-radiative recombination, Auger recombination, or the creation of defects (81) as shown in Figure 4.7

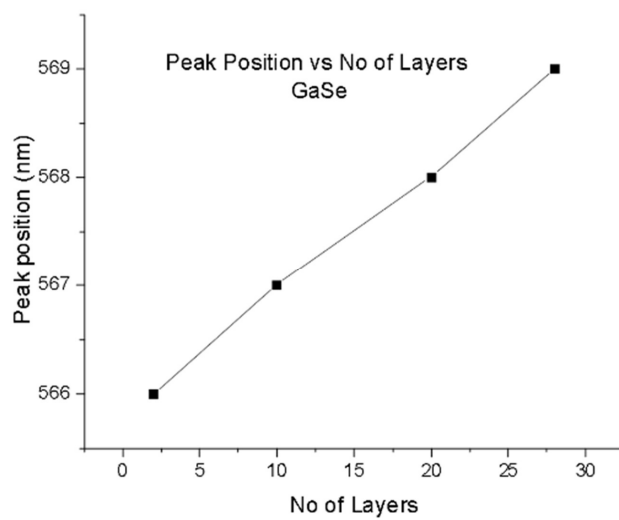


Figure 4.5: Peak position of the different Number of layers of GaSe

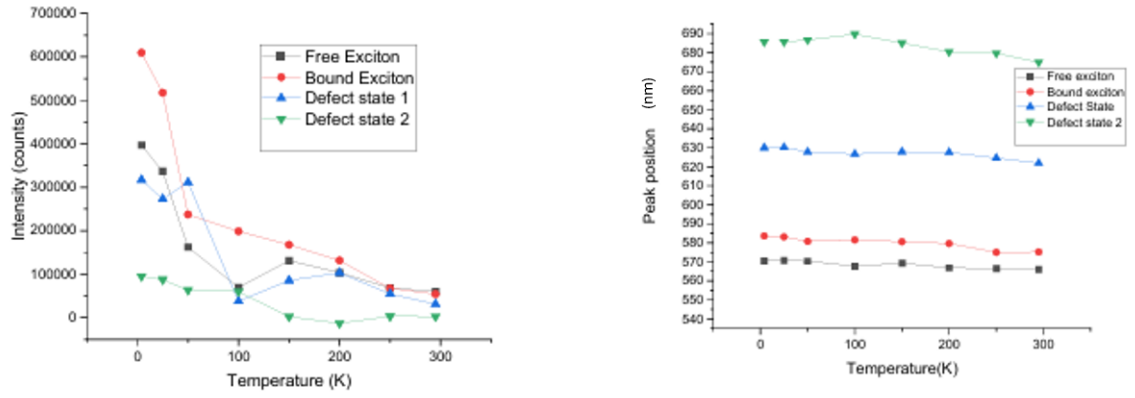


Figure 4.6: (Left side): A plot of PL spectra of different excitons at various temperatures in GaSe (Right side): Peaks of different PL spectra at various temperatures of GaSe

The behavior of the PL with varying excitation intensity can provide insights into the material's quality, defect density, and carrier dynamics. For instance, a rapid saturation of PL intensity at low excitation levels might indicate high defect density, leading to increased non-radiative recombination. Conversely, a linear or near-linear increase over a wide range of excitation intensities suggests high crystalline quality and low defect density (95).

4.4 Conclusion and Summary

We studied the dynamics of excitons in a partially encapsulated GaSe under a widely varied temperature of 4 K to 295 K. This temperature-dependent investigation conducted between 4K and 295 K reveals that the photoluminescence (PL) undergoes a red-shift as a result of a reduction in the band gap. Simultaneously, the intensity of the PL drops due to thermally induced nonradiative recombination, due to an increase in the electronphonon interaction. The latest findings expand our understanding of the different levels of excitons and deep defects in 2D GaSe. This knowledge is crucial for the future use of GaSe in nano-optoelectronics, particularly when it comes to manipulating its optical properties.

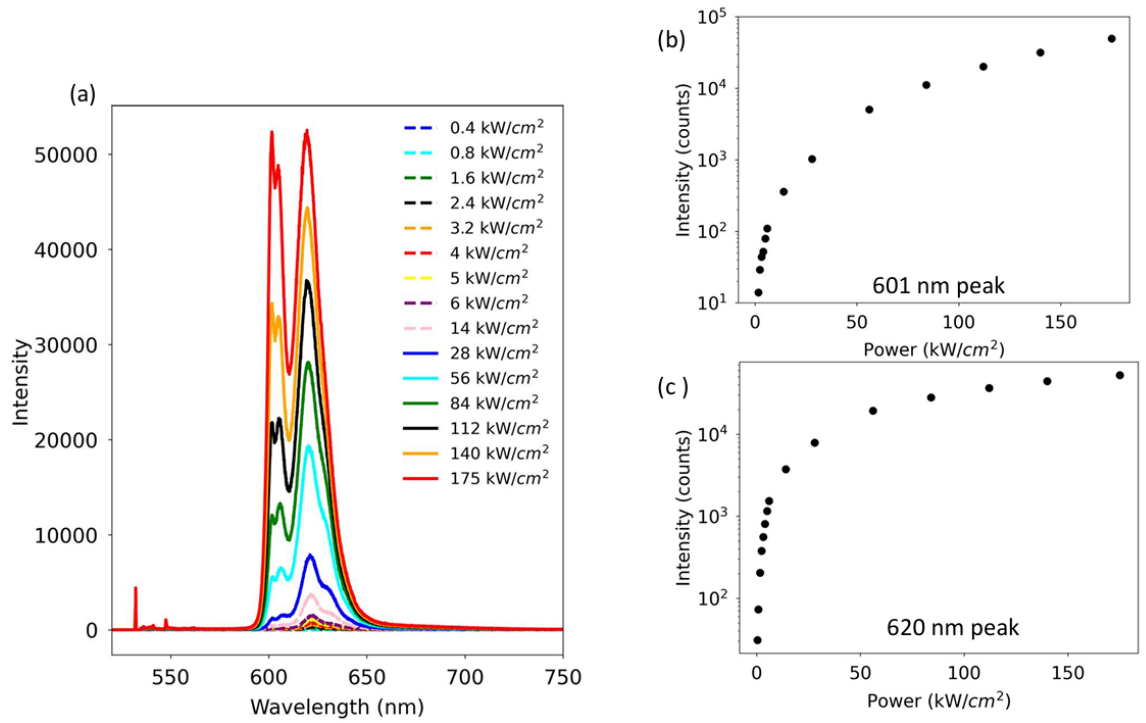


Figure 4.7: (a) Different behaviours of excitons at different excitation power (b) intensity response at 601 nm wavelength (c) intensity response at 620 nm wavelength

Chapter 5

Understanding the effect of composition on the structure and electrical property of $\text{PdSe}_{2-x}\text{Te}_x$

5.1 Introduction

Two-dimensional (2D) transition metal dichalcogenides (TMDs) have garnered considerable attention because to their diverse phase structures and intriguing features, making them particularly appealing for use in electrical and optoelectronic devices. The many polymorphs seen in Transition Metal Dichalcogenides (TMDs) frequently exhibit significantly distinct physical phenomena. The alloying technique has emerged as a diverse and stable means of manipulating the electrical structures of TMDs, which has resulted in a broadening of the potential applications for these devices. The broad applicability of transistor devices has led to substantial interest in the polymorphic phase transition in TMDs. Previous studies have successfully achieved alloying of TMDs with different phase configurations and bandgap values. Various polymorphic configurations arise from either the trigonal prismatic or octahedral coordination of the metal atoms. The stacking order of atomic planes and

potential distortions both influence the resulting configurations. The most commonly observed arrangements include: 1T (trigonal), 2H (hexagonal), 3R (rhombohedral), 1T' (monoclinic phase derived from distorted 1T), and Td (orthorhombic phase originating from distorted 1T). When it comes to TMDs, the many polymorphs frequently exhibit a wide range of radically diverse physical phenomena. Amongst the TMDs, TaSe₂ has a high degree of polymorphism, surpassing other transition metal dichalcogenides (TMDs) in terms of its polymorphic nature. For instance, there are four different Polymorphs (2H, 3R, 1T and 1T') . In 2H and 3R Polytypes, Ta can be found in Se-Ta-Se layers stacked along the c axis of the hexagonal (or rhombohedral) cell in trigonal prismatic coordination with different periodicity in their stacking order. However, in the 1T (T: trigonal) type, which is one of the other polymorphs, Ta is found in octahedral coordination in the Se-Ta-Se layers and the layer stacking along the c-axis of the trigonal cell. Within the TaSe_{2-x}Te_x system, there is coexistence of charge density wave (CDW) and superconductivity at different ranges of temperatures.

PdSe₂ typically crystallizes in a layered orthorhombic structure, whereas PdTe₂ commonly adopts a trigonal structure. The orthorhombic structure of PdSe₂ features puckered layers, resulting in strong anisotropy in its physical properties. This structure leads to unique electronic characteristics, such as high carrier mobility and anisotropic thermal conductivity, which are beneficial for electronic and thermoelectric applications (96). PdTe₂, on the other hand, with its trigonal structure, exhibits metallic behavior and hosts interesting topological properties. The difference in chalcogen atoms (Se vs. Te) leads to variations in interlayer interactions and bond strengths, further influencing their electronic structures. PdTe₂'s structure enables the existence of topological surface states (97). Therefore, these distinctive features in the structure and electronic characteristics of PdSe₂ and PdTe₂ motivate us to investigate the potential structural evolution or transformation, along with the corresponding alterations in electrical transport behavior within the PdSe_{2-x}Te_x

system. It opens new opportunities for investigating the structural evolution and changes in electronic property.

5.2 Methods and Approaches

The $\text{PdSe}_{2-x}\text{Te}_x$ crystals were produced by self-flux techniques. The Pd ingots (99.95 percent, Alfa Aesar), Se shots (99.999 percent, Alfa Aesar), and Te pieces (99.999 percent, Alfa Aesar) were mixed using the appropriate stoichiometric doping ratio, perform the process in an Ar glove box with a total moisture and oxygen content below 0.1 ppm. The source elements were inserted into a silica tube, which was subsequently sealed tightly under vacuum conditions and placed within a box furnace (98) The temperature was gradually raised to 800°C and maintained at that level for a duration of 3 days, after which the furnace was allowed to fall down to room temperature. Here we prepared few layer $\text{PdSe}_{2-x}\text{Te}_x$ alloys with different Te composition concentrations by employing the Au-assisted exfoliation method due to the strong interlayer interactions of these materials. Figure 5.1 by combining Raman spectroscopy, atomic resolution z-contrast STEM, and DFT calculation, we revealed how the structural transition and correlated optical properties changes with different Te composition in these alloys. The FET devices of different alloys were also fabricated using e-beam lithography and we observed the semiconductor to metallic transition with Te doping increasing in these alloys.

5.3 Results and Discussion

5.3.1 Optical characterization of different alloys – Raman and simulation

We confirmed using Raman spectroscopy measurements the many distinct phases that are associated with the various polymorphs that exist between PdSe_2 and PdTe_2 .

PdSe₂ which is a puckered pentagonal structure with an orthorhombic lattice as reported by oyedele (96) and PdTe₂ has recently gained significant interest due to its experimental confirmation as a type-II Dirac semimetal with space group P3m1. The Raman measurement data presented in Figure 5.2 demonstrates that the PdSe₂ orthorhombic structure is retained for values of x ranging from 0 to 0.3 in the Se rich region, However we observed a phase transition from orthorhombic to monoclinic between $x = 0.5$ and 0.8. There are three distinct peaks in the bulk phase of PdSe_{1.2}Te_{0.8}, which describes a monoclinic phase. Another phase transition from monoclinic to 1 T phase was observed between the values of $x = 0.8$ and 0.9 showing a reduction the peak points from three to two. Finally 1 T phase from $x = 0.9$ was observed down to PdTe₂ only with these two peaks red-shifting in that direction. We also compared the few layer PdSe_{2-x}Te_x system only for values of $x = 0.2, 0.5, 0.9$ and 1.0 and observed similarity in the Raman peaks between the PdSe₂ and PdSe_{1.5}Te_{0.5}), however Te $x = 0.9$ and 1 shows only two peaks as shown in Figure 5.3.

5.3.2 Structural transition in alloys by STEM

Few layers of some specific alloys of PdSe_{2-x}Te_x e.g. $x = 0.2, 0.5, 1, 2$ flakes were first prepared by mechanical exfoliation using the gold assisted method onto a SiO₂ substrate and then transferred with PPC to Quantifoil gold TEM grids using a 0.25 M KOH solution to dissolve the SiO₂ as shown Figure 2.5. The Optical Image Figure 5.4 reveals the the different spots with thick and thin flakes. Prior to STEM observation, the samples underwent baking at a temperature of 100 °C under vacuum conditions. The Nion Ultra STEM100 microscope operating at 60 kV was used to acquire the medium angle annular dark-field images (MAADF). We confirmed through STEM that PdSe_{1.8}Te_{0.2} maintains the orthorhombic structure of PdSe₂ but the Te atoms are randomly distributed, filling vacancies created by Se atoms.

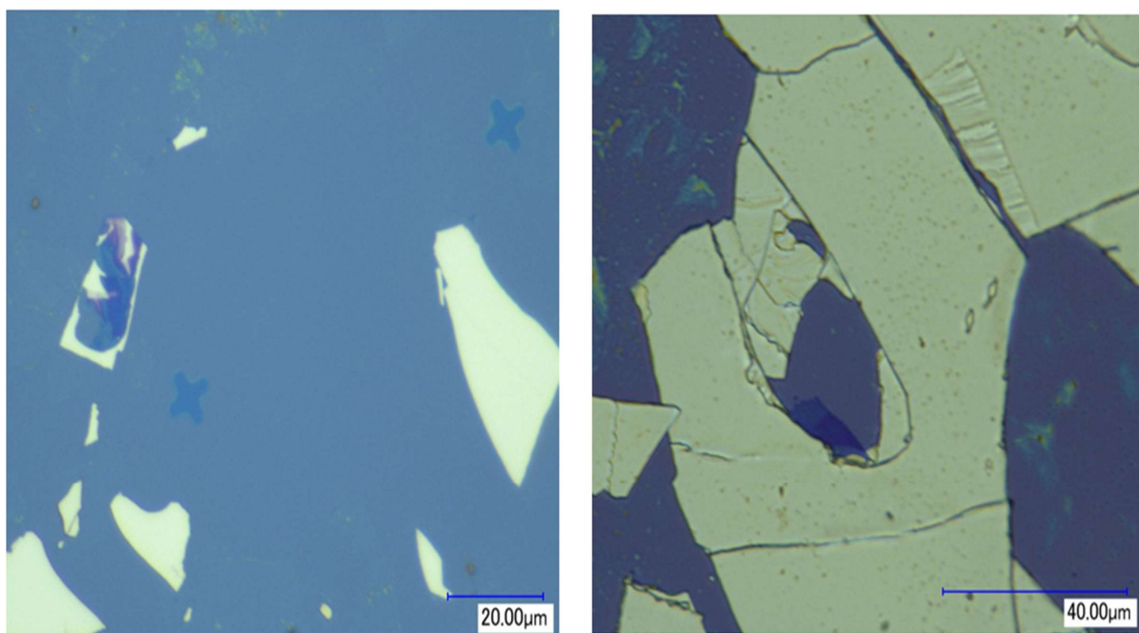


Figure 5.1: Flakes of PdSe₂-PdTe₂

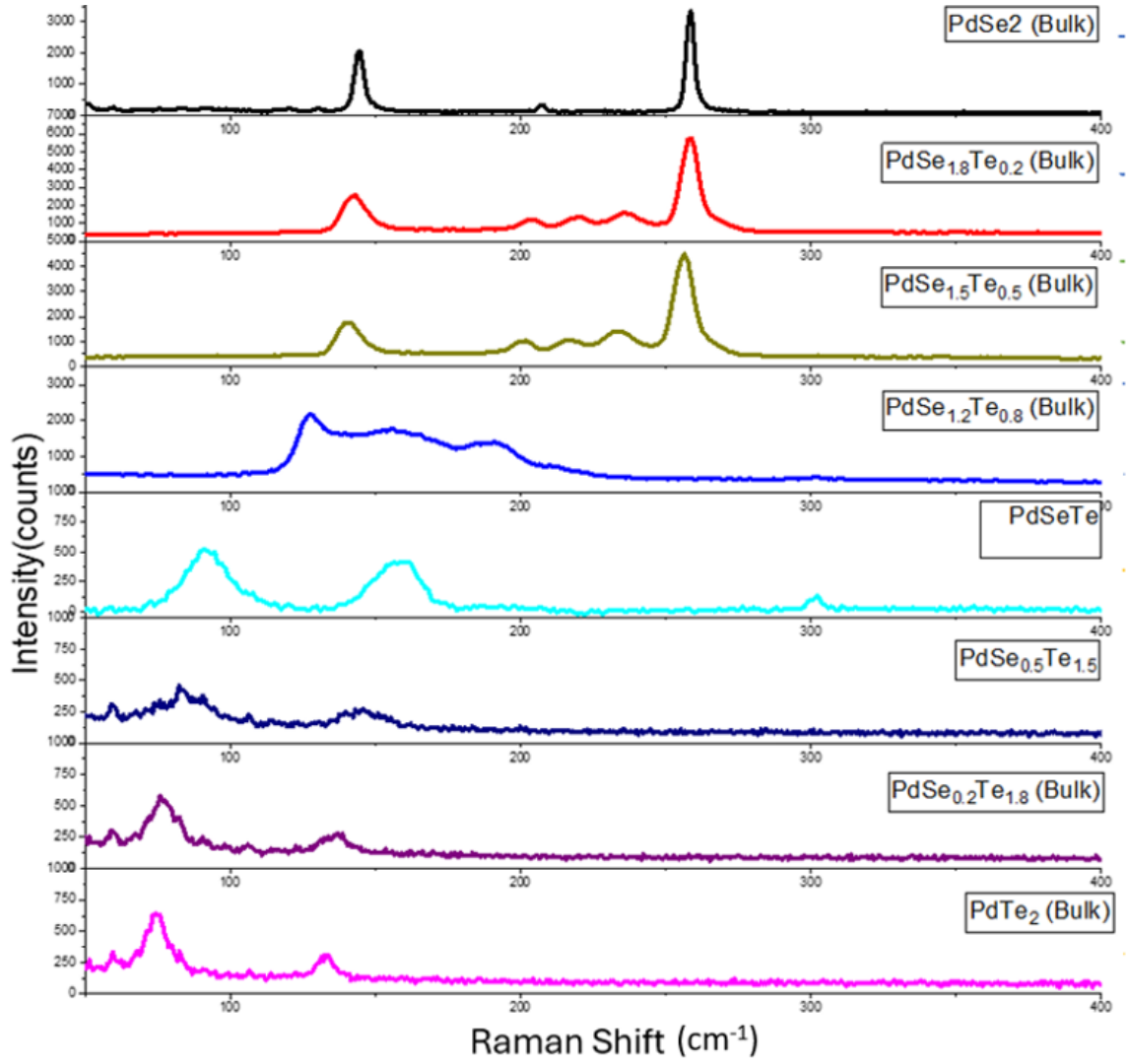


Figure 5.2: Raman spectra of different composition between bulk PdSe₂-PdTe₂

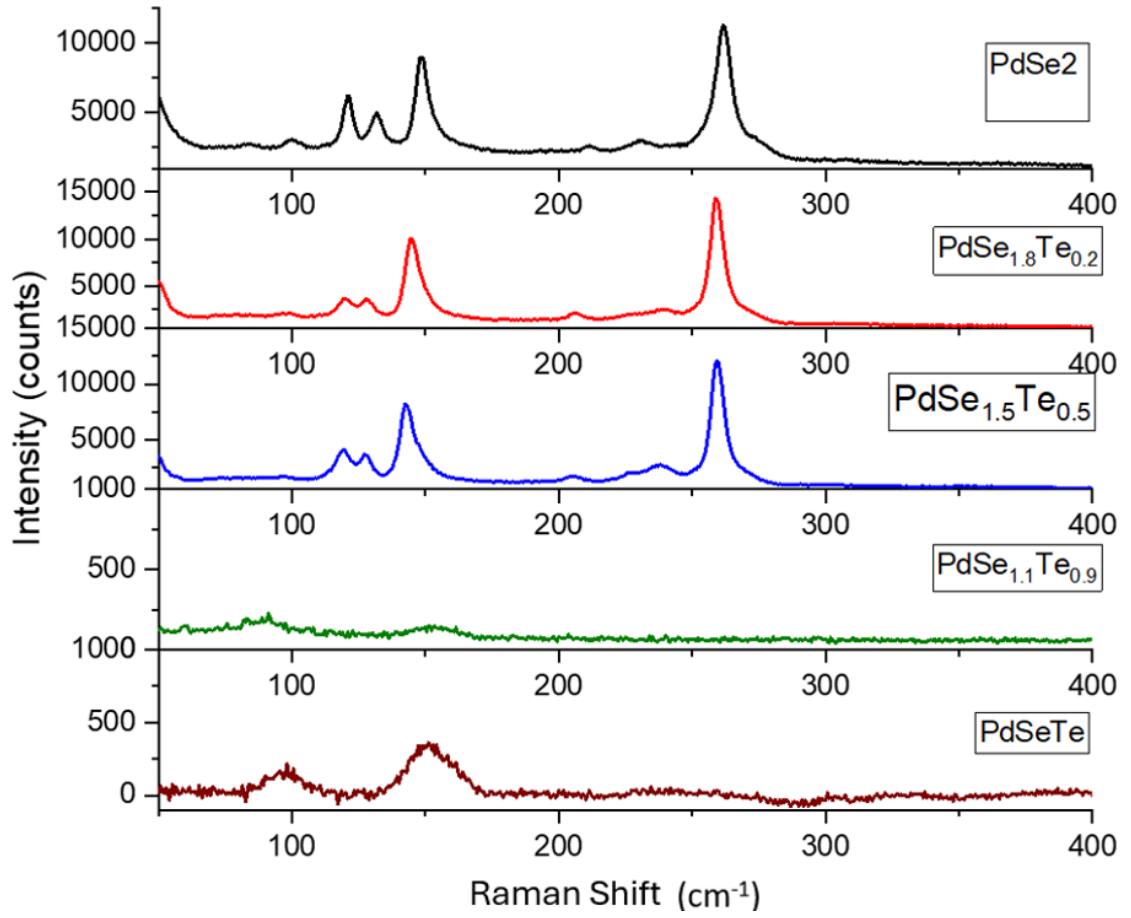


Figure 5.3: Raman spectra of different composition between few-layer PdSe₂ and PdSeTe

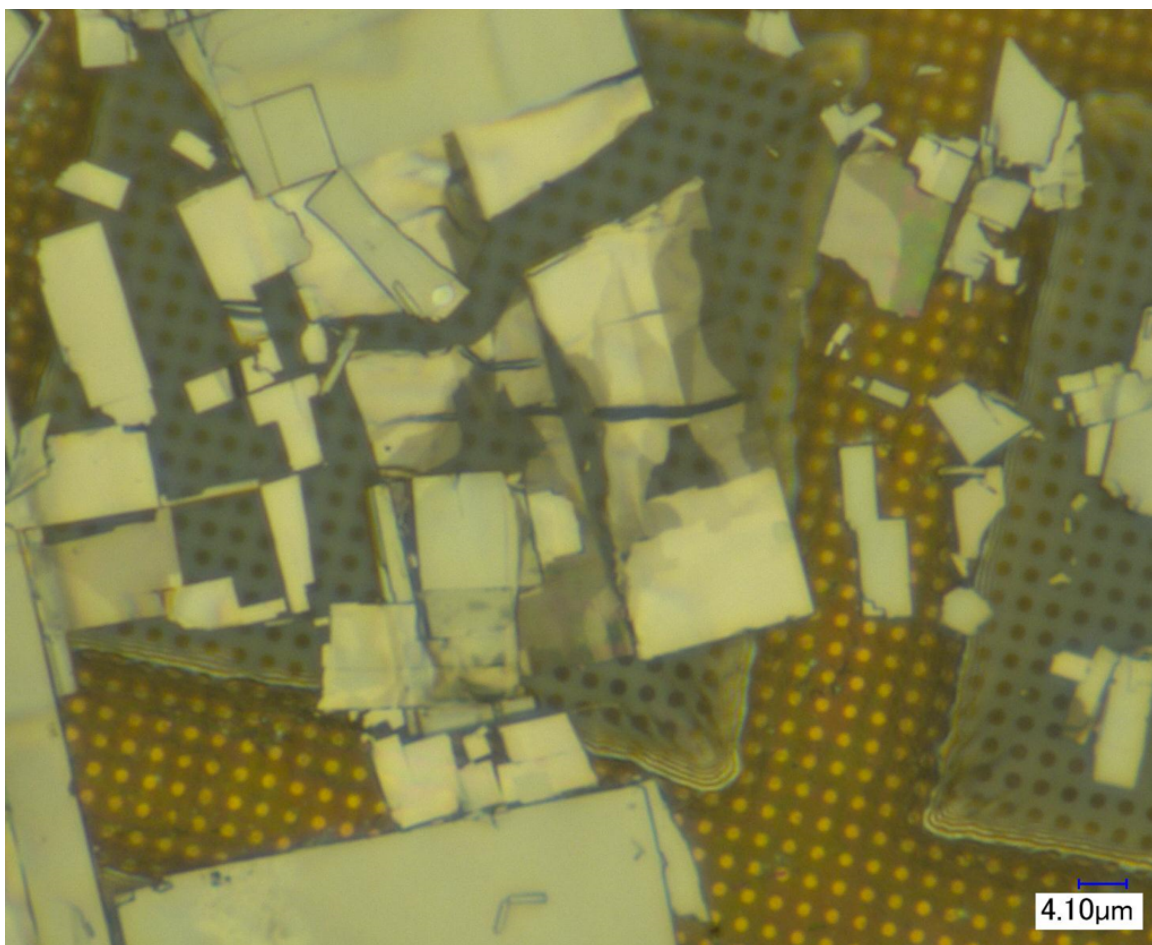


Figure 5.4: Optical images of PdSe_{1.5}Te_{0.5} flakes transferred on TEM grid

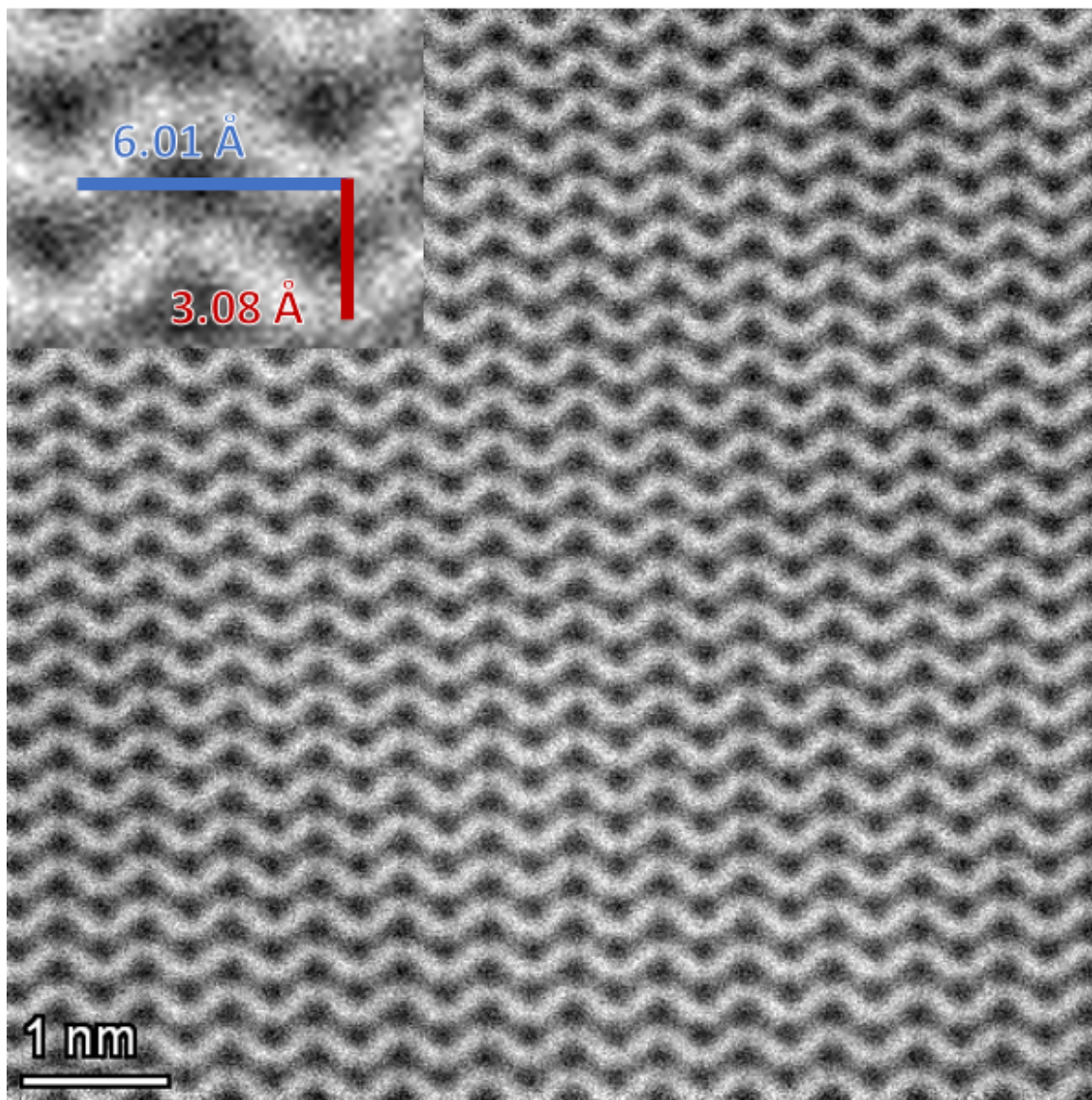


Figure 5.5: Atomic resolution structure of few-layer $\text{PdSe}_{1.5}\text{Te}_{0.5}$

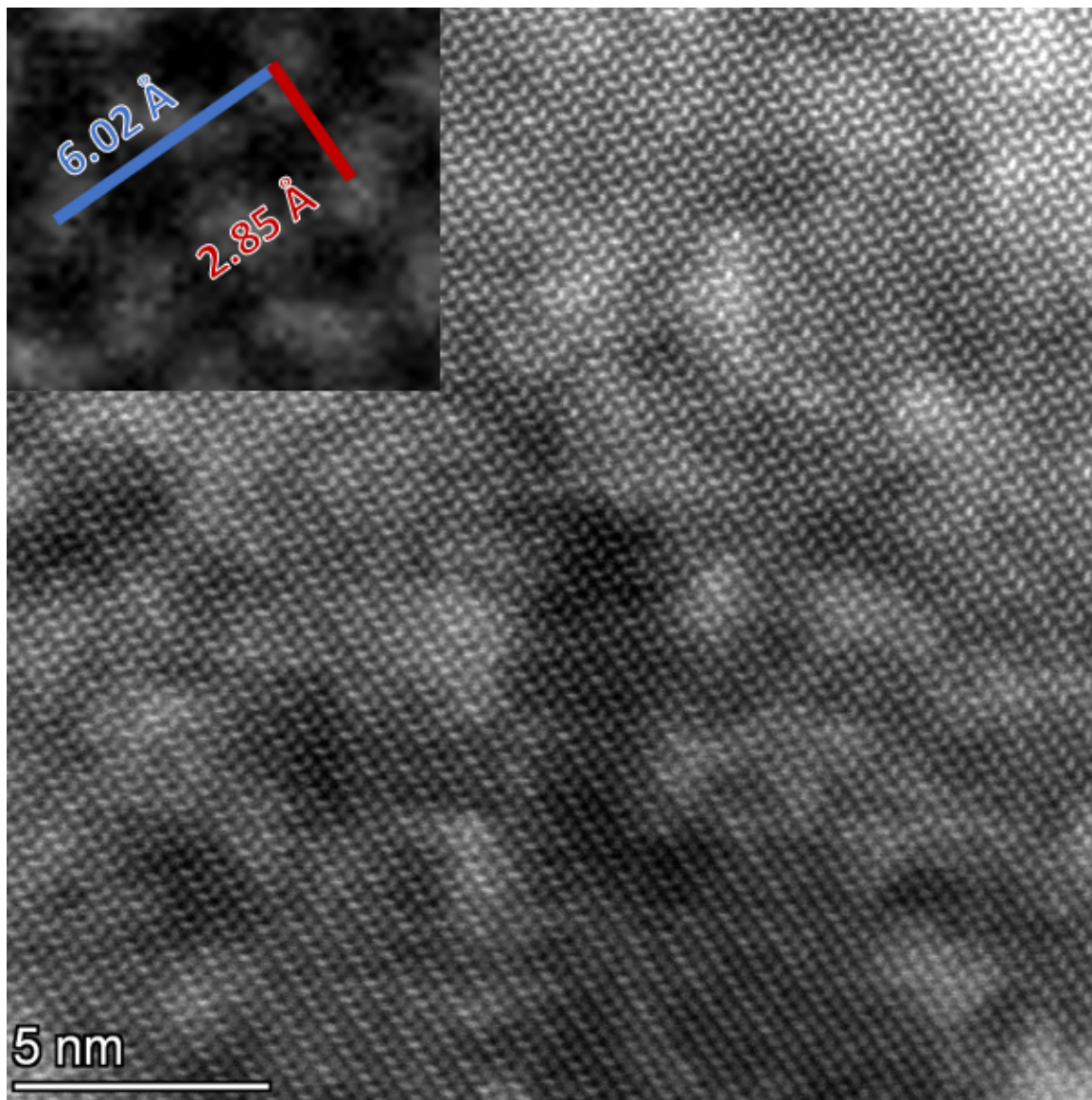


Figure 5.6: Atomic resolution structure of few-layer $\text{PdSe}_{1.8}\text{Te}_{0.2}$

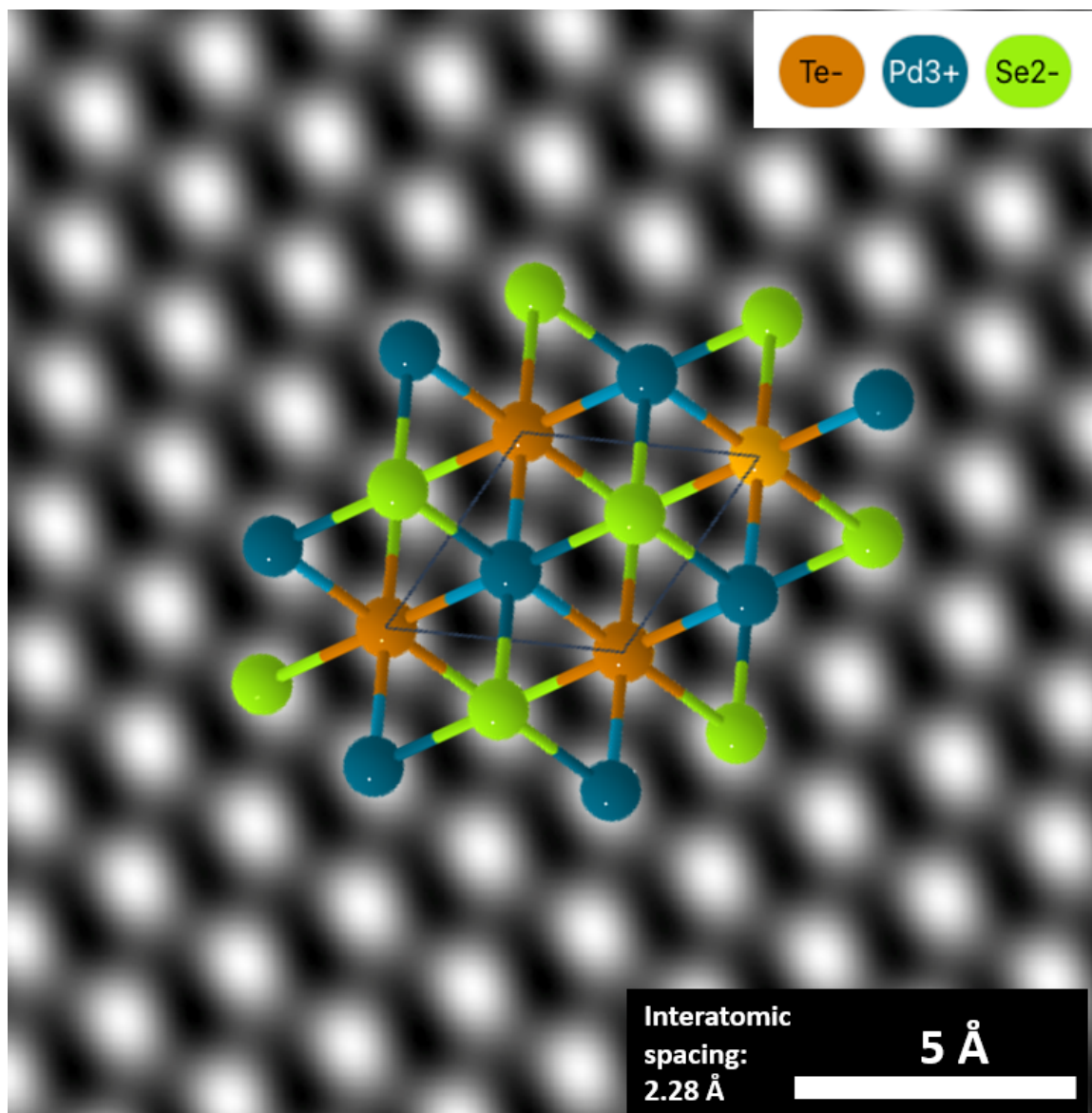


Figure 5.7: Atomic resolution structure of few-layer PdSeTe

Figure 5.8, Figure 5.9, Figure 5.10 compares the experimental results and the simulated Raman spectra for PdSe₂, PdSeTe and PdTe₂.

5.3.3 Composition-dependent electrical properties of the alloys

Tellurium acts as an n-type dopant in many semiconductor materials. The Increase in concentration of Te in the PdSe_{2-x}Te_x system introduces extra electrons into the conduction band. As a result, there is an increase in the carrier concentration that influences the position of the Fermi level, which directly impacts the electrical properties of the alloy. we examine the transport characteristics of 2D PdSe_{1.8}Te_{0.2} and PdSe_{1.5}Te_{0.5}, we fabricated field effect transistor (FET) devices employing a four terminal, back-gate arrangement as shown in Figure 5.11. Figure 5.12 displays the graph of the drain current (I_{ds}) in relation to the back gate voltage (Vg) for a standard 10nm PdSe_{1.8}Te_{0.2} device with a drain bias of 1.0 V. The device demonstrates N-type transport properties. Same procedure was developed for PdSe_{1.5}Te_{0.5}, Figure 5.13 reveals a P-type transport properties. Therefore, the electrical transport characteristics of the PdSe_{2-x}Te_x system is altered as a result of Te doping.

PdSe₂ has been reported to be ambipolar as reported (96), however we observe a change from ambipolar to n-type for PdSe_{1.8}Te_{0.2} as shown in Figure 5.12 then to p-type for PdSe_{1.5}Te_{0.5} as shown in Figure 5.13.

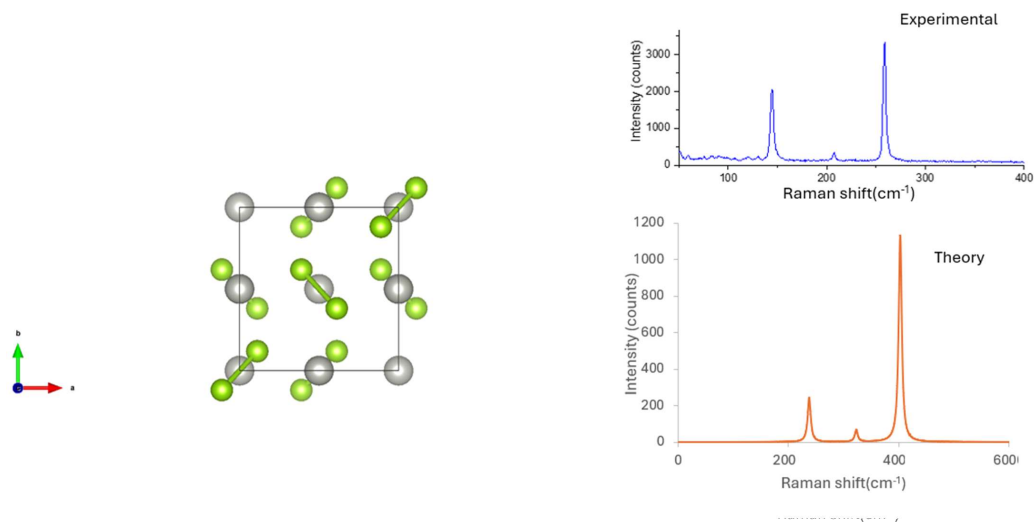


Figure 5.8: Right side- Raman plot of PdSe_2 and Left side- top view of the atomic structure of PdSe_2

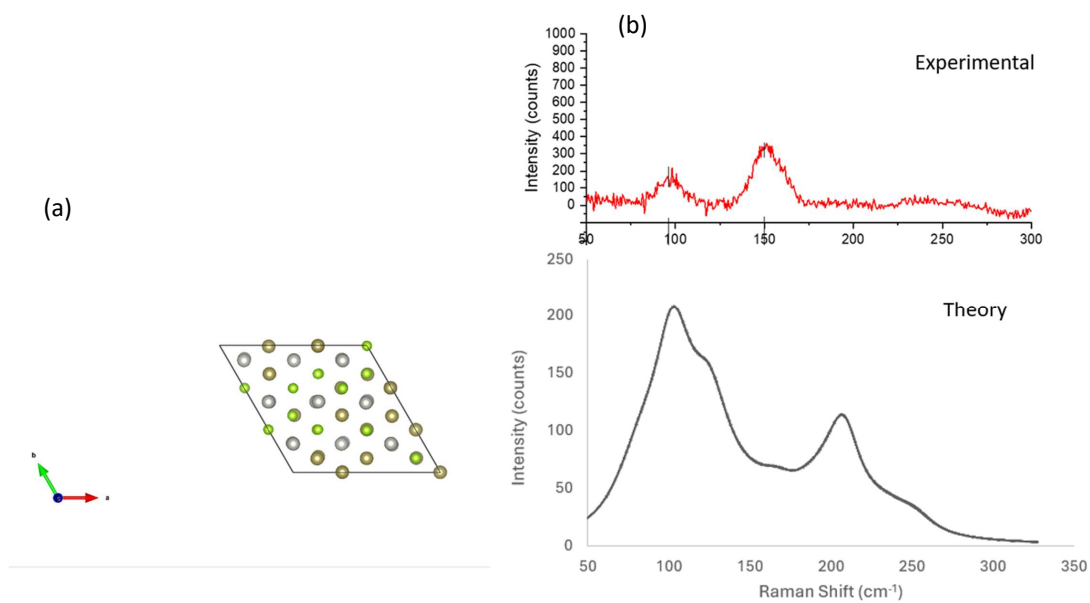


Figure 5.9: Right side- Raman plot of both experimental and theory of thin PdSeTe and Left side- top view of the atomic structure of PdSeTe

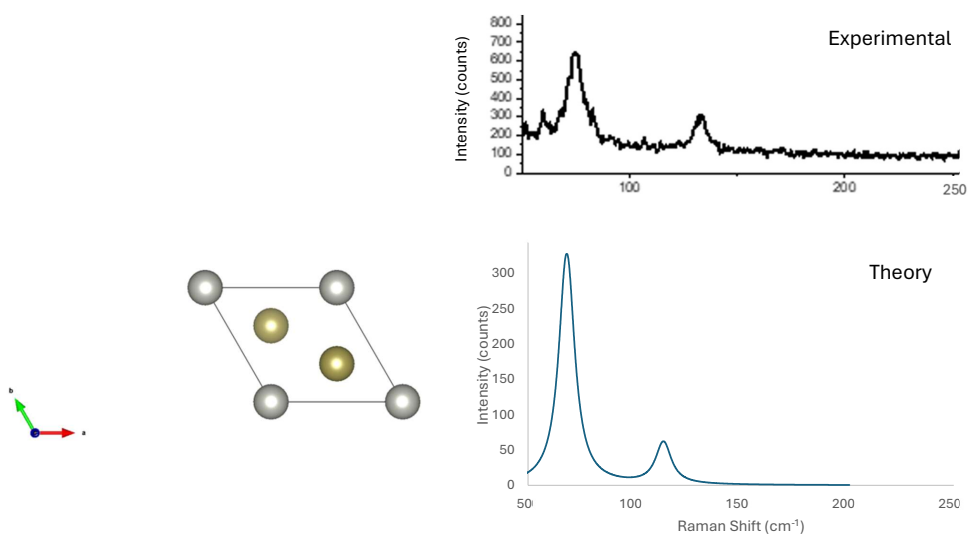


Figure 5.10: Right side- Raman plot of both experimental and theory PdTe₂ and Left side- top view of the atomic structure of PdTe₂

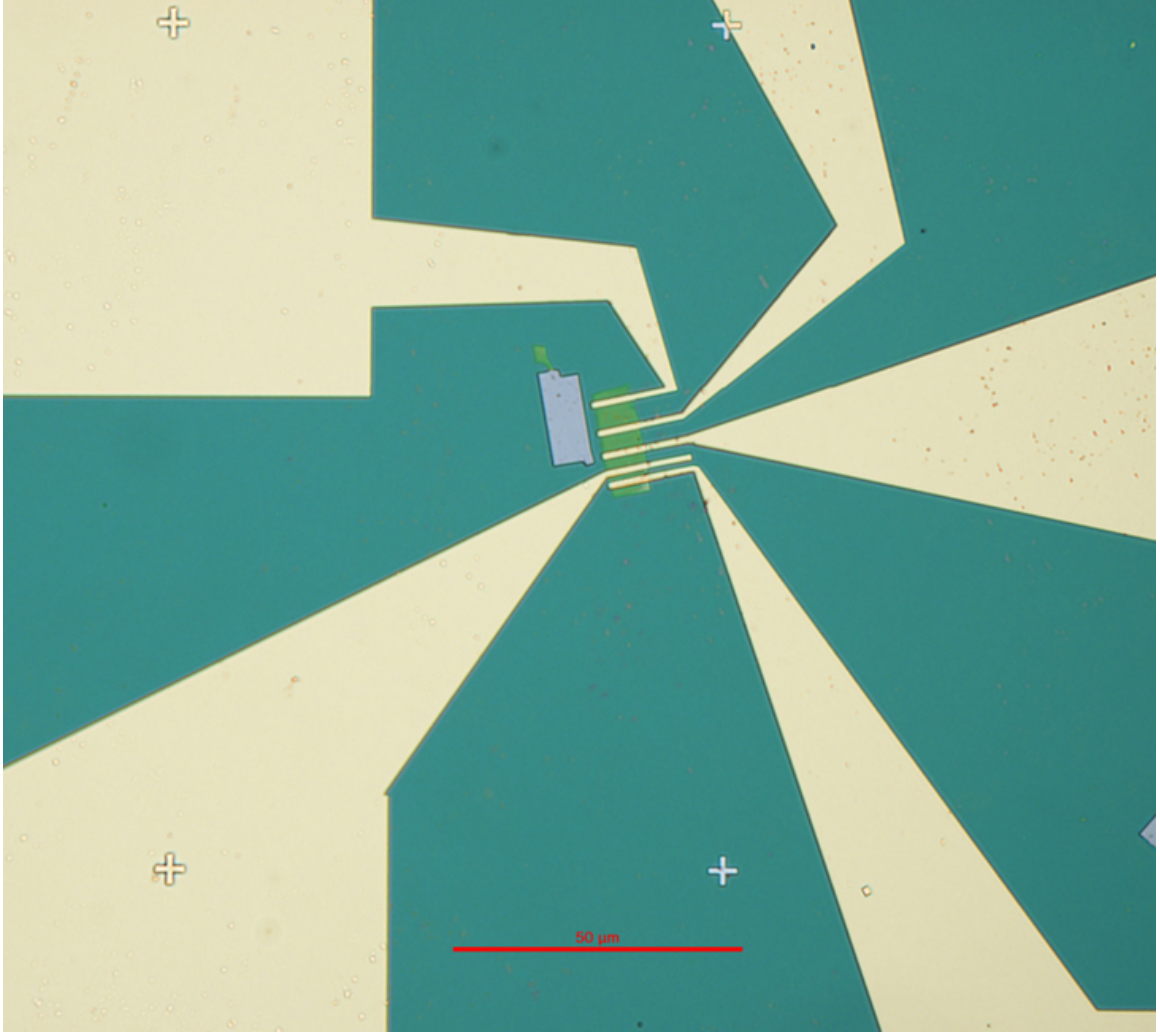


Figure 5.11: Device design for PdSe_{2-x}Te₂ flakes

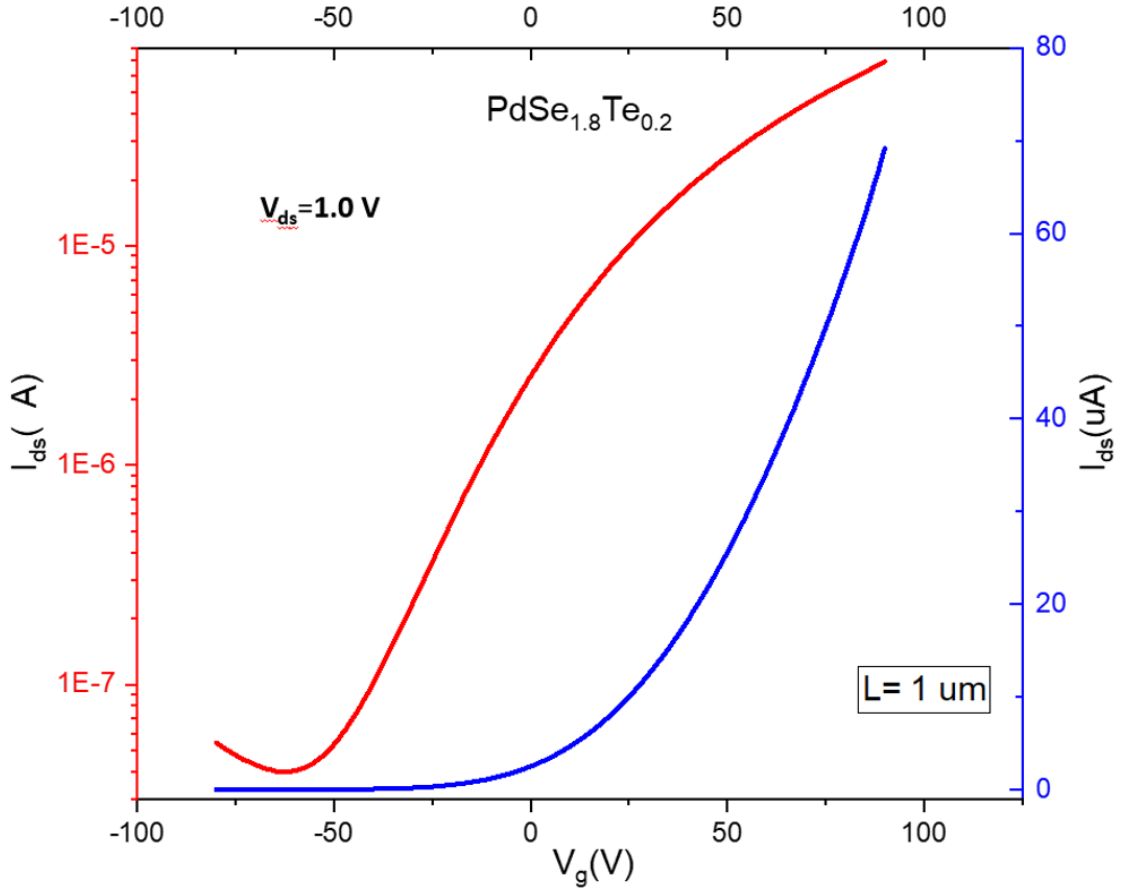


Figure 5.12: Transfer curve of a typical few-layer $\text{PdSe}_{1.8}\text{Te}_{0.2}$ device

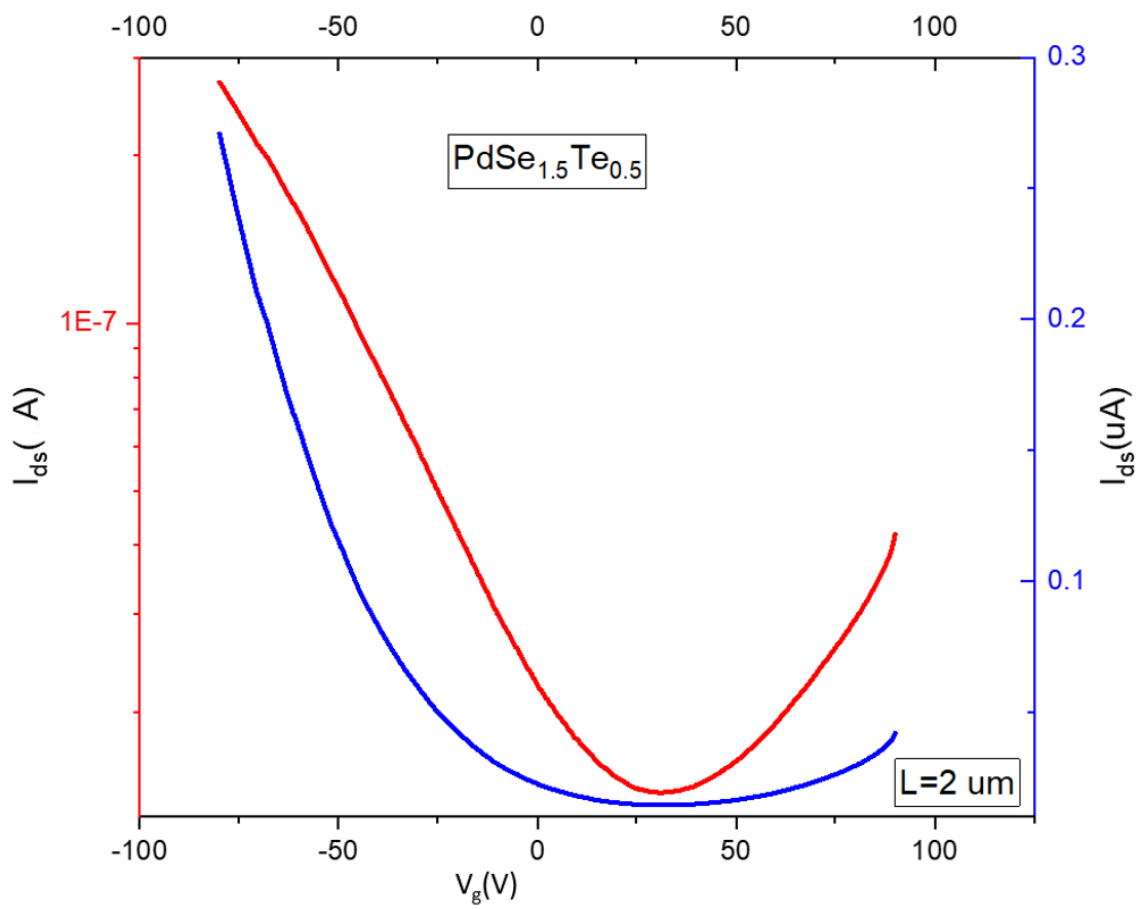


Figure 5.13: Transfer curve of a typical few-layer $\text{PdSe}_{1.5}\text{Te}_{0.5}$ device

5.4 Conclusion and summary

In conclusion, we confirmed using Raman spectroscopy measurements the many distinct phases that are associated with the various polymorphs that exist between PdSe_2 and PdTe_2 . Three distinct phase change were observed, the orthorhombic, monoclinic and 1 T phase. After the exfoliation and wet transfer on TEM grids, we reveal through STEM, the structural evolution within the $\text{PdSe}_{2-x}\text{Te}_x$ system. we also observed a transition from ambipolar to n-type conductivity in $\text{PdSe}_{1.8}\text{Te}_{0.2}$, and subsequently to p-type conductivity in $\text{PdSe}_{1.5}\text{Te}_{0.5}$, as the level of Te doping increases. This increase in doping leads to a higher carrier concentration, which in turn affects the position of the Fermi level. Consequently, the electrical properties of the alloy are directly influenced.

Chapter 6

Conclusion

6.1 Contributions of thesis

The major contributions of this thesis are as follows;

1. Developed a novel approach of polymer-free transfer of high quality graphene on TEM grid thereby avoiding contamination produced from the use of polymers as confirmed using the SEM and Raman Spectroscopy.
2. Fabrication of Van der Waals Heterostructure of Graphene-PdSe₂-Graphene using a hybrid of Wet and Dry transfer to ensure clean interface of the top graphene-PdSe₂ and the bottom graphene-PdSe₂. This helps to investigate phase transformation of PdSe₂ using laser irradiation.
3. Isolation of PdSe₂ nanosheets and fabrication of Van der Waals Heterostructure of PdSe₂ nanosheets using a dry transfer to ensure clean interface between stacked PdSe₂.PdSe₂ nanosheets (NSs) and nanostacks (NS) NSs exhibited memcapacitive behavior and resistive switching in a vertical configuration, which is especially prominent at the interface of the stacked PdSe₂ nanosheets. This further reveals the role of clean interface in the functionality of 2D materials.

4. Demonstrate the partial encapsulation of GaSe with hBN to study the the effect of hBN encapsulation on excitons under a varied temperature from 4K to 295k. We showed that the behavior of excitons in Few-layer GaSe is significantly impacted by the interaction between hBN and GaSe layers in hBN/GaSe. This was determined through detailed photoluminescence (PL) studies, including an examination of the temperature dependence of PL intensity.
5. Demonstrate the isolation of various alloys between the PdSe₂ and PdTe₂ revealing how the structural transition and correlated optical properties changes with different Te doping concentration in these alloys. we also observed the semiconductor to metallic transition with Te doping increasing in these alloys. PdSe₂ devices has been shown to exhibit ambipolar behavior. we have observed a transition from ambipolar to n-type device in PdSe_{1.8}Te_{0.2}, and subsequently to p-type device in PdSe_{1.5}Te_{0.5}, as the level of Te doping increases. This increase in doping leads to a higher carrier concentration, which in turn affects the position of the Fermi level. Consequently, the electrical properties of the alloy are directly influenced.

Bibliography

- [1] Novoselov KS, Mishchenko A, Carvalho A, Castro Neto A. 2D materials and van der Waals heterostructures. *Science*. 2016;353(6298):aac9439. [xii](#), [5](#)
- [2] Geim AK, Novoselov KS. The rise of graphene. *Nature materials*. 2007;6(3):183-91. [1](#)
- [3] Mayorov AS, Gorbachev RV, Morozov SV, Britnell L, Jalil R, Ponomarenko LA, et al. Micrometer-scale ballistic transport in encapsulated graphene at room temperature. *Nano letters*. 2011;11(6):2396-9. [1](#)
- [4] Balandin AA. Thermal properties of graphene and nanostructured carbon materials. *Nature materials*. 2011;10(8):569-81. [1](#)
- [5] Moser J, Barreiro A, Bachtold A. Current-induced cleaning of graphene. *Applied Physics Letters*. 2007;91(16). [1](#)
- [6] Shanmugam V, Mensah RA, Babu K, Gawusu S, Chanda A, Tu Y, et al. A review of the synthesis, properties, and applications of 2D materials. *Particle & Particle Systems Characterization*. 2022;39(6):2200031. [4](#)
- [7] Mannix AJ, Kiraly B, Hersam MC, Guisinger NP. Synthesis and chemistry of elemental 2D materials. *Nature Reviews Chemistry*. 2017;1(2):0014. [4](#)
- [8] Alam S, Chowdhury MA, Shahid A, Alam R, Rahim A. Synthesis of emerging two-dimensional (2D) materials—Advances, challenges and prospects. *FlatChem*. 2021;30:100305. [4](#)

- [9] Wang F, Wang Z, Wang Q, Wang F, Yin L, Xu K, et al. Synthesis, properties and applications of 2D non-graphene materials. *Nanotechnology*. 2015;26(29):292001. [4](#)
- [10] Zhang F, Momeni K, AlSaud MA, Azizi A, Hainey MF, Redwing JM, et al. Controlled synthesis of 2D transition metal dichalcogenides: from vertical to planar MoS₂. *2D Materials*. 2017;4(2):025029. [4](#)
- [11] Lu Z, Neupane GP, Jia G, Zhao H, Qi D, Du Y, et al. 2D materials based on main group element compounds: phases, synthesis, characterization, and applications. *Advanced Functional Materials*. 2020;30(40):2001127. [4](#)
- [12] Choi SH, Yun SJ, Won YS, Oh CS, Kim SM, Kim KK, et al. Large-scale synthesis of graphene and other 2D materials towards industrialization. *Nature Communications*. 2022;13(1):1484. [4](#)
- [13] Zavabeti A, Jannat A, Zhong L, Haidry AA, Yao Z, Ou JZ. Two-dimensional materials in large-areas: synthesis, properties and applications. *Nano-Micro Letters*. 2020;12:1-34. [4](#)
- [14] Gao E, Lin SZ, Qin Z, Buehler MJ, Feng XQ, Xu Z. Mechanical exfoliation of two-dimensional materials. *Journal of the Mechanics and Physics of Solids*. 2018;115:248-62. [7](#)
- [15] Islam MA, Serles P, Kumral B, Demingos PG, Qureshi T, Meiyazhagan A, et al. Exfoliation mechanisms of 2D materials and their applications. *Applied Physics Reviews*. 2022;9(4). [7](#)
- [16] Gao E, Lin SZ, Qin Z, Buehler MJ, Feng XQ, Xu Z. Mechanical exfoliation of two-dimensional materials. *Journal of the Mechanics and Physics of Solids*. 2018;115:248-62. [7](#)
- [17] Liu F. Mechanical exfoliation of large area 2D materials from vdW crystals. *Progress in Surface Science*. 2021;96(2):100626. [7](#)

- [18] Sinclair RC, Suter JL, Coveney PV. Micromechanical exfoliation of graphene on the atomistic scale. *Physical Chemistry Chemical Physics*. 2019;21(10):5716-22. [7](#)
- [19] Bohr J. Adhesive tape exfoliation: Why it works for graphene. *Europhysics Letters*. 2015;109(5):58004. [7](#)
- [20] Cai X, Luo Y, Liu B, Cheng HM. Preparation of 2D material dispersions and their applications. *Chemical Society Reviews*. 2018;47(16):6224-66. [7](#)
- [21] Desai SB, Madhvapathy SR, Amani M, Kiriya D, Hettick M, Tosun M, et al. Gold-mediated exfoliation of ultralarge optoelectronically-perfect monolayers. *Adv Mater*. 2016;28(21):4053-8. [8](#)
- [22] Heyl M, Burmeister D, Schultz T, Pallasch S, Ligorio G, Koch N, et al. Thermally activated gold-mediated transition metal dichalcogenide exfoliation and a unique gold-mediated transfer. *physica status solidi (RRL)–Rapid Research Letters*. 2020;14(11):2000408. [8](#)
- [23] Velicky M, Donnelly GE, Hendren WR, McFarland S, Scullion D, DeBenedetti WJ, et al. Mechanism of gold-assisted exfoliation of centimeter-sized transition-metal dichalcogenide monolayers. *ACS nano*. 2018;12(10):10463-72. [8](#)
- [24] Huang Y, Pan YH, Yang R, Bao LH, Meng L, Luo HL, et al. Universal mechanical exfoliation of large-area 2D crystals. *Nature communications*. 2020;11(1):2453. [8](#), [9](#)
- [25] Jones AC, Hitchman ML. Chemical vapour deposition: precursors, processes and applications. Royal society of chemistry; 2009. [9](#)
- [26] Saeed M, Alshammari Y, Majeed SA, Al-Nasrallah E. Chemical vapour deposition of graphene—Synthesis, characterisation, and applications: A review. *Molecules*. 2020;25(17):3856. [9](#)

- [27] Sun L, Yuan G, Gao L, Yang J, Chhowalla M, Gharahcheshmeh MH, et al. Chemical vapour deposition. *Nature Reviews Methods Primers*. 2021;1(1):5. [9](#)
- [28] Ashfold MN, May P, Rego C, Everitt N. Thin film diamond by chemical vapour deposition methods. *Chemical Society Reviews*. 1994;23(1):21-30. [9](#)
- [29] Lim H, Yoon SI, Kim G, Jang AR, Shin HS. Stacking of two-dimensional materials in lateral and vertical directions. *Chemistry of Materials*. 2014;26(17):4891-903. [11](#)
- [30] Onodera M, Masubuchi S, Moriya R, Machida T. Assembly of van der Waals heterostructures: exfoliation, searching, and stacking of 2D materials. *Japanese Journal of Applied Physics*. 2020;59(1):010101. [11](#), [12](#)
- [31] Sung SH, Schnitzer N, Brown L, Park J, Hovden R. Stacking, strain, and twist in 2D materials quantified by 3D electron diffraction. *Physical Review Materials*. 2019;3(6):064003. [11](#), [12](#)
- [32] Zhang W, Wang Q, Chen Y, Wang Z, Wee AT. Van der Waals stacked 2D layered materials for optoelectronics. *2D Materials*. 2016;3(2):022001. [11](#), [22](#)
- [33] Hu Z, Liu ZB, Tian JG. Stacking of exfoliated two-dimensional materials: a review. *Chinese Journal of Chemistry*. 2020;38(9):981-95. [12](#)
- [34] Ye H, Zhou J, Er D, Price CC, Yu Z, Liu Y, et al. Toward a mechanistic understanding of vertical growth of van der Waals stacked 2D materials: a multiscale model and experiments. *Acs Nano*. 2017;11(12):12780-8. [12](#)
- [35] Yang SJ, Choi S, Odongo Ngome FO, Kim KJ, Choi SY, Kim CJ. All-dry transfer of graphene film by van der Waals interactions. *Nano letters*. 2019;19(6):3590-6. [15](#)

- [36] Purdie D, Pugno N, Taniguchi T, Watanabe K, Ferrari A, Lombardo A. Cleaning interfaces in layered materials heterostructures. *Nature communications*. 2018;9(1):5387. [16](#), [20](#)
- [37] Chen Y, Gong XL, Gai JG. Progress and challenges in transfer of large-area graphene films. *Advanced science*. 2016;3(8):1500343. [16](#)
- [38] Van Ngoc H, Qian Y, Han SK, Kang DJ. PMMA-etching-free transfer of wafer-scale chemical vapor deposition two-dimensional atomic crystal by a water soluble polyvinyl alcohol polymer method. *Scientific reports*. 2016;6(1):33096. [16](#)
- [39] Frisenda R, Navarro-Moratalla E, Gant P, De Lara DP, Jarillo-Herrero P, Gorbachev RV, et al. Recent progress in the assembly of nanodevices and van der Waals heterostructures by deterministic placement of 2D materials. *Chemical Society Reviews*. 2018;47(1):53-68. [16](#)
- [40] Watson AJ, Lu W, Guimarães MH, Stöhr M. Transfer of large-scale two-dimensional semiconductors: challenges and developments. *2D Materials*. 2021;8(3):032001. [18](#)
- [41] Zhao Y, Song Y, Hu Z, Wang W, Chang Z, Zhang Y, et al. Large-area transfer of two-dimensional materials free of cracks, contamination and wrinkles via controllable conformal contact. *Nature Communications*. 2022;13(1):4409. [20](#)
- [42] Wakolbinger S, Geisenhof FR, Winterer F, Palmer S, Crimmann JG, Watanabe K, et al. Locally-triggered hydrophobic collapse induces global interface self-cleaning in van-der-Waals heterostructures at room-temperature. *2D Materials*. 2020;7(3):035002. [20](#)
- [43] Yang X, Yan M. Removing contaminants from transferred CVD graphene. *Nano Research*. 2020;13:599-610. [20](#)

- [44] Liao CD, Capasso A, Queirós T, Domingues T, Cerqueira F, Nicoara N, et al. Optimizing PMMA solutions to suppress contamination in the transfer of CVD graphene for batch production. *Beilstein Journal of Nanotechnology*. 2022;13(1):796-806. [20](#)
- [45] Jain A, Bharadwaj P, Heeg S, Parzefall M, Taniguchi T, Watanabe K, et al. Minimizing residues and strain in 2D materials transferred from PDMS. *Nanotechnology*. 2018;29(26):265203. [20](#)
- [46] Yang F, Stando G, Thompson A, Gundurao D, Li L, Liu H. Effect of Environmental Contaminants on the Interfacial Properties of Two-Dimensional Materials. *Accounts of Materials Research*. 2022;3(10):1022-32. [21](#)
- [47] Lee J, Lee S, Yu HK. Contamination-free graphene transfer from Cu-foil and Cu-thin-film/sapphire. *Coatings*. 2017;7(12):218. [21](#)
- [48] Liang X, Sperling BA, Calizo I, Cheng G, Hacker CA, Zhang Q, et al. Toward clean and crackless transfer of graphene. *ACS nano*. 2011;5(11):9144-53. [21](#)
- [49] Lin YC, Jin C, Lee JC, Jen SF, Suenaga K, Chiu PW. Clean transfer of graphene for isolation and suspension. *ACS nano*. 2011;5(3):2362-8. [21](#)
- [50] Pushkarev GV, Mazurenko VG, Mazurenko VV, Boukhvalov DW. Nature of interlayer bonds in two-dimensional materials. *The Journal of Physical Chemistry C*. 2023;127(17):8148-58. [22](#)
- [51] Bian Z, Miao J, Zhao Y, Chai Y. Strong interlayer interaction for engineering two-dimensional materials. *Accounts of Materials Research*. 2022;3(12):1220-31. [22](#)
- [52] Sun Y, Sun Y, Wang R, Liu K. Probing the interlayer mechanical coupling of 2D layered materials-A review. *Progress in Natural Science: Materials International*. 2022;32(5):528-37. [22](#)

- [53] Shi Z, Wang X, Sun Y, Li Y, Zhang L. Interlayer coupling in two-dimensional semiconductor materials. *Semiconductor Science and Technology*. 2018;33(9):093001. [22](#)
- [54] Ding Y, Zeng M, Zheng Q, Zhang J, Xu D, Chen W, et al. Bidirectional and reversible tuning of the interlayer spacing of two-dimensional materials. *Nature Communications*. 2021;12(1):5886. [22](#)
- [55] Hu T, Hu M, Li Z, Zhang H, Zhang C, Wang J, et al. Interlayer coupling in two-dimensional titanium carbide MXenes. *Physical Chemistry Chemical Physics*. 2016;18(30):20256-60. [22](#)
- [56] Lang H, Peng Y, Zeng X. Effect of interlayer bonding strength and bending stiffness on 2-dimensional materials' frictional properties at atomic-scale steps. *Applied Surface Science*. 2017;411:261-70. [22](#)
- [57] Seok H, Lee D, Son S, Choi H, Kim G, Kim T. Beyond von Neumann Architecture: Brain-Inspired Artificial Neuromorphic Devices and Integrated Computing. *Advanced Electronic Materials*. 2024;2300839. [24](#)
- [58] Mahata C, Ju D, Das T, Jeon B, Ismail M, Kim S, et al. Artificial synapses based on 2D-layered palladium diselenide heterostructure dynamic memristor for neuromorphic applications. *Nano Energy*. 2024;120:109168. [24](#)
- [59] Li Y, Loh L, Li S, Chen L, Li B, Bosman M, et al. Anomalous resistive switching in memristors based on two-dimensional palladium diselenide using heterophase grain boundaries. *Nature Electronics*. 2021;4(5):348-56. [25](#)
- [60] Wu X, Dhakal P, Kim JG, Hou A, Wang S. Transition Metal Dichalcogenides-Based Memristors for Neuromorphic Electronics. *Journal of Neuromorphic Intelligence*. 2024;1(1). [25](#)

- [61] Huang Z, Li Y, Zhang Y, Chen J, He J, Jiang J. 2D multifunctional devices: from material preparation to device fabrication and neuromorphic applications. *International Journal of Extreme Manufacturing*. 2024;6(3):032003. [25](#)
- [62] Yin X, Tang CS, Zheng Y, Gao J, Wu J, Zhang H, et al. Recent developments in 2D transition metal dichalcogenides: phase transition and applications of the (quasi-) metallic phases. *Chemical Society Reviews*. 2021;50(18):10087-115. [31](#)
- [63] Wang R, Yu Y, Zhou S, Li H, Wong H, Luo Z, et al. Strategies on phase control in transition metal dichalcogenides. *Advanced Functional Materials*. 2018;28(47):1802473. [32](#)
- [64] Voiry D, Mohite A, Chhowalla M. Phase engineering of transition metal dichalcogenides. *Chemical Society Reviews*. 2015;44(9):2702-12. [32](#)
- [65] Abbas G, Li Y, Wang H, Zhang WX, Wang C, Zhang H. Recent advances in twisted structures of flatland materials and crafting moiré superlattices. *Advanced Functional Materials*. 2020;30(36):2000878. [42](#)
- [66] He F, Zhou Y, Ye Z, Cho SH, Jeong J, Meng X, et al. Moiré patterns in 2D materials: a review. *ACS nano*. 2021;15(4):5944-58. [42](#)
- [67] Lau CN, Bockrath MW, Mak KF, Zhang F. Reproducibility in the fabrication and physics of moiré materials. *Nature*. 2022;602(7895):41-50. [42](#)
- [68] Tran K, Choi J, Singh A. Moiré and beyond in transition metal dichalcogenide twisted bilayers. *2D Materials*. 2020;8(2):022002. [43](#)
- [69] Carr S, Massatt D, Fang S, Cazeaux P, Luskin M, Kaxiras E. Twistronics: Manipulating the electronic properties of two-dimensional layered structures through their twist angle. *Physical Review B*. 2017;95(7):075420. [43](#)

- [70] Shabani S, Halbertal D, Wu W, Chen M, Liu S, Hone J, et al. Deep moiré potentials in twisted transition metal dichalcogenide bilayers. *Nature Physics*. 2021;17(6):720-5. [43](#)
- [71] Behura SK, Miranda A, Nayak S, Johnson K, Das P, Pradhan NR. Moiré physics in twisted van der Waals heterostructures of 2d materials. *Emergent Materials*. 2021;4:813-26. [43](#)
- [72] Mak KF, Lee C, Hone J, Shan J, Heinz TF. Atomically thin MoS₂: a new direct-gap semiconductor. *Physical review letters*. 2010;105(13):136805. [46](#), [47](#)
- [73] Splendiani A, Sun L, Zhang Y, Li T, Kim J, Chim CY, et al. Emerging photoluminescence in monolayer MoS₂. *Nano letters*. 2010;10(4):1271-5. [46](#)
- [74] Ferneliuss NC. Properties of gallium selenide single crystal. *Progress in crystal growth and characterization of materials*. 1994;28(4):275-353. [46](#), [47](#)
- [75] Camara M, Mauger A, Devos I. Electronic structure of the layer compounds GaSe and InSe in a tight-binding approach. *Physical Review B*. 2002;65(12):125206. [46](#)
- [76] Golovynskyi S, Irfan I, Bosi M, Seravalli L, Datsenko OI, Golovynska I, et al. Exciton and trion in few-layer MoS₂: Thickness-and temperature-dependent photoluminescence. *Applied Surface Science*. 2020;515:146033. [47](#)
- [77] Mooser E, Schlüter M. The band-gap excitons in gallium selenide. *Il Nuovo Cimento B (1971-1996)*. 1973;18(1):164-208. [47](#)
- [78] Camassel J, Merle P, Mathieu H, Chevy A. Excitonic absorption edge of indium selenide. *Physical Review B*. 1978;17(12):4718. [47](#)
- [79] Rahaman M, Bejani M, Salvan G, Lopez-Rivera SA, Pulci O, Bechstedt F, et al. Vibrational properties of GaSe: a layer dependent study from experiments to theory. *Semiconductor Science and Technology*. 2018;33(12):125008. [47](#)

- [80] Jie W, Chen X, Li D, Xie L, Hui YY, Lau SP, et al. Layer-dependent nonlinear optical properties and stability of non-centrosymmetric modification in few-layer GaSe sheets. *Angewandte Chemie International Edition*. 2015;54(4):1185-9. [47](#), [54](#)
- [81] Del Pozo-Zamudio O, Schwarz S, Sich M, Akimov I, Bayer M, Schofield R, et al. Photoluminescence of two-dimensional GaTe and GaSe films. *2D Materials*. 2015;2(3):035010. [48](#), [55](#)
- [82] Wu Y, Fuh HR, Zhang D, Coileáin CÓ, Xu H, Cho J, et al. Simultaneous large continuous band gap tunability and photoluminescence enhancement in GaSe nanosheets via elastic strain engineering. *Nano Energy*. 2017;32:157-64. [50](#)
- [83] Greben K, Arora S, Harats MG, Bolotin KI. Intrinsic and extrinsic defect-related excitons in TMDCs. *Nano Letters*. 2020;20(4):2544-50. [50](#)
- [84] Chen P, Atallah TL, Lin Z, Wang P, Lee SJ, Xu J, et al. Approaching the intrinsic exciton physics limit in two-dimensional semiconductor diodes. *Nature*. 2021;599(7885):404-10. [50](#)
- [85] Zhou M, Wang W, Lu J, Ni Z. How defects influence the photoluminescence of TMDCs. *Nano Research*. 2021;14:29-39. [50](#)
- [86] Zheng W, Jiang Y, Hu X, Li H, Zeng Z, Wang X, et al. Light emission properties of 2D transition metal dichalcogenides: fundamentals and applications. *Advanced Optical Materials*. 2018;6(21):1800420. [50](#)
- [87] Deng W, Zheng Z, Li J, Zhou R, Chen X, Zhang D, et al. Electrically tunable two-dimensional heterojunctions for miniaturized near-infrared spectrometers. *Nature communications*. 2022;13(1):4627. [50](#)
- [88] Qiu Z, Trushin M, Fang H, Verzhbitskiy I, Gao S, Laksono E, et al. Giant gate-tunable bandgap renormalization and excitonic effects in a 2D semiconductor. *Science advances*. 2019;5(7):eaaw2347. [50](#)

- [89] Voevodin VG, Voevodina OV, Bereznaya SA, Korotchenko ZV, Morozov AN, Sarkisov SY, et al. Large single crystals of gallium selenide: growing, doping by In and characterization. *Optical Materials*. 2004;26(4):495-9. [54](#)
- [90] Gauthier M, Polian A, Besson J, Chevy A. Optical properties of gallium selenide under high pressure. *Physical Review B*. 1989;40(6):3837. [54](#)
- [91] Capozzi V, Montagna M. Optical spectroscopy of extrinsic recombinations in gallium selenide. *Physical Review B*. 1989;40(5):3182. [54](#)
- [92] Li X, Basile L, Yoon M, Ma C, Puzos AA, Lee J, et al. Revealing the preferred interlayer orientations and stackings of two-dimensional bilayer gallium selenide crystals. *Angewandte Chemie International Edition*. 2015;54(9):2712-7. [54](#)
- [93] Peng H, Meister S, Chan CK, Zhang XF, Cui Y. Morphology control of layer-structured gallium selenide nanowires. *Nano letters*. 2007;7(1):199-203. [55](#)
- [94] Usman M, Golovynskyi S, Dong D, Lin Y, Yue Z, Imran M, et al. Raman scattering and exciton photoluminescence in few-layer GaSe: Thickness-and temperature-dependent behaviors. *The Journal of Physical Chemistry C*. 2022;126(25):10459-68. [55](#)
- [95] Tang Y, Xie W, Mandal KC, McGuire JA, Lai CW. Optical and spin polarization dynamics in GaSe nanoslabs. *Physical Review B*. 2015;91(19):195429. [58](#)
- [96] Oyedele AD, Yang S, Liang L, Puzos AA, Wang K, Zhang J, et al. PdSe₂: pentagonal two-dimensional layers with high air stability for electronics. *Journal of the American Chemical Society*. 2017;139(40):14090-7. [61](#), [63](#), [71](#)
- [97] Liu W, Li S, Wu H, Dhale N, Koirala P, Lv B. Enhanced superconductivity in the Se-substituted 1T-PdTe₂. *Physical Review Materials*. 2021;5(1):014802. [61](#)

- [98] Liu W, Osanloo MR, Wang X, Li S, Dhale N, Wu H, et al. New Verbeekite-type polymorphic phase and rich phase diagram in the PdSe₂-x Te_x system. Physical Review B. 2021;104(2):024507. [62](#)

Appendix

Appendix A

Appendix

A.1 A List of Publications

1. Sabine M Neumayer, **Olugbenga Olunloyo**, Petro Maksymovych, Kai Xiao
"Nanoscale Probing of Electrical Memory Effects in van der Waals Layered
PdSe₂" *ACS Applied Materials Interfaces* 16, no.3, 3665-3673(2024)
2. Ondrej Dyck, **Olugbenga Olunloyo**, Kai Xiao, Benjamin Wolf, Thomas M
Moore, Andrew R Lupini, Stephen Jesse 'A Versatile Side Entry Laser System
for Scanning Transmission Electron Microscopy' *arXiv:2407.09461 [physics.app-
ph]*
3. Lasseter, J. S. Gellerup, S. Ghosh, S. J. Yun, R.Vasudevan,. Unocic R. R,
Olunloyo O, et al., "Selected Area Manipulation of MoS₂ via Focused Electron
Beam-Induced Etching for Nanoscale Device Editing." *ACS Applied Materials
Interfaces* 16(7), 9144 (2024)
4. Ningxin Li, Tara Jabegu, Rui He, Seokjoon Yun, Sujoy Ghosh, Diren Maraba,
Olugbenga Olunloyo, et al., "Covalently-Bonded Laminar Assembly of Van
der Waals Semiconductors with Polymers: Toward High-Performance Flexible
Devices" *Small*. 2310175 (2024)

5. Vlassiounk, I, Sergei S, Alexander P, **Olugbenga O**, et al., "Armor for Steel: Facile Synthesis of Hexagonal Boron Nitride Films on Various Substrates." *Advanced Materials Interfaces* 11, no. 1 2300704 (2024):
6. Boebinger, M G., Courtney B, Li-Ping D, Sudhajit M, **Olugbenga O**, Yiling Yu, Kai X et al., "The atomic drill bit: Precision controlled atomic fabrication of 2D materials." *Advanced Materials* 35, no. 14 2210116 (2023):
7. Aisha Okmi, Xuemei Xiao, Yue Zhang, Rui He, **Olugbenga Olunloyo**, et al., "Discovery of Graphene-Water Membrane Structure: Toward High-Quality Graphene Process." *Advanced Science* 9 (26), 2201336
8. Elizaveta Tiukalova, **Olugbenga Olunloyo**, et al., "Probing Atomic Structure and Excitons in 2D Heterostructures Through Cryogenic STEM-EELS" *In preparation*
9. **Olugbenga Olunloyo**, et al., "The effect of Te doping on the structure and electrical property of $\text{PdSe}_{2-x}\text{Te}_x$ " *In preparation*

Vita

Olugbenga Olunloyo had his B.Sc. Engineering physics at Obafemi Awolowo University, Ile-Ife. Later, he earned a Master's degree in Physics with distinction from Obafemi Awolowo University, where he focused on Quantum Phase Transitions of the Spin 3/2 Blume-Emery-Griffiths Model in Transverse Field. He later pursued a Ph.D. program at the University of Tennessee, Knoxville. He worked with Dr. Kai Xiao in the Center for Nanophase Materials Science at Oak Ridge National Laboratory, where he developed novel techniques for fabricating heterostructure